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## Synthesis and polymerization of several ester substituted epoxides.

John Muggee  
*University of Massachusetts Amherst*

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SYNTHESIS AND POLYMERIZATION OF SEVERAL  
ESTER SUBSTITUTED EPOXIDES

A Dissertation Presented

By

JOHN MUGGEE

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

DOCTOR OF PHILOSOPHY

February 1982

Polymer Science and Engineering

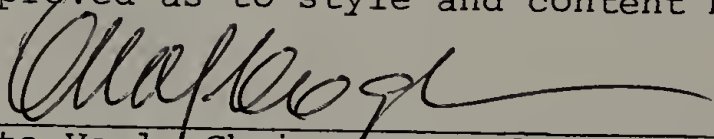
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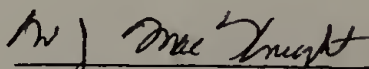
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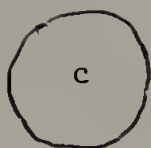
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JOHN MUGGEE

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The author also gratefully acknowledges the financial support of the Materials Research Laboratory and NSF grants DMR-78-13953 and DMR-80-17058.

## ABSTRACT

### Synthesis and Polymerization of Several Ester Substituted Epoxides

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Directed by: Professor Otto Vogl

Novel ester substituted poly(alkylene oxides) were prepared from ester substituted epoxide monomers, where the ester groups were separated from the epoxide groups by a series of 0 to 7 methylene spacer groups. The reactivity of these monomers using coordinate and cationic initiators was examined, with the objective of determining the proximity effect of the ester groups on the polymerizability of the monomers.

Homopolymerizations of the ester substituted monomers using the  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$  (1/0.5/1) coordinate initiator system demonstrated a strong proximity effect of the ester groups on the monomer reactivity. Those monomers with 0 to 3 spacer groups gave polymers in much lower yields with lower molecular weights than the monomers with 4 to 7 spacer groups. The polymers were semicrystalline, and became more rubbery as the number of spacer groups

increased.

Copolymerizations of the ester substituted monomers having 1, 2, and 5 spacer groups with several cyclic ethers, using the  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$  (1/0.5/1) initiator system, also demonstrated a strong proximity effect. Copolymers of the ester substituted monomer with 1 spacer group were produced in very low yields, while copolymers of the ester substituted monomer with 2 spacer groups were produced in low to good yields. Copolymers of the ester substituted monomer with 5 spacer groups were produced in good to high yields. The level of incorporation of the ester substituted monomers into the copolymers was generally >80%. Many of the copolymers were semicrystalline.

Cationic homopolymerizations of the ester substituted monomers having 1, 2, and 5 spacer groups were carried out using  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  and  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}$  (1/0.5) as initiators. The polymers from the  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  initiated polymerizations were low molecular weight, ranging from viscous liquids to paste-like solids. The monomers with 1 and 5 spacer groups gave high molecular weight polymers when the  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}$  (1/0.5) initiator system was used, while the monomer with 2 spacer groups gave a low molecular weight material.

Anionic homopolymerizations of the ester substituted monomers with 1, 2, and 5 spacer groups were

attempted, but were unsuccessful. Propylene oxide could be polymerized, however.

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## C H A P T E R    I

### INTRODUCTION

This dissertation describes the synthesis of a series of ester substituted poly(alkylene oxides) by the ring opening polymerization of the corresponding ester substituted epoxide monomers. The ester groups are separated from the epoxide polymerization site by 0 to 7 methylene spacer groups. These studies represent the first example of a series of polymers with functional groups separated from the polymer main chain by a regular and well defined number of methylene spacer groups. These studies are a continuation of the work in these laboratories concerning the preparation of ester substituted poly(alkylene oxides) in particular, and the much larger effort concerning the preparation of functionally substituted polymers in general.

This introductory chapter is concerned primarily with the preparation and characteristics of functionally substituted poly(alkylene oxides). Section I deals with the preparation of poly(alkylene oxides) by anionic, cationic, and coordinate polymerizations. Some general characteristics and limitations for each synthetic route are discussed. Section II discusses previous studies concerning the preparation of functionally substituted poly(alkyl-

ene oxides). Emphasis is placed on the effect of the functional group on the polymerizability of the monomer, and on the properties of the resultant polymer. This discussion will provide suitable background material for understanding the polymerization behavior of the monomers used in this work and the properties of the resultant polymeric materials.

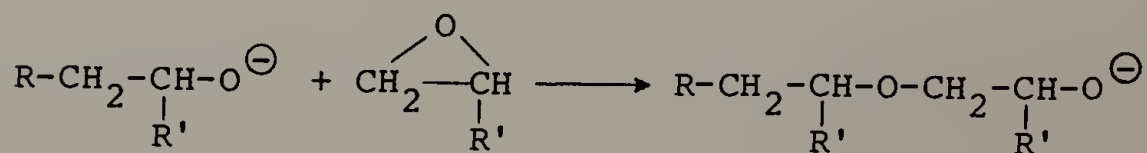
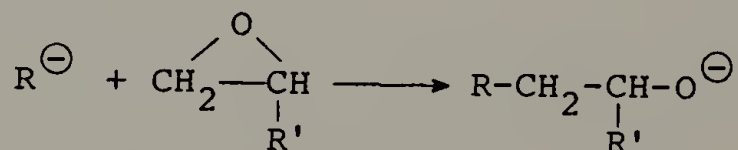
## I. Preparation of Alkylene Oxide Polymers

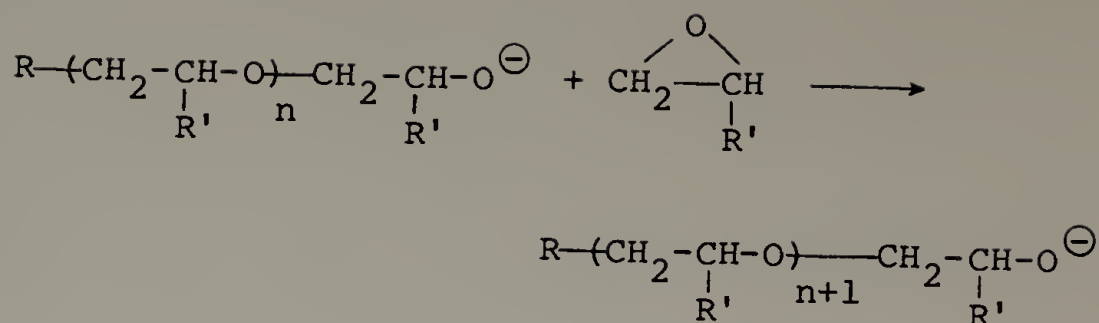
A. General background. The preparation of alkylene oxide polymers via ring opening polymerization of the corresponding cyclic ethers has been known for more than a century.<sup>1-4</sup> This early work dealt with the preparation of low molecular weight polymers from ethylene oxide using anionic and cationic initiators. Since those early studies, poly(alkylene oxides) have been prepared from various epoxides, oxetanes, tetrahydrofurans, oxepane, 1,4-epoxycyclohexane, cyclic formals, and trioxane. The ease of preparation of the substituted polymers varies considerably depending on the monomer. Substituted polymers can not be prepared from substituted trioxanes, and only with difficulty from substituted tetrahydrofurans and cyclic formals. However, substituted polymers from substituted epoxides and oxetanes can be readily prepared, and consequently these have been most intensively studied.

The preparation of poly(alkylene oxides) from the

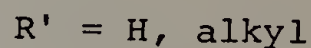
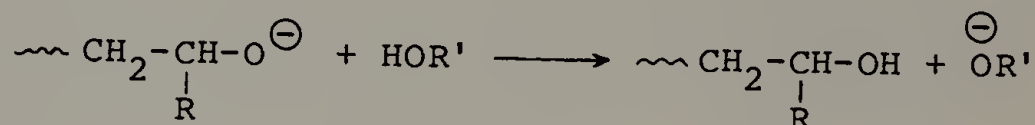
corresponding cyclic ethers has been of both academic and industrial interest. This interest is due, in part, to the wide range of applications for these polymers. The low molecular weight products have found such varied uses as mold release agents, lubricants, pharmaceutical bases, antistatic agents, and polyurethane elastomer soft segments.<sup>5</sup> High molecular weight poly(alkylene oxides), which have, for the most part, only been known for 25 years, vary in usage from amorphous rubbers<sup>6</sup> to crystalline thermoplastics.<sup>7</sup>

B. Anionic polymerization. The only class of cyclic ethers which can be polymerized anionically are the epoxides.<sup>8-10</sup> The ether linkage is basic in the Lewis sense, and only the epoxides possess sufficient ring strain to permit anionic polymerization.<sup>11,12</sup> These polymerizations have been proposed to proceed by a step growth mechanism with an alkoxide anion as the propagation center.<sup>13,14</sup>

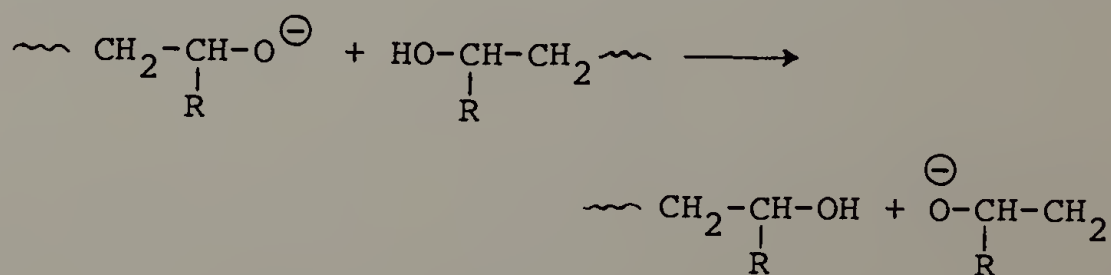




Evidence to support this conclusion was the increase in molecular weight with conversion, and the activity of various sodium alkoxides of ethylene oxide oligomers as initiators. However, the initiators used in these studies have been either aqueous or alcoholic solutions of alkali metal hydroxides or alkoxides, and both water and alcohol can act as chain transfer agents by donating protons.



The formed hydroxide or alkoxide can act as an initiator, thereby maintaining the kinetic chain. The glycols formed by such a transfer can themselves act as transfer agents,

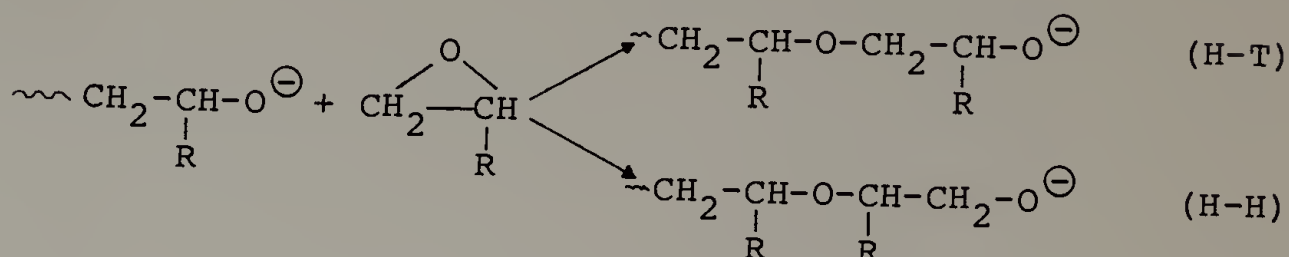


resulting in a situation where all end groups are of equal reactivity, hence a step growth mechanism. When an

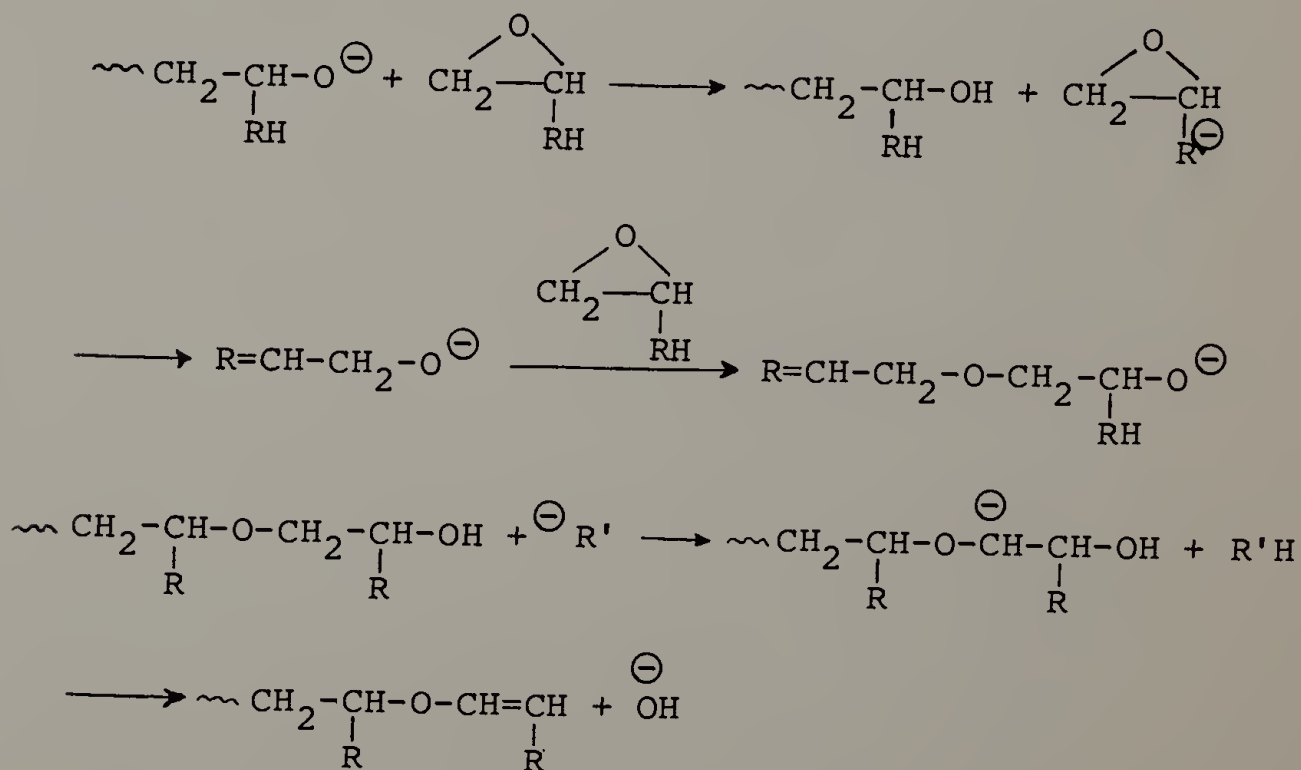
initiator free of active hydrogen species, such as solid potassium hydroxide, is used, polymerization occurs by a chain growth mechanism, as indicated by a constant molecular weight during polymerization.<sup>15</sup> It appears that in the absence of active hydrogen compounds (water, alcohol), the polymerizations proceed by a chain growth mechanism, but when these compounds are present a step growth mechanism is followed. Other initiators which have been used include primary, secondary, and tertiary amines, and alkali metals.<sup>16</sup>

As is the case with other anionic polymerizations, electron withdrawing groups stabilize the alkoxide propagation centers in epoxide polymerizations. Studies of the methoxide ion initiated polymerizations of ethylene, propylene, and isobutylene oxides showed the rate of polymerization decreased in the order ethylene oxide > propylene oxide > isobutylene oxide, indicating that electron donation (by induction) from the alkyl groups decreases the reactivity of the epoxides.<sup>17</sup> Ring substituent effects on the potassium tert-butoxide initiated polymerizations of phenylglycidyl ethers have been studied.<sup>18</sup> It was shown that electron withdrawing groups, such as o- and p-chloro substituents, promote polymerization, while electron releasing groups, such as p-methoxy or -methyl substituents, retard polymerization. Propagation of substituted epoxides occurs predominantly by attack of the alkoxide ion at the

unsubstituted primary carbon atom of the epoxide ring,<sup>19</sup> resulting in the formation of almost pure head-to-tail (H-T) polymer instead of head-to-head (H-H).

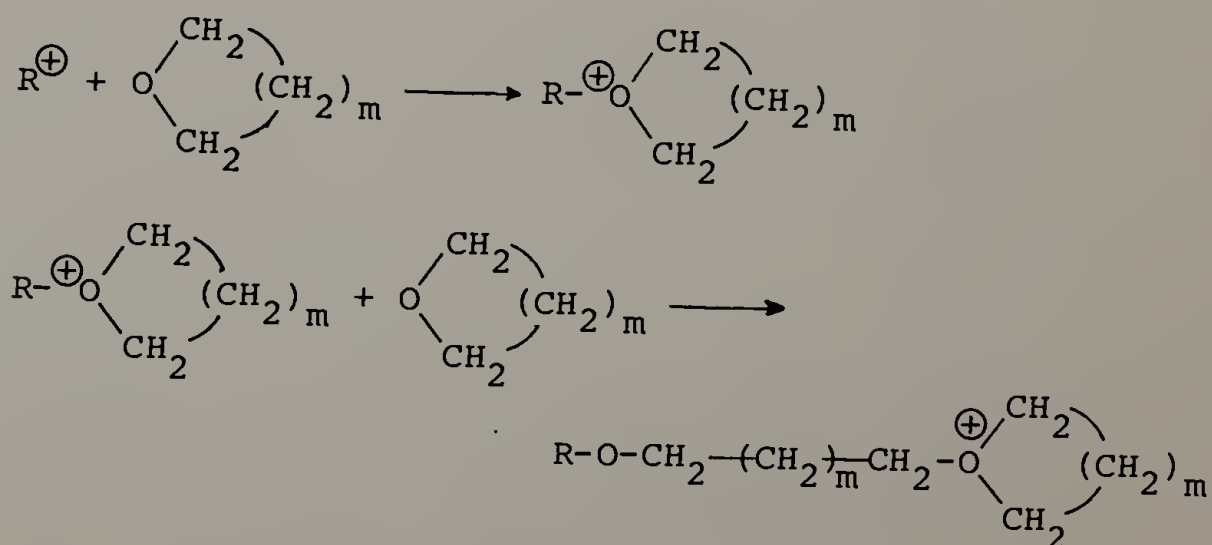


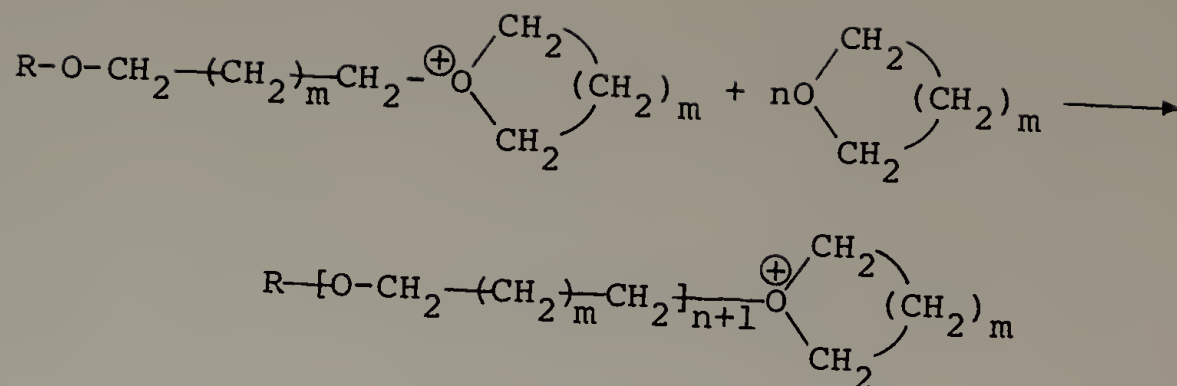
The polymers produced from anionic epoxide polymerizations are typically low molecular weight materials, ranging from a few hundred to several thousand, and appear as viscous liquids or waxy solids. Low molecular weights are achieved because of facile transfer and termination reactions, as shown below.



These polymerizations are normally carried out at elevated temperatures<sup>20</sup> because of the low reactivity towards anionic polymerization exhibited by epoxides, although room temperature polymerizations have been carried out.<sup>13,17</sup> The molecular weight of the polymers decrease with an increase in polymerization temperature.<sup>9</sup>

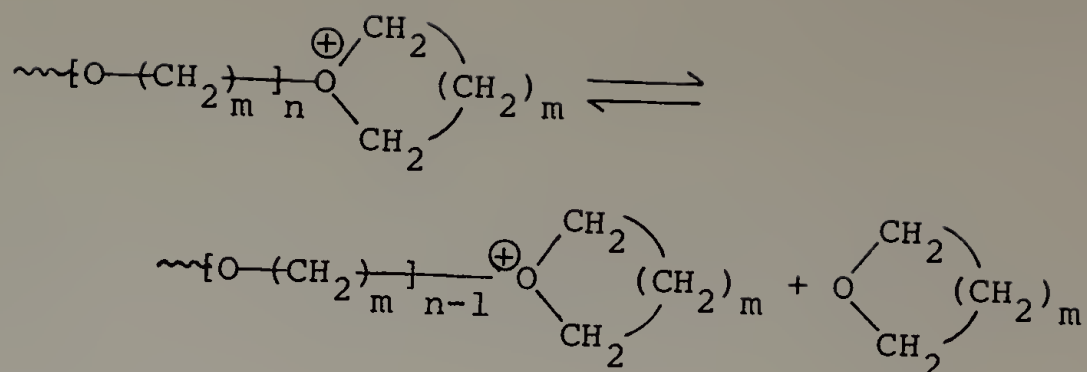
C. Cationic polymerization. Unlike anionic polymerizations of cyclic ethers, cyclic ethers of many different ring sizes may be polymerized cationically.<sup>8-10</sup> The reason for this is the same one which limits anionic cyclic ether polymerizations to epoxides; the ether linkage is basic in the Lewis sense.<sup>11,12</sup> The cyclic ether monomers may include up to three oxygen atoms, but most polymerization studies have dealt with monomers with one oxygen atom. Polymerization proceeds by a chain growth mechanism in which the propagation site is an oxonium ion. Initiators which are commonly used for cyclic ether polymerizations include



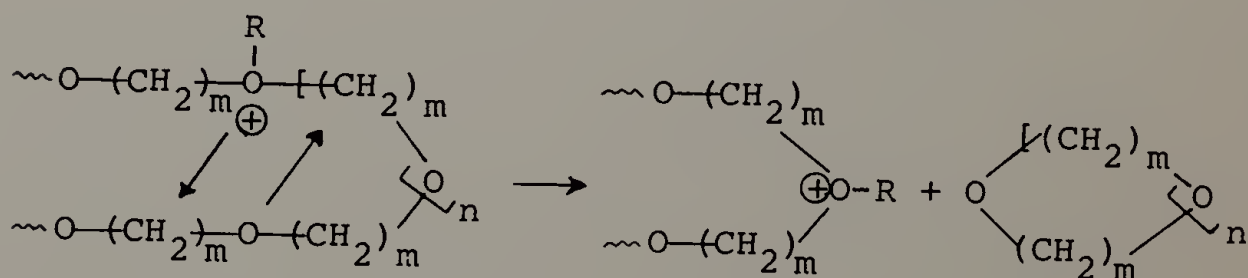
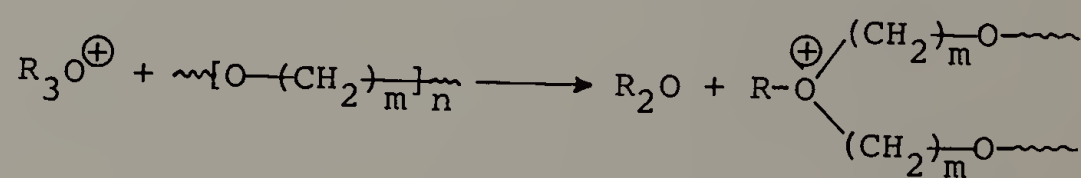


strong protonic acids such as trifluoromethanesulfonic acid, carbenium ions such as alkyl trifluoromethanesulfonates and triphenylmethyl hexachloroantimonate, oxonium ions such as triethyloxonium tetrafluoroborate, and Lewis acids such as boron trifluoride ( $\text{BF}_3$ ) and phosphorous pentoxide.

The polymerizability of cyclic ethers depends on ring strain and ring size. The thermodynamic stability of cyclic ethers, most closely associated with ring strain,<sup>21</sup> decreases in the order  $6 > 5 > 7, 12$  and larger  $> 8$  to  $11 > 4 > 3$ .<sup>10</sup> From these results, it can be seen that the 3 and 4 membered rings possess the greatest amount of ring strain, and are therefore most reactive towards ring opening, while the 5 and 6 membered rings are the least strained, and least reactive towards ring opening. During polymerization, the polymer chains are subject to a propagation-depropagation (or ring-chain) equilibration



governed both by the thermodynamic stability of the ring (the ring strain) and by the kinetic feasibility of forming the ring (ring size). The kinetic feasibility of ring formation decreases as the ring becomes larger. Of these two effects, ring strain is predominant. Cyclic species of different sizes can also be produced during ring-opening polymerizations.<sup>22</sup> Unlike the ring-chain equilibrium, formation of higher cyclic oligomers normally represents an irreversible chain transfer. These cyclic oligomers are produced via a "back-biting" mechanism, as shown below.<sup>23</sup>

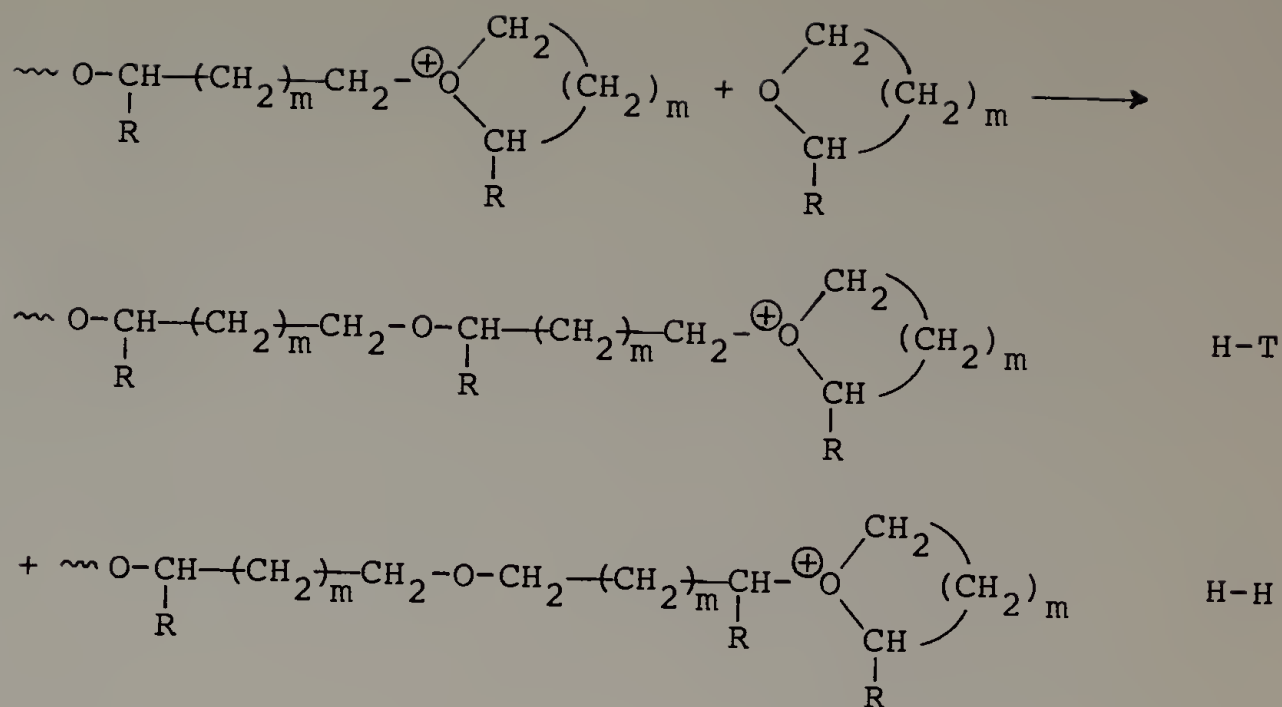


$$n = 1, 2, 3, \dots$$

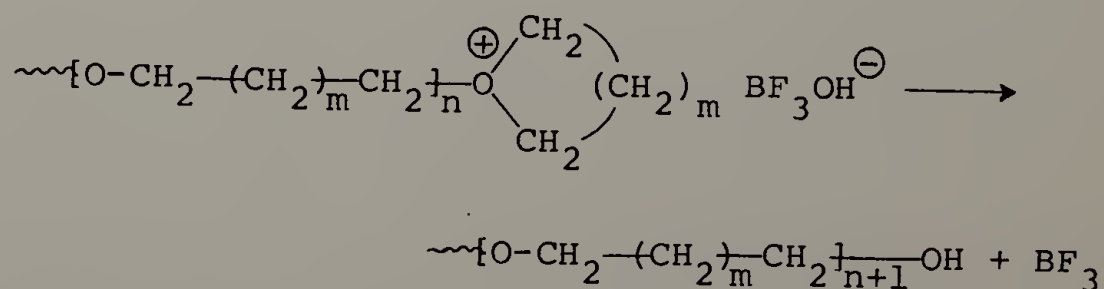
$$m = 2, 3, \dots$$

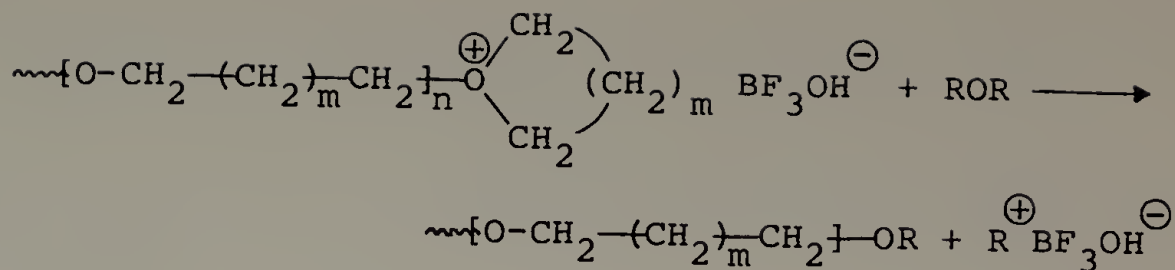
The first step involves an ether exchange reaction resulting in the formation of an oxonium ion in the polymer chain, where  $R_3O^{\oplus}$  may be an initiated monomer or a growing polymer chain. The second step involves an internal ether exchange, resulting in the elimination of different sized cyclic oligomers. The extent to which cyclic oligomer formation occurs depends on the initiator counter ion, temperature, and solvent, temperature being the most important.<sup>24</sup> Generally, as the polymerization temperature is decreased the amount of cyclic oligomer formed decreases.

While propagation in the anionic polymerization of epoxides occurs by a preferential attack of the alkoxide at the primary carbon adjacent to the epoxide oxygen,<sup>19</sup> propagation in cationic polymerizations of cyclic ethers occurs by an essentially random attack of the incoming monomer at either carbon adjacent to the ether oxygen, regardless of substitution. This lack of specificity in addition does not affect polymers from monomers without substituents on the carbons adjacent to the ether oxygen, but polymers from monomers with such substituents have very different backbone structures. Specifically, almost equal numbers of H-T, or normal, and H-H, or abnormal, linkages are formed. Thus, while crystalline polymers can be prepared from substituted epoxide monomers using anionic initiators,<sup>15</sup> only amorphous materials can be prepared from the same monomers using cationic initiators.<sup>25</sup>



Polymers from epoxides prepared using cationic initiators are normally low molecular weight materials similar to those prepared in anionic polymerizations, while higher molecular weights can be achieved from larger ring cyclic ethers. The reason for this is the high reactivity of the epoxides, which not only promotes polymerization, but also transfer and termination reactions. Some of the transfer reactions have been described on previous pages. Termination reactions can occur by attack at the propagation center by counterion decomposition products or fortuitous nucleophilic species present in the reaction system.



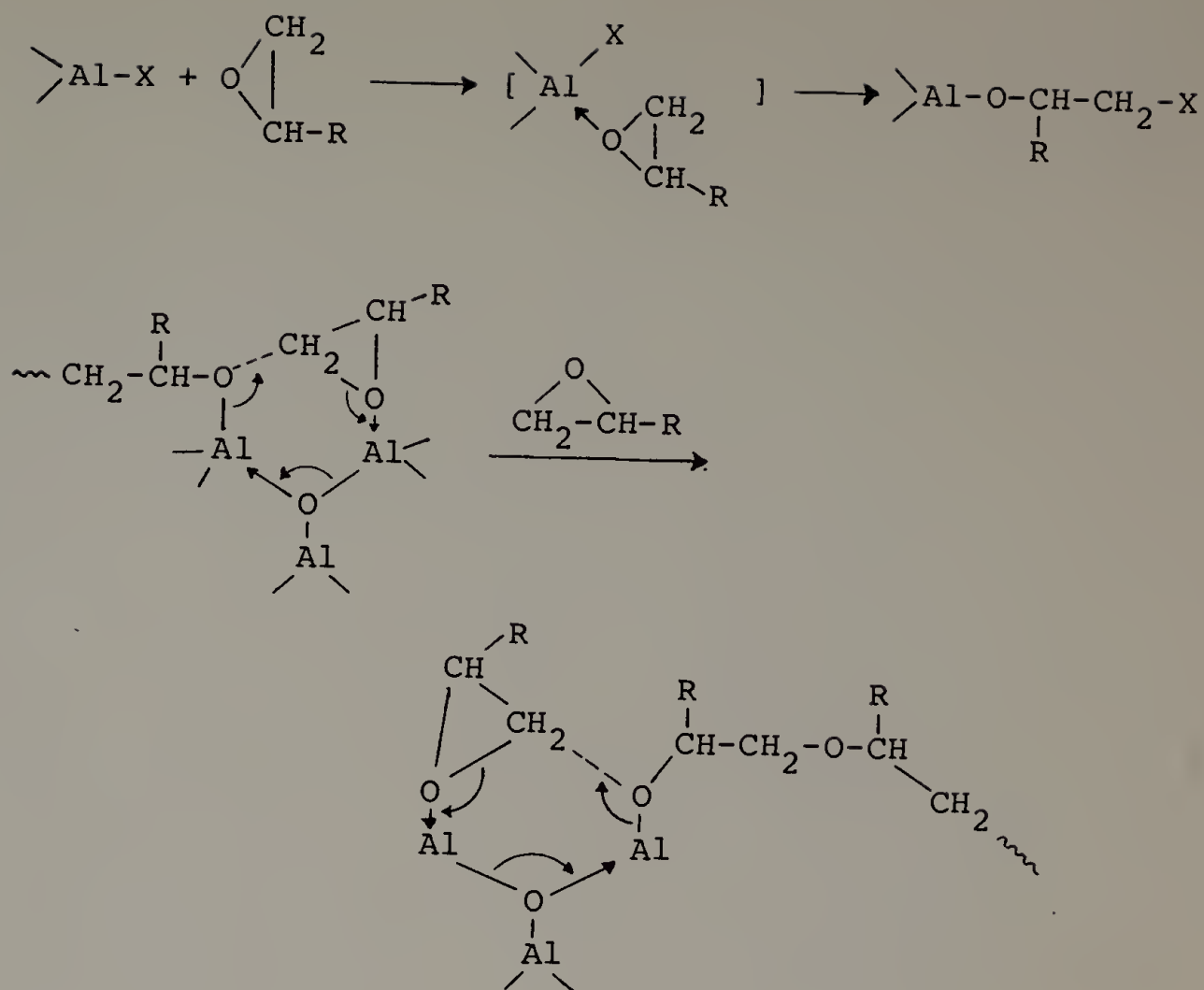


D. Coordinate polymerization. Until the mid-1950s, preparation of high molecular weight poly(alkylene oxides) was only reported in a small number of cases.<sup>26,27</sup> Since then, progress in this area has occurred in two relatively distinct directions. For cyclic ethers with four or more ring members, the greatest advances have come in cationic polymerizations using initiators with stable counterions.<sup>28-30</sup> In the case of the epoxides, the greatest advances have come with the development of a variety of unique and highly effective partially hydrolyzed organometallic initiator systems, or coordinate initiators.<sup>31-34</sup>

The original initiator system recognized as a coordinate initiator was a reaction product between ferric chloride and propylene oxide.<sup>31</sup> This system was prepared by treating a solution of ferric chloride in ether with propylene oxide at 60°C or below, and gave a solid precipitate with the formula  $FeCl_3(C_3H_6O)_{4,5}$  with one inorganic chlorine atom. When this, and similar, initiator systems were used to polymerize ethylene oxide,<sup>31,35,36</sup> propylene oxide,<sup>31,35</sup> styrene oxide,<sup>37</sup> and the epihalohydrins,<sup>36,38,39</sup> high molecular weight, crystalline

materials were produced. A large number of initiator systems have since been developed which have been used to prepare high molecular weight epoxide polymers. Of these, the most important have been based on group II and III organometallics, primarily zinc,<sup>40</sup> aluminum,<sup>33,34</sup> and magnesium<sup>41</sup> alkyl and alkoxide compounds. The initiators are normally monometallic, although bimetallic initiators have been studied.<sup>42,43</sup> The organometallic compounds are coupled by reacting them with water, a diol, or an amine, which effectively reduces the Lewis acidity of the organometallic compound and produces an active initiation center. These initiators may be further modified with regard to Lewis acidity and steric environment by the addition of chelating compounds such as diketones, ketoacids, and hydroxy esters. The most commonly used chelating compound used is acetyl acetone (2,4-pentanedione, AcAc).<sup>44</sup> Given the wide variety of organometallic, coupling, and chelating compounds which can be used, initiators with very different steric and electronic environments can be prepared.

Polymerization of epoxides using the coordinate initiator systems is proposed to proceed without discrete charge formation, as opposed to anionic and cationic polymerizations.<sup>8,9</sup> A proposed mechanism, shown here with aluminum as the metallic atom, is seen as follows.<sup>44</sup> This mechanism is based on several facts. The first concerns



the high molecular weights formed during these polymerizations. Both anionic and cationic epoxide polymerizations are subject to characteristic chain transfer and termination reactions which limit the molecular weights to very low values. If discrete ionic species do not exist, these transfer and termination reactions should be suppressed, allowing propagation to predominate and high molecular weight polymers to be formed. The involvement of more than one metal atom is proposed to account for experimental results showing that inversion of configuration occurs at the ring opening carbon. This result requires a rearward,  $S_N2$

attack by the metal bound alkoxide on the coordinated monomer. Such a result can not be adequately explained if only one metal atom is involved in propagation. While only two metal atoms are shown in this mechanism, it is very possible that more than two are actually involved in propagation. Also, as shown in this mechanism, attack only occurs at the primary carbon atom. However, ring opening can occur at either carbon, leading to some H-H units in the polymers.<sup>44</sup> This is in accord with the coordination of an epoxide to a Lewis acid initiation center, a cationic process. The more acidic (Lewis) and less hindered the initiator site becomes, the more ring opening will occur at the secondary, asymmetric carbon, leading to H-H units. Thus, further classification of these initiators as coordinate anionic or cationic should only be done in rare cases.

## II. Functionally Substituted Polymers-- Preparation and Properties

A. General background. Polymers which are substituted with regularly spaced functional groups have been known almost as long as unsubstituted polymers. Initial research and development in the field of functionally substituted polymers was conducted in order to develop materials with bulk mechanical properties different from the parent unsubstituted polymer. For instance, while polyethylene is a

tough, highly crystalline, non-polar material, substitution on every second carbon atom in the polymer backbone with an amide group gives a brittle, amorphous, water soluble material. These studies have led to the development of many commercially important materials, and have aided in understanding the effect of the functional groups on the polymerization behavior of the monomers. The greatest amount of work has been conducted on polymers with a substituted ethylene backbone, including the acrylates<sup>45</sup> (ester groups), acrylonitriles<sup>46</sup> (nitrile groups), acetates<sup>47</sup> (acetate groups), vinyl halides<sup>48</sup> (halide groups), and acrylamides<sup>49</sup> (amide groups) (Table 1). In all of these cases, the functional group is attached directly to the polymer chain. Functionally substituted polyesters,<sup>50</sup> polyamides,<sup>51</sup> polyurethanes,<sup>52</sup> and polybutadienes<sup>53</sup> have also been prepared, giving materials with bulk mechanical properties much different than those of the parent polymer.

More recently studies have been undertaken to prepare substituted polymers with the goal of utilizing some property of the polymer bound functional group. This property may be a reactivity towards displacement reactions, allowing new functional groups to replace the old,<sup>54</sup> activity as a catalyst for a chemical reaction,<sup>55</sup> or as a spectroscopically active site, such as U.V. absorbers.<sup>56-58</sup> Once again, the greatest amount of work has been conducted on polymers with a substituted ethylene backbone, with some

TABLE 1  
SOME TYPICAL FUNCTIONALLY SUBSTITUTED POLYMERS

Functional Monomer	Polymer Characteristics	Ref.
$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_2=\text{CH}-\text{C}-\text{OR} \\   \\ \text{R}' \end{array}$ <p style="text-align: center;"><math>\text{R}'=\text{H}, \text{Alkyl}</math></p>	<p><math>\text{R}'=\text{H}</math> tough, rubbery materials</p> <p><math>\text{R}'=\text{Alkyl}</math> glassy, brittle to rubbery</p>	45
$\text{CH}_2=\text{CH}-\text{C}\equiv\text{N}$	Brittle, relatively insoluble material, useful in copolymers to impart oil resistance	46
$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_2=\text{CH}-\text{O}-\text{C}-\text{CH}_3 \end{array}$	Amorphous thermoplastic used in adhesives and as poly(vinyl alcohol) precursor	47
$\text{CH}_2=\text{CH}-\text{X}$ <p style="text-align: center;"><math>\text{X}=\text{Halogen}</math></p>	Tough, rigid polymer used both in rigid and flexible forms as moldings, fibers, and sheetings	48
$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_2=\text{CH}-\text{C}-\text{NH}_2 \end{array}$	Hard, glassy polymer. High M.W. polymer gives extremely viscous aqueous solutions.	49
$\begin{array}{c} \text{CH}_2\text{Cl} \\   \\ -\{\text{CH}_2-\text{C}-\text{C}-\text{O}-\} \\   \quad \parallel \\ \text{CH}_2\text{Cl} \quad \text{O} \end{array}$	Highly crystalline material, M.P. 295°C	50
$\begin{array}{c} \text{O} \\ \parallel \\ -(\text{NH}-\text{C}-\text{CH})- \\   \\ \text{CH}_2 \\   \\ \text{CH}_2 \\   \\ \text{O}=\text{C}-\text{O}-\text{CH}_2-\text{CH}_2-\text{C}_6\text{H}_5 \end{array}$		51

TABLE 1 (Continued)

Functional Monomer	Polymer Characteristics	Ref.
$\begin{array}{c} \text{O} \qquad \qquad \text{O} \\ \parallel \qquad \qquad \parallel \\ -\{(\text{CH}_2)_4-\text{O}-\text{C}-\text{N}-\text{CH}_2-\text{CH}_2-\text{N}-\text{C}-\text{O}-\} \\ \qquad \qquad \qquad   \qquad \qquad \qquad   \\ \qquad \qquad \qquad \text{CH}_2 \qquad \qquad \text{R} \\ \qquad \qquad \qquad   \\ \qquad \qquad \qquad \text{CH}_2 \\ \qquad \qquad \qquad   \\ \qquad \qquad \qquad \text{OH} \end{array}$ <p><math>\text{R}=\text{H}, -(\text{CH}_2)_3-\text{CH}=\text{CH}_2</math></p>	Elastomers with high melt viscosity	52
$\begin{array}{c} -(\text{CH}-\text{CH}=\text{CH}-\text{CH}_2)- \\   \\ \text{C}\equiv\text{N} \end{array}$	Amorphous thermoplastic	53
$\begin{array}{c} -(\text{CH}_2-\text{C}=\text{CH}-\text{CH}_2)- \\   \\ \text{C}\equiv\text{N} \end{array}$	Semicrystalline thermoplastic	

work having been conducted with various condensation polymers. These substituted polymers also have, with few exceptions, the functional group directly attached to the polymer backbone. This may introduce considerable steric hindrance to the functional group, which in turn can lead to a serious decrease in reactivity.<sup>59,60</sup>

A major class of substituted polymers which has utilized the polymer bound functional groups, both to modify bulk mechanical properties and for chemical modifications, are the poly(alkylene oxides). This class of polymers will be described in the next section.

B. Functional epoxides. Until the coordinate initiator systems for epoxide polymerization were developed, the field of epoxide polymers was limited to a very small number of simple monomers. Since that time, however, the field has broadened considerably, and almost every class of substituted epoxides has been studied. A survey of the monomers which have been studied is shown in Table 2. Many different substituted poly(alkylene oxides) have been prepared by carrying out substitution reactions on polymers such as poly(epichlorohydrin). However, the substitution reactions can rarely be carried out to completion without significantly altering the molecular weight of the polymers, making this a technique which has been ill-suited for the preparation of pure substituted poly(alkylene oxide)

TABLE 2  
FUNCTIONAL EPOXIDE POLYMERS

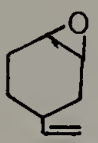
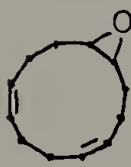




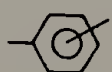
Functional Epoxide	Polymer Characteristics	Ref.
$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{CH}_2 - \text{CH} - \text{CH} = \text{CH}_2 \end{array}$	rubbery	62-66
$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{CH}_2 - \text{CH} - \text{CH}_2 - \text{CH}_2 - \text{CH} = \text{CH}_2 \end{array}$		67,68
$\begin{array}{c} \text{O} \quad \text{CH}_3 \\ \diagup \quad \diagdown \quad   \\ \text{CH}_2 - \text{CH} - \text{C} - \text{CH} = \text{CH}_2 \\ \quad \quad   \\ \quad \quad \text{CH}_3 \end{array}$	elastomer, useful potting compound	69
	useful as cross-link site	64
	useful as cross-link site	64
$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{CH}_2 - \text{CH} - \text{CH}_2 - \text{O} - \text{CH} = \text{CH}_2 \end{array}$		70
$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{CH}_2 - \text{CH} - \text{CH}_2 - \text{O} - \text{CH}_2 - \text{CH} = \text{CH}_2 \end{array}$	useful as cross-link site	70
$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{CH}_2 - \text{CH} - \text{CH}_2 - \text{O} - \{ \text{CH}_2 - \text{CH}_2 - \text{O} \}_n - \text{C} = \text{CH}_2 \\ \quad \quad \quad \quad \quad \quad \quad \quad   \\ \quad \quad \quad \quad \quad \quad \quad \quad \text{CH}_2\text{X} \end{array}$ <p><math>n=0-6 \quad \text{X}=\text{Cl}, \text{Br}, \text{I}</math></p>	tough, rubbery, translucent, easily vulcanized	71
$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{CH}_2 - \text{CH} - \text{CH}_2\text{X} \end{array}$ <p><math>\text{X}=\text{F}, \text{Cl}, \text{Br}</math></p>	highly crystalline	38,39
	amorphous	72



TABLE 2 (Continued)

Functional Epoxide	Polymer Characteristics	Ref.
$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{R}-\text{CH}-\text{CH}-(\text{CH}_2-\text{O})_n-\text{A}-(\text{NR}'\text{R}'')_{n'} \end{array}$ <p> <math>\text{R}', \text{R}''</math> alkyl, aryl, haloaryl, etc.  <math>\text{A}</math> alkylene, cycloalkylene, arylene  <math>n'</math> 1-3  <math>n</math> 0-1  <math>\text{R} (\text{R}'\text{R}''\text{N})_n-\text{A}-(\text{O}-\text{CH}_2)_n-</math> </p>	Tacky elastomers	80
$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{CH}_2-\text{CH}-\text{CH}_2-\text{NR}_1\text{R}_2 \end{array}$ <p><math>\text{R}_1, \text{R}_2</math> alkyl</p>	Low molecular weight, oily materials	81
$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{CH}_2-\text{CH}-\text{CH}_2-\text{N} \end{array}$ 	Low molecular weight, oily material	82
$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{CH}_2-\text{CH}-\text{CH}_2-\text{N} \end{array}$ 	Low molecular weight, oily material	82
$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{R}-\text{CH}-\text{CH}-\text{Y}-\text{OSi} \begin{array}{l} \diagup \text{R}' \\ \diagdown \text{R}'' \\ \text{R}''' \end{array} \end{array}$ <p> <math>\text{Y}-(\text{CR}_1\text{R}_2)_n</math> , <math>-(\text{CR}_1\text{R}_2)_n</math>  ,  <math>-(\text{CR}_1\text{R}_2)_n</math>  ,  </p>	Hydrophilic elastomeric or thermoplastic materials	83

(continued next page)

TABLE 2 (Continued)

Functional Epoxide	Polymer Characteristics	Ref.
$R_1, R_2, R', R'', R''' \quad \text{H, alkyl, cycloalkyl, haloalkyl, aryl, etc.}$ $R \quad R_1, R_2, Y-\text{OSi} \begin{array}{l} \nearrow R' \\ \text{---} R'' \\ \searrow R''' \end{array}$		
$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{CH}_2 \text{---} \text{CH} \text{---} \text{Si}(\text{CH}_3)_3 \end{array}$	Low molecular weight, oily materials	84
$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{CH}_2 \text{---} \text{CH} \text{---} \text{CH}_2 \text{---} \text{O} \text{---} \text{Si}(\text{CH}_3)_3 \end{array}$		
$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{CH}_2 \text{---} \text{CH} \text{---} \text{CH}_2 \text{OH} \end{array}$	Low molecular weight, viscous oils	85, 86, 87
$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{CH}_3 \text{---} \text{C} \text{---} \text{CH} \text{---} \text{C}(=\text{O}) \text{---} \text{CH}_3 \\   \\ \text{CH}_3 \end{array}$		88
$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{CH}_2 \text{---} \text{CH} \text{---} \text{CH}_2 \text{---} \text{O} \text{---} \text{C}_6\text{H}_3(\text{OH})(\text{C}(=\text{O})\text{C}_6\text{H}_5) \\   \\ \text{R} \end{array}$ $\text{R} = \text{H, CH}_3, \text{ t-C}_4\text{H}_9$	Low molecular weight, oily materials	89
$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{CH}_2 \text{---} \text{CH} \text{---} \text{C}(=\text{O}) \text{---} \text{H} \end{array}$	Low molecular weight, oily materials	90, 91, 92, 94
$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{CH}_2 \text{---} \text{C} \text{---} \text{CH} \\   \\ \text{CH}_3 \end{array}$		94
$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{CH} \text{---} \text{C} \text{---} \text{CH} \\   \quad   \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$		

(continued next page)

TABLE 2 (Continued)


Functional Epoxides	Polymer Characteristics	Ref.
$  \begin{array}{c}  \text{O} \\  \diagup \quad \diagdown \\  \text{CH} - \text{CH} - \text{CH} \\    \quad \quad \parallel \\  \text{CH}_3 \quad \quad \text{O}  \end{array}  $	<div style="text-align: center;">  </div>	93
$  \begin{array}{c}  \text{O} \\  \diagup \quad \diagdown \\  \text{CH}_2 - \text{CH} - \text{CH}_2 - \text{R}  \end{array}  $ <p> <math>\text{R} = \text{CH}_2\text{CN}, \text{CH}_2\text{CH}_2\text{CN},</math>  <math>\text{CH}_2\text{OCH}_2\underset{\text{Cl}}{\text{CH}}\text{CN},</math>  <math>\text{CH}_2\text{OCH}_2\text{CN}, \text{CH}_2\text{OCH}_2\text{CH}_2\text{CN},</math>  <math>\text{CH}_2\text{OCH}_2\text{OCH}_2\text{CH}_2\text{CN}</math> </p>		97
$  \begin{array}{c}  \text{O} \\  \diagup \quad \diagdown \\  \text{CH}_2 - \text{CH} - \text{C} \begin{array}{l} \parallel \\ \text{NH}_2 \end{array}  \end{array}  $		98
$  \begin{array}{c}  \text{O} \\  \diagup \quad \diagdown \\  \text{CH} - \text{CH} - \text{C} \begin{array}{l} \parallel \\ \text{NR}''_2 \end{array} \\    \\  \text{R}'  \end{array}  $ <p> <math>\text{R}' = \text{alkyl, aryl}</math>  <math>\text{R}'' = \text{alkyl}</math> </p>		99
$  \begin{array}{c}  \text{O} \\  \diagup \quad \diagdown \\  \text{CH}_2 - \text{CH} - \text{CH}_2 - \text{N} \begin{array}{c} \diagup \quad \diagdown \\ \text{O} \quad \text{O} \end{array}  \end{array}  $	Low molecular weight, oily material	100
$  \begin{array}{c}  \text{O} \\  \diagup \quad \diagdown \\  \text{CH}_2 - \text{CH} - \text{C} \begin{array}{l} \parallel \\ \text{OR} \end{array}  \end{array}  $ <p> <math>\text{R} = \text{C}_{1-4} \text{ alkyl}</math>  <math>\text{R} = \text{C}_{2-10} \text{ alkyl, aralkyl, aryl}</math>  <math>\text{R} = \text{C}_2\text{H}_5</math> </p>	Tough, somewhat rubbery, semi- crystalline materials	101 102-104 105-110

TABLE 2 (Continued)

Functional Epoxides	Polymer Characteristics	Ref.
$\text{C}_2\text{H}_5-\text{O}-\overset{\text{O}}{\parallel}\text{C}-\text{CH}-\overset{\text{O}}{\triangle}-\text{CH}-\overset{\text{O}}{\parallel}\text{C}-\text{O}-\text{C}_2\text{H}_5$	Low molecular weight, oily material	111
$\text{CH}_3\text{O}-\overset{\text{O}}{\parallel}\text{C}-\text{CH}-\overset{\text{O}}{\triangle}-\text{CH}-\overset{\text{O}}{\parallel}\text{C}-\text{OCH}_3$	Low molecular weight, oily material	112
$\text{CH}_2-\overset{\text{O}}{\triangle}-\text{CH}-\overset{\text{O}}{\parallel}\text{C}-\text{OM}$	Low molecular weight, very viscous oil	86
M=alkali metal		

homopolymers. Therefore, those polymers will not be considered.

A considerable amount of effort has been directed towards the development of amorphous poly(alkylene oxides), such as the homopolymers of propylene oxide and epichlorohydrin, and a 50:50 ethylene oxide:epichlorohydrin copolymer, into commercial rubbers.<sup>61</sup> Several of these studies have dealt with vinyl substituted epoxides as a means of introducing crosslinking sites into these polymers. Butadiene monoxide has been most widely mentioned in this regard,<sup>62-65</sup> and its incorporation gives polymers which can be cured using standard sulfur vulcanization recipes. Butadiene monoxide has also been homopolymerized by <sup>60</sup>Co gamma irradiation, resulting in the formation of the vinyl substituted polymer in poor yields.<sup>66</sup> Evidence to support the claim of epoxide polymerization includes the absence of epoxide bands and the presence of a strong ether band in the I.R. spectrum, and the fact that polymerization proceeds virtually unchanged in the presence of radical inhibitors. Diallyl monoxide (3-butenyl oxirane)<sup>67,68</sup> has been copolymerized with THF, 3,3-bis(chloromethyl)oxetane, and propylene oxide using a  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}$  initiator system. The THF and 3,3-bis(chloromethyl)oxetane copolymers were shown to be useful rubbers after vulcanization. Copolymerization with propylene oxide ( $r_1$ ) demonstrated that diallyl monoxide ( $r_2$ ) is considerably less reactive than propylene oxide

under these conditions ( $r_1 = 1.93 \pm 0.18$ ;  $r_2 = 0.08 \pm 0.01$ ). Homo- and copolymerizations of 3,3-dimethyl-4,5-epoxy-1-pentene(1,1-dimethyl-2-propenyloxirane), which possesses no allylic hydrogens, with propylene oxide using the  $\text{Zn}(\text{C}_2\text{H}_5)_2/\text{H}_2\text{O}$  (1/0.5) initiator system have been studied.<sup>69</sup> The absence of allylic hydrogens in the polymers results in materials with better oxidative stability. Polymerizations were carried out at 80°C for 24 hours in benzene and gave low molecular weight materials in yields of 10 to 60%. The homopolymer was described as being a useful potting compound. The copolymer was readily halogenated and gave fire-resistant materials incapable of producing HCl or HBr. Several unsaturated cycloaliphatic epoxides have been copolymerized with saturated epoxides, such as propylene oxide and epichlorohydrin, to give sulfur vulcanizable polymers.<sup>64</sup> The polymerizations involved 1,2-epoxy-4-vinylcyclohexane and 1,2-epoxy-5,9-cyclododecadiene using  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$  (1/0.5/0.5,1) initiator systems, and gave high molecular weight elastomers.

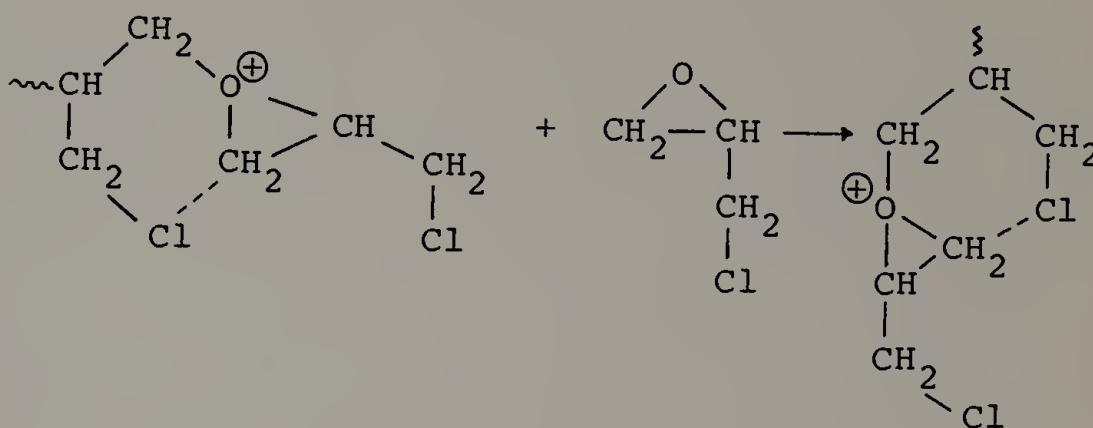
Vinyl substituted glycidyl ethers have also been used to introduce crosslinking sites into epoxide polymers, and have been studied as homopolymers as well. High temperature (130°C) coordinate polymerizations of vinyl glycidyl ether were studied using several solvents and initiators, and it was demonstrated that the order of the reactions was independent of the dielectric constant of the

solvent and the aluminum alkoxide used as the initiator.<sup>70</sup> Halomethyl vinyl glycidyl ethers, synthesized by the reaction of glycerol dihalohydrins with various alkylene oxides, were homo- and copolymerized with several saturated epoxide monomers using  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$  initiators.<sup>71</sup> The polymers were tough, translucent elastomers which could be crosslinked without sulfur, thereby avoiding problems such as poor oil, solvent, and heat resistance found in sulfur cured rubbers.

The most widely studied group of substituted epoxide monomers is the halogen substituted epoxides. The halogen substituted polymers have been studied extensively due to the excellent bulk properties which many of the high molecular weight polymers possess, the relatively high flame resistance these polymers exhibit, and the ability to carry out substitution reactions at the halogen bearing center. Of these polymers, the polyepihalohydrins have been studied the most. The first high molecular weight polyepihalohydrins, the fluoro-, chloro-, and bromo-substituted polymers, were highly crystalline polymers prepared using a  $\text{FeCl}_3$ ·propylene oxide or epichlorohydrin initiator system.<sup>38,39</sup> These polymers were tough thermoplastics. In contrast, the first high molecular weight amorphous polyepihalohydrins, prepared using both the  $\text{Al}(\text{iso-C}_4\text{H}_9)_3/\text{H}_2\text{O}$  (1/0.5) and  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$  (1/0.5/0.5) initiator systems, were found to be excellent

elastomers.<sup>72</sup> They were also found to be vulcanizable, and yielded polymers with high tensile strength and excellent solvent resistance.

Unlike most epoxide monomers, the epihalohydrins can be polymerized to high molecular weights using cationic as well as coordinate initiators.<sup>73</sup> However, a mechanism involving ultimate unit coordination has been proposed to explain the formation of high molecular weight polymer using cationic initiators, and is shown below. In this



mechanism, the halogen atom serves as an electron donor to stabilize the electron deficient ring through a 6-membered ring intermediate. While this mechanism differs fundamentally from that proposed for coordinate anionic polymerizations, it is apparent that an increase in the electron density of the propagation site, effectively moderating the charge density, results in stabilization of the propagation site. Thus, this situation more closely resembles the coordinate anionic than cationic (ionic) polymerizations.

Several halogenated glycidyl ethers have also been polymerized. 2-Chloroethyl glycidyl ether has been polymerized using cationic initiators to give low molecular weight (M.W. 1124) materials.<sup>75</sup> Post reaction of this polymer with various amino compounds gave insoluble materials which were described as being useful for dehydrating paper pulp. Polymerization of this same monomer using coordinate initiators gave high molecular weight elastomeric materials.<sup>74</sup> Post reactions of these polymers were carried out to give graft copolymers and phosphorous substituted polymers. Halomethyl glycidyl ethers have been homo- and copolymerized with saturated epoxide monomers using  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$  initiators, giving tough, translucent elastomers suitable for non-sulfur cross-linking.<sup>71</sup>

A series of 1,1-disubstituted epoxides, including several halogenated monomers such as 1,1-difluoro, dichloro, dibromo, bis(fluoromethyl), bis(chloromethyl), and bis(bromomethyl)ethylene oxides, have been polymerized cationically to give low molecular weight polymers which were described as useful positive photoresists.<sup>76</sup> Various halogenated 1,2-disubstituted epoxides have been polymerized and have been found to yield interesting high molecular weight thermoplastic materials. Polymerizations of a 70:30 trans:cis 1,4-dichloro-2,3-epoxybutane mixture and the pure trans monomer were carried out at  $-78^\circ\text{C}$  in

dichloromethane using the  $\text{Al}(\text{iso-C}_4\text{H}_9)_3/\text{H}_2\text{O}$  (1/0.7) initiator system and gave high molecular weight crystalline polymers.<sup>54</sup> Post reaction of these polymers with metal thiosulfates gave materials useful as coatings, adhesives, sizing agents, and emulsifiers. The extent of substitution of the chlorine atoms with thiosulfate groups was always very low. Studies of the polymerizations of the pure cis- and trans-1,4-dichloromethyl-2,3-epoxybutanes under the same conditions indicated that polymers with very different properties were produced.<sup>77</sup> The cis-monomer yielded a racemic-diisotactic polymer with a melting point of 235°C, while the trans monomer yielded a meso-diisotactic with a melting point of 145°C. Using an AcAc modified  $\text{AlR}_3/\text{H}_2\text{O}$  initiator system, only low conversions to polymer were obtained in the homo- and copolymerization of the cis-isomer with ethylene oxide. The low reactivity of the cis-monomer using the AcAc-modified initiator was postulated to occur due to steric hindrance encountered on approach of the monomer to the initiator site, and a decrease in the epoxide oxygen basicity due to the electron withdrawing chloromethyl groups, decreasing the coordinating power of the monomer to the initiator.<sup>77</sup>

Polymerizations of several other classes of substituted epoxides have been studied, but the examples for each class are fewer in number and in less detail. Those examples present in the literature will be discussed in the

following pages.

One example of a polymerization of a nitro-substituted epoxide is present in the patent literature. 2-Fluoro-2,2-dinitroethyl glycidyl ether, prepared from allyl alcohol, 1,1-dinitroethylene, perchloryl fluoride, and a peracid, was polymerized at room temperature using several Lewis acids as initiators, and gave liquid materials with molecular weights of 800 to 2700.<sup>78</sup> The polymers were developed for use as energetic (oxygen supplying) binders in explosives formulations.

Homo- and copolymerizations of cyclic epoxy sulfones have been studied using several coordinate initiators.<sup>79</sup> The epoxy substituted 5, 6, and 7-membered cyclic sulfones were homo- and copolymerized with several common epoxide and oxetane monomers at 50°C for 30 to 40 hours using the  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$  (1/0.5/0.5),  $\text{Al}(\text{iso-C}_4\text{H}_9)_3/\text{H}_2\text{O}$  (1/0.5), and  $\text{Mg}(\text{C}_8\text{H}_{17})_2/\text{NH}_3$  (1/0.6) initiator systems. Very high initiator concentrations were necessary for these polymerizations, especially in the case of the homopolymerizations, where initiator concentrations up to 20 mole% based on monomer were required to achieve yields normally less than 20%. The polymerizations yielded ether insoluble, ether soluble, and water soluble fractions, varying from one another in degree of polymerization and crystallinity. The ether insoluble homopolymer of 3,4-epoxysulfolane was found to be a medium to highly

crystalline material with a melting point of 307 to 344°C. The ether soluble homopolymer was found to be a low to medium crystallinity polymer with a melting point of 142 to 193°C, while the water soluble polymer ranged from an amorphous to slightly crystalline material with a melting point of 118 to 166°C. The polymers were hydrophilic materials suggested for uses as yarns, fabrics, coatings, and adhesives.

The polymerizations of several amino substituted epoxides have been described in the literature. A variety of cyclic and acyclic mono- and 1,2-diamino substituted epoxides have been homo- and copolymerized at 30 to 50°C for 2 to 100 hours using the  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$  (1/0.5/0.5, 1),  $\text{Al}(\text{iso-C}_4\text{H}_9)_3/\text{H}_2\text{O}$  (1/0.5), and  $\text{Mg}(\text{C}_2\text{H}_5)_2/\text{NH}_3$  (1/0.5) initiator systems.<sup>80</sup> As in the case of the sulfolane substituted epoxides,<sup>79</sup> very high initiator concentrations, 10 to 20 mole% based on monomer, were required to produce polymers in yields normally less than 20%. Incorporation of the amino substituted epoxides into the copolymers typically was only 20 to 25% of that in the monomer feed solution. The polymers were described as tacky, elastomeric materials in their unquaternized form, while being tacky elastomers to hard, solid films in their quaternized form, and were proposed as useful flocculating agents, textile sizes, and paper coatings. A series of epi-N,N-dialkylaminohydrins were polymerized using the  $\text{Al}(\text{C}_2\text{H}_5)_3/$

$\text{H}_2\text{O}$  (1/0.5,1,1.5),  $\text{Zn}(\text{C}_2\text{H}_5)_2/\text{H}_2\text{O}$  (1/0.5), and  $\text{Zn}(\text{C}_2\text{H}_5)_2/\text{CH}_3\text{OH}$  (1/1.95) initiator systems.<sup>81</sup> The polymers were produced in yields of 5 to 30%, and were only low molecular weight, oily materials. In both of these examples, the low yields and molecular weights have been attributed to the greater nucleophilicity of the amino groups compared to the epoxide groups, resulting in a preferential coordination, or reaction, of the amino group with the initiators. This is most evident in the more acidic (Lewis) initiators of the latter example, where no chelating agents were used. Indole and carbazole substituted epoxide monomers, prepared by reacting the sodium salts of indole and carbazole with epichlorohydrin, have been polymerized at room temperature for 1 week using KOH as initiator in hexamethylphosphoramide.<sup>82</sup> The indole substituted polymer was obtained in a 93% yield, and the carbazole substituted polymer was obtained in a 69% yield.

A variety of silyl substituted epoxides have been polymerized, although the polymers were not always isolated in that form. A series of mono- and bisilyl esters of epoxy alcohols have been prepared and homo- and copolymerized with several common epoxide and oxetane monomers using the  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$  (1/0.5/0.5,1) and  $\text{Al}(\text{iso-C}_4\text{H}_9)_3/\text{H}_2\text{O}$  (1/0.5) initiator systems.<sup>83</sup> The polymerizations gave high molecular weight materials in good yields, but were not isolated in their silyl ester form. Instead, they were

isolated as the corresponding hydroxyl substituted polymers after treating the polymers with active hydrogen compounds, such as methanol, during the workup. The hydroxyl substituted polymers were soluble in water, methanol, and dilute aqueous base, and were suggested to be useful as flocculating agents, fibers, films, and rigid or elastomeric foams. Optically active polymers from racemic trimethylsilyl-ethylene oxide and trimethylsilyl glycidyl ether have been prepared using optically active coordinate initiators such as  $\text{Zn}(\text{C}_2\text{H}_5)_2/1\text{-menthol}$  (1/1.5) and  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/1\text{-menthyl ethyl ether}$ .<sup>84</sup> The polymers, produced in yields of 7 to 78% with intrinsic viscosities of 0.1 to 0.2 dl/g, showed only a small optical activity ( $[\alpha]_{\text{D}}^{25} = 2.5$ ), indicating a small amount of asymmetric induction.

Only one hydroxyl substituted epoxide, glycidol, has been polymerized. Several anionic initiators have been tested in room temperature polymerizations of glycidol, and it was found that conversion increased with time while the molecular weight stayed constant at approximately 440, or a degree of polymerization of 6.<sup>85</sup> This result is hardly surprising since each monomer unit can act as an efficient chain transfer agent by donating its hydroxyl proton. These polymers, described as viscous oils, showed no unsaturation by infrared spectroscopy. Anionic polymerization of glycidol using initiators such as 1,2,4-trimethylpiperazine has been mentioned in a patent, but no

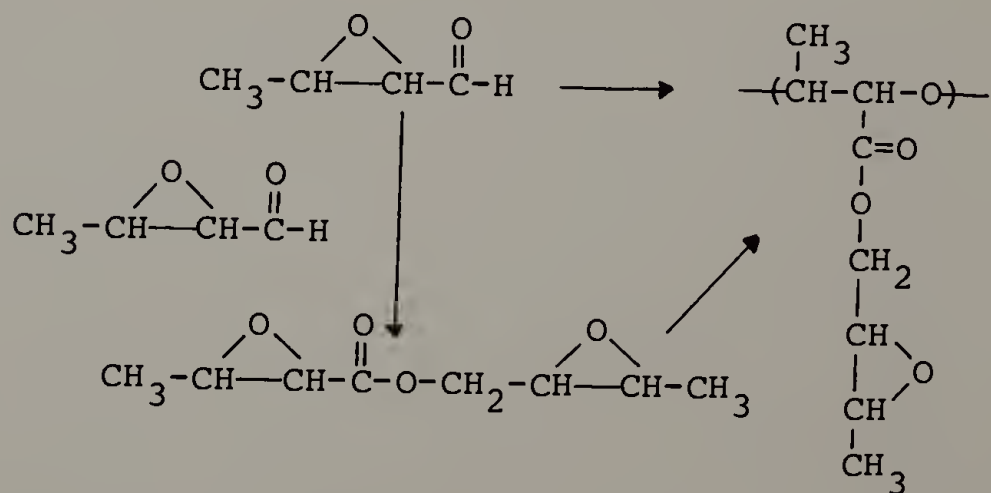
experimental details were presented.<sup>86</sup> Homo- and copolymerizations of glycidol with several common epoxide monomers have been carried out using alkyl or alkoxide substituted Group II or III metals as initiators, but once again, no details were presented.<sup>87</sup>

One example of the polymerization of a ketone substituted epoxide has been presented. 3,4-Epoxy-4-methyl-2-pentanone was copolymerized with 3-chloromethyloxetane using the  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}$  (1/1) initiator system, and its activity was compared to propylene oxide and methyl glycidyl ether in this system.<sup>88</sup>

Several derivatives of 2-hydroxybenzophenone-glycidyl ether have been polymerized using strong protonic and Lewis acid initiators to give oligomeric materials claimed to be useful as U.V. absorbers.<sup>89</sup> For example, 2-hydroxybenzophenoneglycidyl ether was polymerized for 3 hours at  $-50^\circ\text{C}$  using  $\text{SnCl}_4$  as initiator to give an oligomer with a molecular weight of 1020, or a degree of polymerization of 4.

The polymerization of aldehyde substituted epoxides has been studied from theoretical and practical points of view. In early patents assigned to Shell Oil Co., glycid-aldehyde was polymerized using anionic<sup>90</sup> and cationic<sup>91</sup> initiators, such as tertiary amines and Lewis acids, respectively, and gave low molecular weight polymers in both cases. Polymerization of glycidaldehyde was studied

at  $-78^{\circ}\text{C}$  and room temperature using  $\text{Al}(\text{iso-C}_3\text{H}_7\text{O})_3$  and  $\text{Al}(\text{C}_2\text{H}_5)_3$  as initiators, and it was found that the final products depended on the polymerization temperature.<sup>92</sup> A polyacetal, obtained by polymerization through the aldehyde groups, was produced at  $-78^{\circ}\text{C}$ , while a substituted poly(ethylene oxide), obtained by polymerization through the epoxide groups, was produced at room temperature. More recently, the polymerizations of glycidaldehyde and some methyl derivatives have been examined in greater detail.<sup>93,94</sup> These studies have shown that instead of forming simple aldehyde substituted poly(alkylene oxides) or epoxide substituted polyacetals, polymers with very different structures were obtained. In the bulk polymerization of 1-methylglycidaldehyde using  $\text{Al}(\text{iso-C}_3\text{H}_7\text{O})_3$ , a low molecular weight polymer of 2,3-epoxybutyl-1-methyl glycidate was produced.<sup>93</sup> The mechanism for this polymerization is shown below. The first step involves the



dimerization of the monomer induced by the initiator to

give the Tishchenko reaction product. The second step involves polymerization of this dimer through the glycidate epoxide group. The same polymerization mechanism was noted in the polymerizations of glycidaldehyde, 2-methylglycid-aldehyde, and 1,2-dimethylglycidaldehyde in bulk and solution at  $-78$ ,  $20$ , and  $50^{\circ}\text{C}$  using  $\text{Al}(\text{iso-C}_3\text{H}_7\text{O})_3$  as the initiator.<sup>94</sup> Polymerization times of 120 to 2200 hours were used, and polymers with degrees of polymerization of 6 to 18 were formed in yields up to 100%.

Despite the strong complexes formed between nitrile groups and the metal alkyls and alkoxides used as coordinate initiators,<sup>95</sup> several nitrile substituted epoxides have been polymerized. Polymerizations of glycidonitrile, dimethyl glycidonitrile, tetracyanoethylene oxide, and epicyanohydrin were attempted using the  $\text{FeCl}_3 \cdot \text{propylene oxide}$  and  $\text{Zn}(\text{C}_2\text{H}_5)_2/\text{H}_2\text{O}$  initiator systems, but even at very high initiator concentrations, up to 41 mole% based on monomer, no polymers were obtained.<sup>96</sup> Successful homo-, co-, and terpolymerizations of several nitrile substituted epoxides with ethylene or propylene oxides and allyl glycidyl ether, and epichlorohydrin were carried out when the stronger  $\text{Al}(\text{iso-C}_4\text{H}_9)_3/\text{H}_2\text{O}/\text{AcAc}$  (1/0.5/0.5) initiator system was used.<sup>97</sup> Attempts were also made to carry out the same polymerizations using  $\text{FeCl}_3 \cdot \text{propylene oxide}$  or  $\text{Zn}(\text{C}_2\text{H}_5)_2/\text{H}_2\text{O}$  initiator systems, but these were unsuccessful. The monomers prepared and studied were epicyanohydrin,

1,2-epoxy-4-cyanobutane, 2-cyano-2-chloroethyl glycidyl ether, cyanomethyl glycidyl ether, 2-cyanoethyl glycidyl ether, and 2-cyanoethoxymethyl glycidyl ether. Homopolymerizations were carried out at 50°C for 18 to 20 hours using initiator concentrations from 20 to 65 mole% based on monomer, giving tough, snappy elastomers in yields from 10% for 1,2-epoxy-4-cyanobutane to 98% for cyanomethyl glycidyl ether. Epicyanohydrin was not polymerizable under these reaction conditions. In copolymerizations of cyanomethyl glycidyl ether and 2-cyanoethyl glycidyl ether with epichlorohydrin using initiator concentrations of 4 to 38 mole% based on monomer, copolymers with 1 to 2 times the amount of nitrile substituted monomer in the monomer feed were produced in good yields. This behavior was also seen in terpolymerizations of the same monomers with ethylene or propylene oxides and allyl glycidyl ether, except when the nitrile substituted monomer was only present in low concentrations in the monomer feed. After vulcanization, the co- and terpolymers exhibited good solvent and ozone resistance, and good low temperature flexibility. This study showed two general trends seen in other substituted epoxide polymerization systems; first, the initiator concentration required for giving good yields of polymers can be decreased as the nitrile substituted monomer concentration is decreased, and second, at constant initiator concentrations, the yield and molecular weight of copolymers

decrease as the nitrile substituted monomer concentration increases.

The polymerizations of several amide and oxazolidone substituted epoxides have also been studied. Glycidamine has been polymerized using  $\text{ZnR}_2$  or  $\text{AlR}_3/\text{H}_2\text{O}/\text{R}'\text{NH}_2$  initiator systems, and good yields of the homopolymer were obtained.<sup>98</sup> N,N-Dialkyl-1-alkyl or arylglycidamides have been copolymerized with ethylene oxide using  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}$ /ethylene oxide (1/0.5 to 1/1 to 3) initiator systems, and gave polymers with molecular weights from 50,000 to 150,000.<sup>99</sup> These copolymers were then tested as plasma substitutes. N-Glycidyl-2-oxazolidone has been studied in both cationic and anionic polymerization systems.<sup>100</sup> Anionic polymerizations were attempted in 1,4-dioxane at 70°C using triethylamine and sodium methoxide as initiators, but no polymer was produced. Under the same conditions using  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  and  $\text{AlCl}_3$  as initiators, low yields, from 13 to 33%, of polymers with inherent viscosities of approximately 0.5 dL/g were produced. When lower reaction temperatures were used, a stable complex between the monomer and initiator formed as seen by a decrease in both the carbonyl and epoxide infrared frequencies. Cationic copolymerizations with styrene were carried out and gave styrene rich copolymers.

Several investigators have been involved over the years in studying polymerizations of carboxylic acid ester

substituted epoxide monomers. The homo- and copolymers of these materials are of interest both because of the properties which the ester and other carboxylate derivatives impart to the polymers, and because of the reactivity of these groups toward further chemical reactions. Polymerization of ester substituted epoxides was first reported when several lower alkyl glycidates were polymerized using the  $\text{Al}(\text{iso-C}_4\text{H}_9)_3/\text{THF}$  (1/1) and a mixture of  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}$  (1/0.6) and  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$  (1/0.5/1) initiator systems.<sup>101</sup> The polymers were described as tough, somewhat rubbery materials shown to be highly crystalline by X-ray diffraction possessing inherent viscosities greater than 0.2 dL/g. No yields or further characterization of the polymers were given. Various alkyl glycidates have been copolymerized with trioxane in bulk and gas phase cationic polymerizations.<sup>102-104</sup> The copolymers were prepared in good yields, from 50 to 90%, but were of lower molecular weight and base stability than corresponding trioxane-ethylene oxide copolymers. It was found that the yields and molecular weights of the copolymers decreased as the concentration of the alkyl glycidate was increased in the monomer feed. Cleavage of the ester groups with a suitable base, such as sodium hydroxide, was carried out to give the carboxylate form of the copolymers, the first example of poly(alkylene oxide) ionomers, or ionic group containing polymers. Further studies of the co- and terpolymeriza-

tions of ethyl glycidate with trioxane and 1,3-dioxolane using cationic initiators confirmed the low reactivity for the alkyl glycidates found in the earlier studies.<sup>105-108</sup> The co- and terpolymers were converted to their ionomer form and characterized using calorimetric, dynamic mechanical, and dielectric techniques, and showed that ionic clustering similar to that found in polyethylene-based ionomers existed. Cationic homo- and copolymerizations of ethyl glycidate with THF using triethyloxonium tetrafluoroborate, and methyl and ethyl trifluoromethanesulfonates as initiators have recently been studied.<sup>109</sup> Homopolymerizations carried out at 35°C gave approximately two-thirds of a tetrameric species, probably the cyclic tetramer, and one third of a linear polymer with a molecular weight of 1200. Copolymerizations of ethyl glycidate with THF under conditions precluding THF homopolymerization gave 2:1 THF:ethyl glycidate copolymers of low molecular weight. The copolymer composition was explained by a penultimate effect of the ethyl glycidate units. The low reactivity of ethyl glycidate towards polymerization was attributed to the low nucleophilicity of the epoxide oxygen and possible side reactions involving the ester groups.

The copolymerization of ethyl glycidate with several cyclic ethers using coordinate initiators has recently been investigated.<sup>110</sup> Ethyl glycidate was copolymerized with propylene oxide, 1-butene oxide, and oxetane

using the  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$  (1/0.3/0.5) initiator system, and gave good yields of high molecular weight polymers. The  $\text{Zn}(\text{C}_2\text{H}_5)_2/\text{H}_2\text{O}$ ,  $\text{Zn}(\text{C}_2\text{H}_5)_2/\text{CH}_3\text{NO}_2$ ,  $\text{FeCl}_3 \cdot \text{propylene oxide}$ , and  $\text{Al}(\text{iso-C}_3\text{H}_7\text{O})_3$  initiator systems were also tested, but were found to be ineffective as initiators. Incorporation of ethyl glycidate into the copolymers was found to be approximately 10% of the concentration in the monomer feed, and as the ethyl glycidate concentration in the monomer feed was raised, both the yield and molecular weight of the resultant polymer decreased. These copolymers were also converted to their carboxylate salt and carboxylic acid forms by first treating the polymers with a base, followed by an acid.

Diester substituted epoxide monomers have also been polymerized. Polymerization of diethyl-2,3-epoxy-1,4-butanedioate was carried out at  $60^\circ\text{C}$  for 1 hour using  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  as initiator gave oligomeric species with an average degree of polymerization of 4.2.<sup>111</sup> Dimethyl-2,3-epoxy-1,4-butanedioate was polymerized at  $40^\circ\text{C}$  using  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  as initiator and gave an oligomer with an average degree of polymerization of 3.<sup>112</sup> Hydrolysis of the ester groups of this oligomer gave a material found to be useful as a detergent builder.

Alkali metal glycidates have been polymerized anionically using 1,2,4-trimethylpiperazine as the initiator.<sup>86</sup> The polymerizations were carried out at  $100^\circ\text{C}$  for

40 hours and gave light tan, extremely viscous materials. Poly(glycidic acid) was prepared from this polymer by passing an aqueous solution of the polymer through a cation exchange resin. The poly(glycidic acid) produced in this way was a tan, very viscous oil described as being useful as alkali soluble resin, thickener, and flocculant intermediates.

From the examples of polymerizations of substituted epoxides presented on the previous pages, some conclusions may be drawn. First, it appears that as the polarity of the functional group increases, the reactivity of the epoxide toward polymerization decreases. This may be due to a decrease in the nucleophilicity of the epoxide oxygen caused by the electron withdrawing effect of the functional group and/or a competition between the epoxide and functional groups for the initiator. Proximity of the functional group to the epoxide also appears to affect the polymerizability of the epoxide, that is, separation of the two groups appears to be beneficial to the polymerization (see reference 97). This may be due to a decrease in the epoxide oxygen nucleophilicity when the functional group is close to the epoxide, or it may be a simple steric effect.

C. Functional oxetanes. Unlike the polymerization of substituted epoxides, where most of the studies have been carried out utilizing coordinate initiator systems, most of

the polymerizations of substituted oxetanes have been carried out using cationic initiators. A survey of the substituted oxetanes which have been polymerized is shown in Table 3.

The oxetane oxygen atom is considerably more nucleophilic than the epoxide oxygen,<sup>113</sup> and this, combined with the significant ring strain of the 4 membered oxetane ring, renders these monomers very susceptible to cationic polymerization. The rates of the cationic polymerizations of oxetane, 3-methyloxetane, and 3,3-dimethyloxetane were studied, and it was found that the rates increased with substitution, contrary to findings from other ring systems.<sup>114</sup> This trend was attributed to the increasing ease of proceeding from the solvated initial state to the nonsolvated transition state as substitution increases.

Polymerization of the first substituted oxetane was reported in 1954 when 3,3-bis(chloromethyl)oxetane was cationically polymerized at low temperatures.<sup>115</sup> The polymerizations were carried out using  $\text{BF}_3$  and a trace amount of water as the initiator at temperatures ranging from  $-78^\circ\text{C}$  to  $0^\circ\text{C}$ . The high molecular weight polymers were semicrystalline, with a melting point of  $180^\circ\text{C}$ , and were only soluble in various hydrocarbons, chlorinated hydrocarbons, amines, and esters at elevated temperatures. The polymer has excellent electrical and mechanical properties, corrosion resistance, and dimensional stability, and was

TABLE 3  
FUNCTIONAL OXETANE POLYMERS

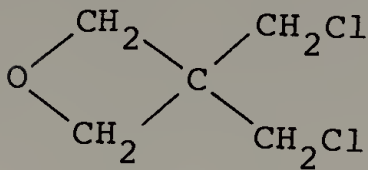
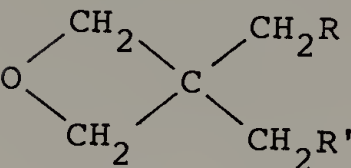
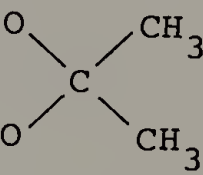
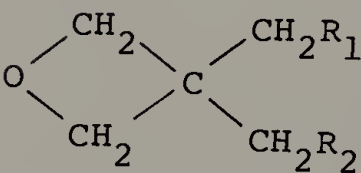
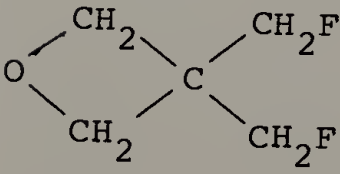
Functional Oxetane	Polymer Characteristics	Ref.
	Semicrystalline, tough thermoplastic	114,115
	Amorphous to semi-crystalline thermoplastics	116
$R = \text{Cl}, R' = \text{O}-\overset{\text{O}}{\parallel}\text{CCH}_3;$ $R = \text{OCCH}_3, R' = \text{OCCH}_3$ $R, R' =$ 		
		117
$R_1 = R_2 = \text{CN}; R_1 = \text{Cl}, R_2 = \text{CH}_3\text{O};$ $R_1 = \text{Cl}, R_2 = \text{C}_2\text{H}_5; R_1 = \text{Cl}, R_2 = \text{CH}_3$		
	Crystalline thermoplastic	118

TABLE 3 (Continued)

Functional Oxetane	Polymer Characteristics	Ref.
$  \begin{array}{c}  \text{CH}_2 \quad \text{CH}_2\text{X} \\  \diagdown \quad \diagup \\  \text{O} \quad \text{C} \\  \diagup \quad \diagdown \\  \text{CH}_2 \quad \text{CH}_2\text{X}  \end{array}  $ <p>X=F, Cl, Br, I</p>	Semicrystalline thermoplastics	119
$  \begin{array}{c}  \text{CH}_2 \quad \text{CH}_2\text{Cl} \\  \diagdown \quad \diagup \\  \text{O} \quad \text{C} \\  \diagup \quad \diagdown \\  \text{CH}_2 \quad \text{CH}_2\text{OH}  \end{array}  $		120
$  \begin{array}{c}  \text{CH}_2 \quad \text{R}_1 \\  \diagdown \quad \diagup \\  \text{O} \quad \text{C} \\  \diagup \quad \diagdown \\  \text{CH}_2 \quad \text{R}_2  \end{array}  $ <p> <math>\text{R}_1=\text{R}_2=\text{F}, \text{Cl}, \text{Br}, \text{CH}_2\text{F}, \text{CH}_2\text{Cl},</math>  <math>\text{CH}_2\text{OH}, \text{CN}, \text{CH}_2\text{CN},</math>  <math>\text{CH}_2\text{OC}(=\text{O})\text{CH}_3</math> </p>		121
$  \begin{array}{c}  \text{CH}_2 \quad \text{CH}_2\text{-S-CH}_3 \\  \diagdown \quad \diagup \\  \text{O} \quad \text{C} \\  \diagup \quad \diagdown \\  \text{CH}_2 \quad \text{CH}_2\text{-S-CH}_3  \end{array}  $	Semicrystalline thermoplastics	122
$  \begin{array}{c}  \text{CH}_2 \quad \text{CH}_2\text{-S-CH}_2\text{-CH}_2\text{-CH}_2 \\  \diagdown \quad \diagup \\  \text{O} \quad \text{C} \\  \diagup \quad \diagdown \\  \text{CH}_2 \quad \text{CH}_2\text{-S-CH}_2\text{-CH}_2\text{-CH}_2  \end{array}  $		
$  \begin{array}{c}  \text{CH}_2 \quad \text{CH}_2\text{-S-C=O} \\  \diagdown \quad \diagup \\  \text{O} \quad \text{C} \\  \diagup \quad \diagdown \\  \text{CH}_2 \quad \text{CH}_2\text{-S}  \end{array}  $		

(continued next page)

TABLE 3 (Continued)

Functional Oxetane	Polymer Characteristics	Ref.
	Water soluble materials	123
	Semicrystalline elastomers	124
$X=O, S; Z=CH_2CH_2, p+q=2-9;$		
$Z = \text{oxetane ring}, p+q=1-9$		



commercialized by Hercules, Inc. under the tradename Penton. Subsequently, the material has been withdrawn from the marketplace. Polymerizations of several 3,3-disubstituted oxetanes, including the 3,3-bis(chloromethyl), 3-chloromethyl-3-acetoxymethyl, and 3,3-bis(acetoxymethyl) substituted monomers were carried out, and their melting points and water solubility correlated with their structures.<sup>116</sup> The polymerizations were carried out at low temperatures using  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  as the initiator. 7,7-Dimethyl-2,6,8-trioxaspiro[3,5]nonane was also polymerized and subjected to hydrolysis to give the 3,3-bis(hydroxymethyl) substituted oxetane polymer. The acetoxymethyl substituted polymers were amorphous, while the 3,3-bis(chloromethyl) substituted polymer had a melting point of  $180^\circ\text{C}$ . The 3,3-bis(hydroxymethyl) substituted polymer had a melting point above  $280^\circ\text{C}$ . Only the 3,3-bis(acetoxymethyl) substituted polymer was found to be water soluble.

Polymerization of four different disubstituted oxetanes, 3-chloromethyl-3-methyloxetane, 3-chloromethyl-3-ethyloxetane, 3-chloromethyl-3-methoxymethyloxetane, and 3,3-bis(cyanomethyl)oxetane, at  $-100^\circ\text{C}$  to  $20^\circ\text{C}$  using  $\text{BF}_3$  or its etherate as the initiator gave polymers with molecular weights from 10,000 to 60,000.<sup>117</sup> A highly crystalline polymer with a melting point of  $135$  to  $137^\circ\text{C}$  was produced from the polymerization of 3,3-bis(fluoromethyl)oxetane.<sup>118</sup> The polymerizations were carried out at  $-20^\circ\text{C}$  in several

chlorinated solvents using  $\text{BF}_3$  as the initiator, and the polymer was described as being highly resistant to acids and bases, the only soluble in various aromatic, chlorinated hydrocarbon, and cyclic ether solvents above  $80^\circ\text{C}$ .

The entire series of 3,3-bis(halomethyl) substituted polymers was prepared using  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  as the initiator, and it was shown that the melting points of the polymers increase with increasing size of the halogen atom, while the solubility decreases in the same order.<sup>119</sup> The polymer prepared from 3-chloromethyl-3-hydroxymethyloxetane using  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  as the initiator was esterified with a castor oil fatty acid and an acid catalyst to give the fatty acid substituted oxetane polymer.<sup>120</sup> It is surprising that polymerization could occur at all because of the presence of free hydroxyl groups on the monomer. A wide range of substituted oxetanes, such as 3,3-bis(fluoro, chloro, bromo, fluoromethyl, chloromethyl, hydroxymethyl, cyano, cyanomethyl, and acetoxymethyl)oxetanes, have been polymerized and suggested as positive photoresists.<sup>121</sup>

A series of 3,3-bisthio- or thiocarboxylate ester oxetane monomers were prepared and polymerized using  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  or  $\text{PF}_5$  as the initiators with the goal of preparing free mercaptan substituted polymers.<sup>122</sup> Molecular weights up to 21,000 were achieved. Hydrolysis of most of the polymers was successfully accomplished under oxygen free conditions to give the free mercaptan substituted

polymers. The mercaptan substituted polymers had melting points above  $280^{\circ}\text{C}$  and were only soluble in alkaline medium.

Several oxetane polymers with cyclic and acyclic poly(alkylene oxide) substituents have been prepared. Acyclic poly(alkylene oxide) mono- and disubstituted oxetanes were prepared by reacting the sodium salts of 3-ethyl-3-hydroxymethyl-oxetane and 3,3-bis(hydroxymethyl)oxetane with ethylene oxide for 5 hours at  $130^{\circ}\text{C}$ .<sup>123</sup> Following neutralization, the substituted oxetanes were polymerized in benzene for 8 hours at  $80^{\circ}\text{C}$  using  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  as the initiator. The resultant polymers were water soluble, and proposed for uses as surfactants and paper and textile dyeing aides. Spiro cyclic oxygen and sulfur analogs of the acyclic poly(alkylene oxide) substituted oxetanes have been described in a DuPont patent.<sup>124</sup> The substituted oxetanes were prepared by reacting the dianion of an appropriate polyethylene glycol or its S analog with 3,3-bis(chloromethyl)oxetane. Polymerizations were carried out using  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  as the initiator and gave rubbery materials, softening at 180 to  $200^{\circ}\text{C}$ , capable of complexing alkaline earth and alkali metal salts, and, in the case of the S analogs, heavy metals such as mercury. In a closely related example, spiro cyclic poly(alkylene oxide) substituted oxetanes were prepared by reacting 3,3-bis(bromomethyl)oxetane with the disodium alkoxide of an ethylene oxide tetramer.<sup>125</sup> The polymers were prepared using  $\text{BF}_3 \cdot$

$\text{O}(\text{C}_2\text{H}_5)_2$  as the initiator, and were found to be useful in extracting sodium salts from aqueous solutions in a thermally reversible fashion.

A series of phosphate substituted oxetanes have been prepared and polymerized cationically.<sup>126</sup> The substituted oxetane monomers were prepared by reacting a bis-halo substituted oxetane with an ammonium phosphate salt in ethanol, giving monophosphate substituted oxetanes. The polymerizations were carried out in dichloromethane at 40°C using  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  as the initiator and gave white solids which softened near 175°C.

The preceding examples show that, as was seen in the substituted epoxides, the polarity of the functional group affects the polymerizability of the oxetane monomers. Generally, the more polar a functional group is, the less reactive the substituted oxetane is towards polymerization. However, because the oxetane oxygen is more nucleophilic than the epoxide oxygen, and because the substituents on the oxetanes are generally farther removed from the polymerization site than on the epoxides, the observed effect is smaller for the oxetanes than for the epoxides.

D. Functional tetrahydrofurans. There are no references in the literature concerning the polymerization of functionally substituted tetrahydrofurans, and very few dealing with any substituted tetrahydrofurans.<sup>127</sup> Tetrahydrofuran

is much more difficult to polymerize than either oxetane or ethylene oxide because of the stability of the five membered ring, and substitution only serves to increase that inherent stability.

E. Functional 1,3-dioxolanes. While 1,3-dioxolane polymerizes more readily than tetrahydrofuran, substitution of 1,3-dioxolane still greatly reduces its reactivity toward polymerization, and as a consequence, there are few examples of substituted 1,3-dioxolane polymerizations.

Polymerizations of several 2- and 4-substituted 1,3-dioxolanes were attempted at low temperatures using acetic anhydride/perchloric acid (5/1) and acetyl chloride/ $\text{ZnCl}_2$  (1/1) initiator systems.<sup>128</sup> All of the 2-substituted 1,3-dioxolanes, including methyl and phenyl substituents, failed to undergo polymerization. The 4-substituted 1,3-dioxolanes, including methyl and chloromethyl substituents, underwent polymerization, but only gave low molecular weight polymers in yields from 13 to 59%. 4-Phenyl-1,3-dioxolane was successfully polymerized in dichloromethane at  $-35^\circ\text{C}$  using perchloric acid as the initiator, and gave a polymer with an inherent viscosity of 0.06 dL/g.<sup>129</sup>

F. Functional aldehydes. While aldehydes do not polymerize by a ring opening mechanism, their polymerizations are subject to many of the same effects encountered in cyclic ether polymerizations. Consequently, a discussion of the

polymerization of substituted aldehydes should aid in understanding the effects of substituents on the polymerizations of cyclic ethers. Substituted aldehydes which have been polymerized are shown in Table 4.

The most common functionally substituted aldehyde is acrolein. Polymerization of this monomer has predominantly been carried out through the carbon-carbon double bond,<sup>130</sup> although claims have been made that appropriate conditions for polymerization predominantly through the aldehyde group can be chosen.<sup>131</sup> Infrared analysis of the native and hydrogenated polymer was used to show only aldehyde polymerization had occurred. Propiolaldehyde has been homo- and copolymerized with styrene at  $-78^{\circ}\text{C}$  in dichloromethane and THF using  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  as the initiator.<sup>132</sup> The homopolymer was a low molecular weight material found to be unstable at room temperature, even after attempts to stabilize it. The copolymers were low molecular weight materials prepared in low yields shown to contain less than 1% of pendant aldehyde groups.

Recently, the polymerization of allyloxyacetaldehyde in dichloromethane, toluene, and THF at  $-10$  to  $-78^{\circ}\text{C}$  using  $\text{Al}(\text{C}_2\text{H}_5)_3$  and  $\text{AlCl}_2(\text{C}_2\text{H}_5)$  as initiators has been studied.<sup>133</sup> The polymers were semicrystalline, and it was found that the crystallinity increased with the acidity of the initiator. Degradation of the polymers occurred very readily in the presence of air and heat. Polymerization of

TABLE 4  
FUNCTIONAL ALDEHYDE POLYMERS

Functional Aldehyde	Polymer Characteristics	Ref.
$\begin{array}{c} \text{O} \\ \parallel \\ \text{HC}-\text{CH}=\text{CH}_2 \end{array}$	Low molecular weight, oily material	131
$\begin{array}{c} \text{O} \\ \parallel \\ \text{HC}-\text{C}\equiv\text{CH} \end{array}$	Low molecular weight, oily material	132
$\begin{array}{c} \text{O} \\ \parallel \\ \text{HC}-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}=\text{CH}_2 \end{array}$	Semicrystalline thermoplastic	133
$\begin{array}{c} \text{O} \\ \parallel \\ \text{HC}-\text{CH}_2-\text{CH}_2-\text{S}-\text{CH}_2-\text{CH}=\text{CH}_2 \end{array}$		134
$\begin{array}{c} \text{O} \\ \parallel \\ \text{HC}-\text{CH}_2\text{Cl} \end{array}$	Amorphous or semi-crystalline materials	135
$\begin{array}{c} \text{O} \\ \parallel \\ \text{HC}-\text{CH}_2-\text{CH}_2\text{Cl} \end{array}$	Semicrystalline thermoplastic	136
$\begin{array}{c} \text{O} \\ \parallel \\ \text{HC}-\text{CH}-\text{CH}_2 \\   \quad   \\ \text{Cl} \quad \text{Cl} \end{array}$	Semicrystalline thermoplastic	137
$\begin{array}{c} \text{O} \\ \parallel \\ \text{HC}-\text{CH}_2\text{CH}_2-\text{CN} \end{array}$	Low molecular weight, oily materials and semi-crystalline thermoplastic	138, 139, 141-145
$\begin{array}{c} \text{O} \\ \parallel \\ \text{HC}-(\text{CH}_2)_n-\text{CN} \\ n=1-6 \end{array}$	Low molecular weight materials	140

TABLE 4 (Continued)

Functional Aldehyde	Polymer Characteristics	Ref.
$\begin{array}{c} \text{O} \qquad \qquad \text{O} \\ \parallel \qquad \parallel \\ \text{HC}-\text{CH}_2-\text{CH}_2-\text{OCCH}_3 \end{array}$	Semicrystalline thermoplastic	146,147
$\begin{array}{c} \text{O} \qquad \qquad \text{O} \\ \parallel \qquad \parallel \\ \text{HC}-\text{CH}_2-\text{CH}_2-\text{C}-\text{OCH}_3 \end{array}$	Semicrystalline thermoplastic	147,148

the related allylthiopropionaldehyde has been studied using a variety of Lewis acid initiators.<sup>134</sup> When  $\text{AlBr}_3$  or  $\text{SnCl}_4$  were used as the initiators at  $-48$  to  $-78^\circ\text{C}$ , a mixture of cyclic trimer and linear polymer was obtained, while using  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  as the initiator gave only cyclic trimer. Linear polymers and Tishchenko reaction products were the materials obtained when  $\text{Al}(\text{C}_2\text{H}_5)_3$  or  $\text{Al}(\text{C}_2\text{H}_5)_2(\text{OC}_4\text{H}_9)$  were used as initiators.

Several chlorine substituted aldehydes have recently been polymerized using a variety of initiators. Polymerization of chloroacetaldehyde has been carried out using both cationic and anionic initiators, but the products are quite different from one another.<sup>135</sup> Polymerizations carried out with cationic initiators gave amorphous products, while anionic initiators gave crystalline products. The polymerization of 3-chloropropionaldehyde was found to give products which were both solvent and initiator dependent.<sup>136</sup> The rate of polymerization was solvent dependent, decreasing in the order dichloromethane > toluene > THF, and the amount of crystalline fraction decreased as the initiator acidity increased,  $\text{Al}(\text{C}_2\text{H}_5)_3 > \text{Al}(\text{C}_2\text{H}_5)_3 + \text{Al}(\text{C}_2\text{H}_5)_2\text{Cl} > \text{Al}(\text{C}_2\text{H}_5)_2\text{Cl} > \text{Al}(\text{C}_2\text{H}_5)_3 + \text{Al}(\text{C}_2\text{H}_5)\text{Cl}_2 > \text{Al}(\text{C}_2\text{H}_5)\text{Cl}_2 + \text{Al}(\text{C}_2\text{H}_5)_2\text{Cl} > \text{AlCl}_3$ . If the initiators were rendered more acidic by the addition of  $\text{TiCl}_3$  or  $\text{TiCl}_4$ , no polymerization took place. An increase in the polymer yield was found as the temperature was

lowered to  $-95^{\circ}\text{C}$ , with no polymerization occurring above  $-45^{\circ}\text{C}$ . Copolymerization of 3-chloropropionaldehyde with 3-cyanopropionaldehyde gave soluble, random copolymers.<sup>136</sup> Polymerization of 2,3-dichloropropionaldehyde has been carried out using a variety of aluminum Lewis acid initiators, and it was found that the initiator activity increased with the acidity of the initiator.<sup>137</sup> The polymerizations were carried out in dichloromethane, toluene, and THF at 0 to  $-78^{\circ}\text{C}$  using  $\text{AlCl}_3$ ,  $\text{Al}(\text{C}_2\text{H}_5)\text{Cl}_2$ ,  $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ , and  $\text{Al}(\text{C}_2\text{H}_5)_3$  as initiators, and gave high molecular weight, DMF insoluble polymers.

Several cyano substituted aldehydes have been polymerized, although only 3-cyanopropionaldehyde has been studied in detail. 3-Cyanopropionaldehyde was first polymerized in dichloromethane at  $-78^{\circ}\text{C}$  using a variety of Lewis acid initiators.<sup>138</sup> When  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  or  $\text{Zn}(\text{C}_2\text{H}_5)_2$  were used as initiators, only low molecular polymers were obtained, and modification of  $\text{Zn}(\text{C}_2\text{H}_5)_2$  with small amounts of water gave only a slightly more active initiator. Polymerization using  $\text{Al}(\text{C}_2\text{H}_5)_3$  as the initiator gave a predominance of low molecular weight material, along with a small quantity of high molecular weight amorphous and crystalline material. The DMF insoluble, crystalline polymer had a melting point of 150 to  $170^{\circ}\text{C}$ . Modification of the  $\text{Al}(\text{C}_2\text{H}_5)_3$  initiator with  $\text{TiCl}_4$  resulted in better yields of high molecular weight polymer with lower

crystallinity.<sup>139</sup> Copolymerizations of the  $C_{3-8}$   $\omega$ -cyanoalkylaldehydes with formaldehyde have been carried out at  $-40^{\circ}\text{C}$  using  $\text{Al}(\text{C}_2\text{H}_5)_3$  as the initiator to give low molecular weight,  $\omega$ -cyanoalkylaldehyde-poor copolymers.<sup>140</sup>

3-Cyanopropionaldehyde has also been studied in anionic homo- and copolymerizations. Homopolymerizations were carried out using the lithium or sodium metal/benzophenone initiator systems to give low molecular weight materials.<sup>141</sup> As the initiator concentration was raised, the polymer yield decreased, and the polymer stereoregularity increased. Copolymerizations with dimethylketene at  $-78^{\circ}\text{C}$  in THF have been carried out using the lithium/benzophenone initiator system.<sup>142,143</sup> 3-Cyanopropionaldehyde was incorporated preferentially into the copolymers, but as the concentration of 3-cyanopropionaldehyde in the comonomer feed was increased, both the yields and molecular weights of the copolymers decreased. The same behavior was noted in copolymerizations with methyl isocyanate.<sup>144</sup> When the more reactive phenyl isocyanate was copolymerized with 3-cyanopropionaldehyde, phenyl isocyanate was incorporated preferentially.<sup>145</sup> In none of the homo- or copolymerizations were molecular weights greater than 8,000 achieved.

The polymerization of acetate and ester substituted aldehydes have also been described. 3-Acetoxypromionaldehyde was polymerized using a variety of Lewis and protonic acid initiators to give a variety of products.<sup>146</sup> When HCl

or  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  were used as initiators, cyclic trimers were formed regardless of the reaction temperature used. Cyclic trimers were formed when  $\text{H}_2\text{SO}_4$  was used as the initiator at  $0^\circ\text{C}$ , but a linear polymer was formed at  $-78^\circ\text{C}$ . Linear, crystalline polymers were formed at  $-78^\circ\text{C}$  using  $\text{Al}(\text{C}_2\text{H}_5)_3$  and  $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$  as initiators, the highest yields produced using  $\text{Al}(\text{C}_2\text{H}_5)_3$ . Both the yield and rate of polymerization were found to be solvent dependent, decreasing in the order dichloromethane > THF > toluene. The polymer had a melting point of  $160^\circ\text{C}$ , and was insoluble in all common organic solvents. Copolymerizations of 3-acetoxypromionaldehyde and carbomethoxypromionaldehyde were carried out at  $-78^\circ\text{C}$  in dichloromethane using  $\text{Al}(\text{C}_2\text{H}_5)_3$  and  $\text{Al}(\text{C}_2\text{H}_5)_2(\text{OC}_2\text{H}_5)$  as the initiators, and gave copolymers in higher yields than either of the homopolymers.<sup>147</sup> Optimum polymer yields were obtained when the initiator concentration was 50 mole% based on the monomers, indicating a considerable amount of initiator interaction with the carboxyl groups. The homopolymerization of 3-carbomethoxypromionaldehyde has been studied using several solvents and Lewis acid initiators.<sup>148</sup> The highest yield and molecular weight were obtained using  $\text{Al}(\text{C}_2\text{H}_5)_3$  as the initiator in dichloromethane to give 38% of a highly crystalline, high molecular weight polymer with a melting point of  $150^\circ\text{C}$ . Unlike the 3-acetoxypromionaldehyde homopolymer, the homopolymer of 3-carbomethoxypromionaldehyde was found

to be soluble in chloroform and acetone. The polymer was found to be stable at room temperature, and considerably more so when stabilized by acetate endcapping.

As was found with the substituted oxetanes, most of the functional groups of the substituted aldehydes were separated by at least one methylene group. As a consequence, many of the monomers were readily polymerized. The polarity of the functional groups once again strongly influenced the polymerizability of the monomers. As the functional group increased in polarity, the polymerizability of the monomer decreased.

# CHAPTER II

## EXPERIMENTAL SECTION

### I. Materials

The following chemicals were obtained from the sources indicated.

acetyl acetone	T	magnesium sulfate,	
acetic acid, glacial	F	anhydrous	F
ammonium chloride	F	methanol	F
azelaic acid	A	methyl acrylate	A
benzene	F	molecular sieves (4A)	MCB
boron trifluoride		nitric acid,	
etherate	A	concentrated	F
1-butene oxide	A	oxetane	A
3-butenic acid	A	4-pentenoic acid	P
calcium chloride,		phenyl glycidyl ether	T
anhydrous	F	phenyl magnesium	
calcium hydride	F	bromide	AV
m-chloroperoxybenzoic		pimelic acid	A
acid, technical	A	potassium metal	B
chromium trioxide	F	potassium hydroxide	MCB
cupric acetate	F	propylene oxide	E
di-n-butyl ether	F	pyridine	A
1,2-dichloroethane	A	sebacic acid	A
dichloromethane	F	sodium metal	B
diethyl ether	F	sodium bicarbonate	F
1,4-dioxane	F	sodium bisulfite	B
epichlorohydrin	A	suberic acid	A
ethanol, absolute	A	sulfuric acid	F
n-hexane	F	tetrahydrofuran	F
1-hexene	A	4,4-thiobis(6-tert-	
hydrochloric acid,		butyl-m-cresol)	PB
concentrated	F	p-toluenesulfonic acid	E
lead tetraacetate	A	triethyl aluminum,	
lithium aluminum		neat	ET
hydride	AV	10-undecenoic acid	E

Sources: A = Aldrich Chemical Company; AV = Alfa Ventron, Inc.; B = J.T. Baker Chemical Company; E = Eastman Organic Chemicals; ET = Ethyl Corporation; F = Fisher Scientific Company; MCB = Matheson, Coleman and Bell; PB = Pfaltz and Bauer, Inc.; P = Polysciences, Inc.; T = Tridom-Fluka Chemical Company.

## II. Purification of Solvents and Reagents

Distillations were carried out using either an 18 or 30 cm Vigreux column equipped with a variable reflux ratio distillation head. Reduced pressure distillations were carried out with magnetic stirring under a nitrogen atmosphere.

Acetyl acetone was stirred over calcium hydride for 30 minutes, then distilled (B.P. 133-4°C) and stored under nitrogen.

Benzene was distilled (B.P. 80°C) from a sodium/potassium alloy (5/1 by weight) and stored under nitrogen at 10°C.

Boron trifluoride etherate was distilled (B.P. 64°C/125 mm) and stored under nitrogen.

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

Dichloromethane was refluxed for 12 hours with calcium hydride, then distilled (B.P. 40°C) and stored over molecular sieves.

Diethyl ether was refluxed for four hours with

lithium aluminum hydride, then distilled (B.P. 35°C) immediately before use under nitrogen.

1,4-Dioxane was stirred with anhydrous calcium chloride for twelve hours, filtered, refluxed for twelve hours with sodium metal, then distilled (B.P. 101°C) and stored under nitrogen.

Epichlorohydrin was refluxed for four hours with calcium hydride, then distilled (B.P. 115-7°C) and stored under nitrogen.

n-Hexane was distilled (B.P. 60°C) and stored over molecular sieves.

Methanol was distilled (B.P. 64°C).

Oxetane and propylene oxide were refluxed for twelve hours with calcium hydride, then distilled (B.P. 50°C and 34°C, respectively) and stored under nitrogen.

Phenyl glycidyl ether was distilled (B.P. 70°C/1 mm) and stored under nitrogen.

Tetrahydrofuran was refluxed for twelve hours with lithium aluminum hydride, then distilled (B.P. 66°C) and stored under nitrogen at 10°C.

All other solvents and reagents were used as received.

### III. Preparation of Monomers

A. General procedure for the epoxidation of alkenes with m-chloroperoxybenzoic acid. This procedure is a modification of that described by Schwartz and Blumberg.<sup>149</sup> A three-neck round bottom flask is fitted with a stopper, condenser, and pressure equalizer addition funnel with a nitrogen blanket line while hot, then cooled under a dry nitrogen flow. After cooling, 1.1 mole equivalents of m-chloroperoxybenzoic acid (based on alkene) and a teflon coated magnetic stir bar are added to the flask under positive nitrogen pressure. The peracid should be transferred with a non-metallic spatula, since metals catalyze the decomposition of peracids. The m-chloroperoxybenzoic acid commercially available is 80-90% peracid, with the remainder being m-chlorobenzoic acid. This material may be purified by washing with a suitable buffer system. However, experience has shown that under the experimental conditions described here, the presence of the free acid causes no problems. Sufficient dichloromethane is then added to the flask via syringe to prepare a 20% (wt./vol.) solution. The slurry is stirred for 10 minutes at room temperature, then cooled to 0°C by submerging the flask in an ice/water bath. Most of the free acid impurity is insoluble under these conditions. The addition funnel is then charged with the alkene and sufficient dichloromethane to prepare a 20%

(wt./vol.) solution. The alkene solution is added to the peracid solution over a 15-30 minute period, after which the solution is allowed to warm to room temperature. The reaction is normally completed within 24 hours. After the reaction is completed, the solution is cooled to 0°C to precipitate the free acid from the solution. The reaction mixture is then filtered and the precipitate washed with fresh, cold dichloromethane. The filtrate is washed with excess aqueous sodium bisulfite (to reduce residual peracid), aqueous sodium bicarbonate, and distilled water, then dried over anhydrous magnesium sulfate. After concentration, the pure epoxide is isolated by distillation or recrystallization.

## B. Methyl glycidate.

1. Procedure I. The general procedure described in Chapter II, III.A was used. A solution of methyl acrylate (15 g, 0.17 mole) and dichloromethane (240 ml) was added to a solution of m-chloroperoxybenzoic acid (36 g, 0.17 mole) and dichloromethane (500 ml) at 0°C over a 20 minute period. The reaction was carried out for 17 hours at room temperature and 96 hours at 40°C with stirring under nitrogen. Due to the low conversion (24% by G.C.) and difficulties encountered in the washing procedure (emulsion formation), the reaction was not worked up.

2. Procedure II. A 500 ml single neck round bottom flask was fitted with a condenser and nitrogen blanket while hot, then cooled under a dry nitrogen flow. The flask was charged with m-chloroperoxybenzoic acid (40 g, 0.20 mole), methyl acrylate (15 g, 0.17 mole), 1,2-dichloroethane (320 ml), 4,4-thiobis(6-tert-butyl-m-cresol), (0.10 g, 0.28 mmole), and a teflon coated magnetic stir bar. The mixture was refluxed (83°C) with stirring for 14 hours, then cooled to 0°C and filtered. After washing the precipitate with fresh, cold 1,2-dichloroethane, the filtrate was washed with 4 x 100 ml 10% aqueous sodium bisulfite solution, 4 x 100 ml 5% aqueous sodium bicarbonate solution, and 3 x 100 ml distilled water, and dried over anhydrous magnesium sulfate. Concentration under reduced pressure and distillation yielded 5.5 g (31%) of methyl glycidate (B.P. 88°C/90 mm). The infrared spectrum (NaCl plates) showed absorptions centered at  $1754\text{ cm}^{-1}$  (C=O stretching), and at  $884\text{ cm}^{-1}$  and  $854\text{ cm}^{-1}$  (epoxide C-O-C stretching) (see p. 270). The  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ ) showed peaks at 46.57 ppm ( $\text{CH}_2\text{-}\overset{\text{O}}{\text{C}}$ ), 47.71 ppm ( $\text{-}\overset{\text{O}}{\text{C}}\text{-H}$ ), 52.63 ppm ( $\text{-O-CH}_3$ ), and 170.51 ( $\text{-}\overset{\text{O}}{\text{C}}\text{-O}$ ) (see p. 249).

### C. Methyl-3,4-epoxybutanoate.

1. Methyl-3-butenate. A 100 ml single neck round bottom flask was fitted with a teflon coated magnetic stir bar, and a condenser and nitrogen blanket while hot, then

cooled under a dry nitrogen flow. The flask was charged with 3-butenic acid (10 g, 0.12 mole), anhydrous methanol (38 g, 1.2 moles), and p-toluenesulfonic acid (0.23 g, 1.2 mmole). The mixture was heated at reflux (64°C) with stirring overnight, then cooled to 0°C. The reaction mixture was washed with 2 x 100 ml ice cold 5% aqueous sodium bicarbonate, and the organic phase removed. The aqueous phase was then extracted with 50 ml of diethyl ether, and the organic phases combined. The organic solution was washed with 100 ml of ice cold distilled water and 100 ml of saturated ice cold aqueous sodium chloride solution, then dried over anhydrous magnesium sulfate. Concentration and distillation yielded 7.6 g (63%) of methyl-3-butenate (B.P. 108-9°C). The infrared spectrum (NaCl plates) showed absorptions centered at  $1743\text{ cm}^{-1}$  (C=O stretching),  $1644\text{ cm}^{-1}$  (C=C stretching), and  $995\text{ cm}^{-1}$  and  $924\text{ cm}^{-1}$  (vinyl C-H bending) (see p. 271). The  $^{13}\text{C}$  NMR spectrum (neat) showed peaks at 39.12 ppm ( $-\text{CH}_2-$ ), 51.69 ppm ( $-\text{O}-\text{CH}_3$ ), 118.14 ppm ( $\text{CH}_2=$ ), 131.60 ppm ( $=\text{CH}-$ ), and 171.60 ppm ( $-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{O}$ ) (see p. 245).

2. Methyl-3,4-epoxybutanoate. A solution of methyl-3-butenate (12 g, 0.12 mole) and dichloromethane (50 ml) was added to a solution of m-chloroperoxybenzoic acid (28 g, 0.14 mole) and dichloromethane (180 ml) at 0°C over a 20 minute period. The reaction was carried out for 22 hours at room temperature and 4 hours at 40°C

with stirring under nitrogen. The reaction mixture was worked up, and, after distillation, yielded 8.4 g (60%) of methyl-3,4-epoxybutanoate (B.P. 60°C/13 mm). The infrared spectrum (NaCl plates) showed absorptions centered at  $1741\text{ cm}^{-1}$  (C=O stretching), and at  $922\text{ cm}^{-1}$  and  $839\text{ cm}^{-1}$  (epoxide C-O-C stretching) (see p. 271). The  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ ) showed peaks at 37.94 ppm ( $-\text{CH}_2-$ ), 46.54 ppm ( $\text{CH}_2-\overset{\text{O}}{\text{C}}$ ), 48.01 ppm ( $-\overset{\text{O}}{\text{C}}\text{H}-$ ), 51.80 ppm ( $-\text{O}-\text{CH}_3$ ), and 170.91 ppm ( $-\overset{\text{O}}{\text{C}}-\text{O}$ ) (see p. 249).

D. Methyl-4,5-epoxypentanoate.

1. Methyl-4-pentenoate. A 100 ml single neck round bottom flask was fitted with a teflon coated magnetic stir bar, and a condenser and nitrogen blanket, and the hot glassware was cooled under a dry nitrogen flow. The flask was charged with 4-pentenoic acid (12 g, 0.12 mole), anhydrous methanol (38 g, 1.2 moles), and p-toluenesulfonic acid (0.23 g, 1.2 mmole). The mixture was heated at reflux (64°C) with stirring overnight, then cooled to 0°C. The reaction mixture was worked up in the manner described for the preparation of methyl-3-butenate (Chapter II.III.C.1). Concentration and distillation yielded 8.9 g (66%) of methyl-4-pentenoate (B.P. 128-9°C). The infrared spectrum (NaCl plates) showed absorptions centered at  $1742\text{ cm}^{-1}$  (C=O stretching),  $1643\text{ cm}^{-1}$  (C=C stretching), and  $991\text{ cm}^{-1}$  and  $917\text{ cm}^{-1}$  (vinyl C-H bending)

(see p. 272). The  $^{13}\text{C}$  NMR spectrum (neat) showed peaks at 29.44 ppm ( $=\text{CH}-\text{CH}_2-$ ), 33.59 ppm ( $-\text{CH}_2-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{O}$ ), 51.37 ppm ( $-\text{O}-\text{CH}_3$ ), 115.47 ppm ( $\text{CH}_2=$ ), 137.66 ppm ( $=\text{CH}-$ ), and 172.92 ppm ( $-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{O}-$ ) (see p. 246).

2. Methyl-4,5-epoxypentanoate. A solution of methyl-4-pentenoate (12 g, 0.11 mole) and dichloromethane (50 ml) was added to a solution of m-chloroperoxybenzoic acid (25 g, 0.12 mole) and dichloromethane (150 ml) at  $0^\circ\text{C}$  over a 15 minute period. The reaction was carried out for twelve hours at room temperature with stirring under nitrogen. The reaction mixture was worked up, and, after distillation, yielded 8.3 g (60%) of methyl-4,5-epoxypentanoate (B.P.  $72^\circ\text{C}/9$  mm). The infrared spectrum (NaCl plates) showed absorptions centered at  $1738\text{ cm}^{-1}$  ( $\text{C}=\text{O}$  stretching), and at  $917\text{ cm}^{-1}$  and  $841\text{ cm}^{-1}$  (epoxide  $\text{C}-\text{O}-\text{C}$  stretching) (see p. 272). The  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ ) showed peaks at 27.94 ppm ( $-\overset{\text{O}}{\text{CH}}-\text{CH}_2-$ ), 30.22 ppm ( $-\text{CH}_2-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{O}$ ), 46.78 ppm ( $\text{CH}_2-\overset{\text{O}}{\text{C}}-$ ), 51.12 ppm ( $-\text{O}-\text{CH}_3$ ), 51.54 ppm ( $-\overset{\text{O}}{\text{CH}}-$ ), and 173.23 ppm ( $-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{O}$ ) (see p. 250).

E. General method for the preparation of  $\omega$ -alkenoates by oxidative decarboxylation of half-esters. This procedure is a modification of that described by Bacha and Kochi.<sup>150</sup> A three-neck round bottom flask with a thermometer neck is fitted with a thermometer, a nitrogen inlet tube, a mechanical stirrer with a teflon blade, and a

condenser with a mineral oil bubbler. The flask should be chosen so that the contents of the flask occupy less than one-half of the total flask volume. After flushing the flask with a stream of dry nitrogen for 15 minutes, the flask is charged with 35-40 mole equivalents of benzene (relative to the half-ester), 1.2 mole equivalents of pyridine, 1 mole equivalent of the half-ester, 0.2 mole equivalents of cupric acetate, and 1.6 mole equivalents of lead tetraacetate under a positive nitrogen pressure. The resultant slurry is then flushed with nitrogen for 1 hour with stirring, after which the nitrogen inlet tube is replaced with a condenser and a nitrogen bypass. The contents of the flask are heated very slowly to a reflux with vigorous stirring, shortly after which the reaction begins, as seen by the rapid evolution of carbon dioxide. The heating should be adjusted so that a steady but controllable reflux is maintained for 2 hours. This may necessitate removing the heat source and applying external cooling. Accompanying the reaction is a color change from a deep forest green to a dark brown. The reaction mixture is allowed to cool to room temperature, and is washed with excess 10% (wt./vol.) aqueous nitric acid, 5% (wt./vol.) aqueous sodium bicarbonate, and distilled water. The organic solution becomes a pale golden yellow following the acid wash. The solution is then concentrated and distilled to yield the pure  $\omega$ -alkenoate ester.

F. Methyl-5,6-Epoxyhexanoate.

1. Monomethyl pimelate. This procedure is a modification of that described by Swann et al. A 500 ml single neck round bottom flask was fitted with a condenser and a nitrogen bypass, and the hot glassware was cooled under a dry nitrogen flow. The flask was charged with pimelic acid (150 g, 0.92 mole), dimethyl pimelate (79 g, 0.42 mole), di-n-butyl ether (43 ml), concentrated hydrochloric acid (37%) (21 ml), and a teflon coated magnetic stir bar; the flask contents were dissolved by heating the mixture with stirring- to 110°C (approximately 1 hour). Methanol (24 g, 0.75 mole) was added to the flask through the condenser, and the reaction mixture was refluxed for 2 hours with stirring under nitrogen. A further addition of methanol (11 g, 0.34 mole) was followed by another 2 hour reflux period, after which the reaction mixture was cooled to room temperature. The aqueous layer was removed and discarded, and the remaining material was washed with 100 ml of distilled water. After removing the aqueous layer and discarding it, and drying the remaining material over anhydrous magnesium sulfate, distillation yielded 107 g (68%) of monomethyl pimelate (B.P. 165°C/10 mm). The infrared spectrum (NaCl plates) showed absorptions centered at  $1745\text{ cm}^{-1}$  (ester C=O stretching) and  $1715\text{ cm}^{-1}$  (acid C=O stretching). (see p. 273).

2. Methyl-5-hexenoate. A 2 liter round bottom flask was charged with benzene (800 ml), pyridine (26 g, 0.33 mole), monomethyl pimelate (51 g, 0.29 mole), cupric acetate (9.6 g, 0.05 mole), and lead tetraacetate (200 g, 0.45 mole). The reaction was carried out for 2 hours at reflux under nitrogen. The reaction mixture was worked up, and, after distillation, yielded 8.2 g (22%) of methyl-5-hexenoate (B.P. 60°C/20 mm). The infrared spectrum (NaCl plates) showed absorptions centered at  $1742\text{ cm}^{-1}$  (C=O stretching),  $1641\text{ cm}^{-1}$  (C=C stretching), and  $995\text{ cm}^{-1}$  and  $913\text{ cm}^{-1}$  (vinyl C-H bending) (see p. 273). The  $^{13}\text{C}$  NMR spectrum (neat) showed peaks at 24.69 ppm ( $-\underline{\text{CH}}_2-$ ), 33.53 ppm ( $=\text{CH}-\underline{\text{CH}}_2-$ ,  $-\underline{\text{CH}}_2-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{O}$ ), 51.04 ppm ( $-\text{O}-\underline{\text{CH}}_3$ ), 115.32 ppm ( $\underline{\text{CH}}_2=$ ), 138.28 ppm ( $=\underline{\text{CH}}-$ ), and 172.99 ppm ( $-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{O}$ ) (see p. 246).

3. Methyl-5,6-epoxyhexanoate. A solution of methyl-5-hexenoate (6.0 g, 0.05 mole) and dichloromethane (29 ml) was added to a solution of m-chloroperoxybenzoic acid (11 g, 0.06 mole) and dichloromethane (60 ml) at 0°C over a 10 minute period. The reaction was carried out for 12 hours at room temperature with stirring under nitrogen. The reaction mixture was worked up, and after distillation, yielded 3.7 g (55%) of methyl-5,6-epoxyhexanoate (B.P. 85°C/8 mm). The infrared spectrum (NaCl plates) showed absorptions centered at  $1738\text{ cm}^{-1}$  (C=O stretching), and at  $920\text{ cm}^{-1}$  and  $834\text{ cm}^{-1}$  (epoxide C-O-C

stretching) (see p. 274). The  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ ) showed peaks at 21.57 ppm ( $-\text{CH}_2-$ ), 31.94 ppm ( $-\overset{\text{O}}{\text{CH}}-\text{CH}_2-$ ), 33.65 ppm ( $-\text{CH}_2-\overset{\text{O}}{\text{C}}-\text{O}$ ), 46.68 ppm ( $\text{CH}_2-\overset{\text{O}}{\text{C}}-$ ), 51.42 ppm ( $-\text{O}-\text{CH}_3$ ), 51.70 ppm ( $-\overset{\text{O}}{\text{CH}}-$ ), and 173.56 ppm ( $-\overset{\text{O}}{\text{C}}-\text{O}$ ) (see p. 250).

G. Methyl-6,7-epoxyheptanoate.

1. Monomethyl suberate. The reaction flask was charged with suberic acid (77 g, 0.44 mole), dimethyl suberate (44 g, 0.22 mole), di-n-butyl ether (28 ml), concentrated hydrochloric acid (37%) (15 ml), and a teflon coated magnetic stir bar, and the contents were allowed to dissolve. Methanol was added to the flask in two portions (13 g, 0.40 mole and 6.3 g, 0.20 mole) and allowed to react as previously described. The reaction mixture was worked up, and after distillation, yielded 49 g (60%) of monomethyl suberate (B.P.  $167-9^\circ\text{C}/10\text{ mm}$ ). The infrared spectrum showed absorptions centered at  $1745\text{ cm}^{-1}$  (ester  $\text{C}=\text{O}$  stretching) and  $1715\text{ cm}^{-1}$  (acid  $\text{C}=\text{O}$  stretching) (see p. 274).

2. Methyl-6-heptenoate. A 2 liter round bottom flask was charged with benzene (800 ml), pyridine (24 g, 0.30 mole), monomethyl suberate (48 g, 0.25 mole), cupric acetate (8.8 g, 0.04 mole), and lead tetraacetate (184 g, 0.42 mole). The reaction was carried out for 2 hours at reflux under nitrogen. The reaction mixture was worked up,

and after distillation, yielded 11 g (32%) of methyl-6-heptenoate (B.P. 80°C/30 mm). The infrared spectrum (NaCl plates) showed absorptions centered at 1742  $\text{cm}^{-1}$  (C=O stretching), 1641  $\text{cm}^{-1}$  (C=C stretching), and 995  $\text{cm}^{-1}$  and 912  $\text{cm}^{-1}$  (vinyl C-H bending) (see p. 275). The  $^{13}\text{C}$  NMR spectrum (neat) showed peaks at 24.93 ppm ( $-\text{CH}_2-\text{CH}_2-\overset{\text{O}}{\parallel}\text{C}-\text{O}$ ), 28.95 ppm ( $=\text{CH}-\text{CH}_2-\text{CH}_2-$ ), 33.88 ppm and 34.00 ppm ( $=\text{CH}-\text{CH}_2-$  and  $-\text{CH}_2-\overset{\text{O}}{\parallel}\text{C}-\text{O}$ ), 51.11 ppm ( $-\text{O}-\text{CH}_3$ ), 114.83 ppm ( $\text{CH}_2=$ ), 138.81 ppm ( $=\text{CH}-$ ), and 173.18 ppm ( $-\overset{\text{O}}{\parallel}\text{C}-\text{O}$ ) (see p. 247).

3. Methyl-6,7-epoxyheptanoate. A solution of methyl-6-heptenoate (10 g, 70 mmole) and dichloromethane (36 ml) was added to a solution of m-chloroperoxybenzoic acid (16 g, 82 mmole) and dichloromethane (100 ml) at 0°C over a 10 minute period. The reaction was carried out for 11 hours at room temperature with stirring under nitrogen. The reaction mixture was worked up, and after distillation, yielded 8.6 g (77%) of methyl-6,7-epoxyheptanoate (B.P. 85-6°C/3 mm). The infrared spectrum (NaCl plates) showed absorptions centered at 1738  $\text{cm}^{-1}$  (C=O stretching), and at 919  $\text{cm}^{-1}$  and 836  $\text{cm}^{-1}$  (epoxide C-O-C stretching) (see p. 275). The  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ ) showed peaks at 25.23 ppm ( $-\text{CH}_2-\overset{\text{O}}{\parallel}\text{C}-\text{O}$ ), 26.05 ppm ( $-\overset{\text{O}}{\text{CH}}-\text{CH}_2-\text{CH}_2-$ ), 32.69 ppm ( $-\overset{\text{O}}{\text{CH}}-\text{CH}_2-$ ), 33.99 ppm ( $-\text{CH}_2-\overset{\text{O}}{\parallel}\text{C}-\text{O}$ ), 46.43 ppm ( $\text{CH}_2-\overset{\text{O}}{\text{C}}-$ ), 51.20 ppm ( $-\text{O}-\text{CH}_3$ ), 51.75 ppm ( $-\overset{\text{O}}{\text{CH}}-$ ), and 173.42 ppm ( $-\overset{\text{O}}{\parallel}\text{C}-\text{O}$ ) (see p. 251).

## H. Methyl-7,8-epoxyoctanoate.

1. Monomethyl azelate. The reaction flask was charged with azelaic acid (100 g, 0.54 mole), dimethyl azelate (70 g, 0.32 mole), di-n-butyl ether (30 ml), concentrated hydrochloric acid (37%) (16 ml), and a teflon coated magnetic stir bar, and the contents were allowed to dissolve. Methanol was added to the flask in two portions (15 g, 0.48 mole and 7.6 g, 0.24 mole) and allowed to react as previously described. The reaction mixture was worked up, and after distillation, yielded 73 g (68%) of monomethyl azelate (B.P. 162-5°C/4 mm). The infrared spectrum (NaCl plates) showed absorptions centered at 1745  $\text{cm}^{-1}$  (ester C=O stretching) and 1715  $\text{cm}^{-1}$  (acid C=O stretching) (see p. 276).

2. Methyl-7-octenoate. A 2 liter round bottom flask was charged with benzene (500 ml), pyridine (15 g, 0.19 mole), monomethyl azelate (32 g, 0.16 mole), cupric acetate (5.3 g, 29 mmole), and lead tetraacetate (120 g, 0.26 mole). The reaction was carried out for 2 hours at reflux under nitrogen. The reaction mixture was worked up, and after distillation, yielded 10 g (41%) of methyl-7-octenoate (B.P. 70-1°C/9 mm). The infrared spectrum (NaCl plates) showed absorptions centered at 1742  $\text{cm}^{-1}$  (C=O stretching), 1641  $\text{cm}^{-1}$  (C=C stretching), and 994  $\text{cm}^{-1}$  and 911  $\text{cm}^{-1}$  (vinyl C-H bending) (see p. 276). The  $^{13}\text{C}$  NMR spectrum (neat) showed peaks at 25.23 ppm ( $-\text{CH}_2-\text{CH}_2-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{O}$ ),

29.10 ppm ( $=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-$ ), 34.06 ppm ( $=\text{CH}-\text{CH}_2-$ ,  $-\text{CH}_2-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{O}-$ ), 51.03 ppm ( $-\text{O}-\text{CH}_3$ ), 114.60 ppm ( $\text{CH}_2=$ ), 139.04 ppm ( $=\text{CH}-$ ), and 173.08 ppm ( $-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{O}$ ) (see p. 247).

3. Methyl-7,8-epoxyoctanoate. A solution of methyl-7-octenoate (9.0 g, 58 mmole) and dichloromethane (30 ml) was added to a solution of m-chloroperoxybenzoic acid (14 g, 67 mmole) and dichloromethane (80 ml) at 0°C over a 10 minute period. The reaction was carried out for 6 hours at room temperature with stirring under nitrogen. The reaction mixture was worked up, and after distillation, yielded 6.5 g (65%) of methyl-7,8-epoxyoctanoate (B.P. 89°C/2 mm). The infrared spectrum (NaCl plates) showed absorptions centered at 1739  $\text{cm}^{-1}$  ( $\text{C}=\text{O}$  stretching), and 913  $\text{cm}^{-1}$  and 833  $\text{cm}^{-1}$  (epoxide  $\text{C}-\text{O}-\text{C}$  stretching) (see p. 277). The  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ ) showed peaks at 25.04 ppm ( $-\text{CH}_2-\text{CH}_2-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{O}$ ), 25.89 ppm ( $-\text{CH}-\text{CH}_2-\text{CH}_2-$ ), 29.14 ppm ( $-(\text{CH}_2)_2-\text{CH}_2-(\text{CH}_2)_2-$ ), 32.54 ppm ( $-\text{CH}-\text{CH}_2-$ ), 33.91 ppm ( $-\text{CH}_2-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{O}$ ), 46.60 ppm ( $\text{CH}_2-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-$ ), 51.19 ppm ( $-\text{O}-\text{CH}_3$ ), 51.88 ppm ( $-\text{CH}-$ ), and 173.60 ppm ( $-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{O}$ ) (see p. 251).

I. Methyl-8,9-epoxynonanoate.

1. Monomethyl sebacate. The reaction flask was charged with sebacic acid (91 g, 0.45 mole), dimethyl sebacate (52 g, 0.23 mole), di-n-butyl ether (29 ml), concentrated hydrochloric acid (37%) (15 ml), and a teflon coated magnetic stir bar, and the contents were allowed to

dissolve. Methanol was added to the flask in two portions (13 g, 0.40 mole and 6.4 g, 0.20 mole) and allowed to react as previously described. The reaction mixture was worked up, and after distillation, yielded 50 g (51%) of monomethyl sebacate (B.P. 183-4°C/7 mm). The infrared spectrum (NaCl plates) showed absorptions centered at  $1745\text{ cm}^{-1}$  (ester C=O stretching) and  $1715\text{ cm}^{-1}$  (acid C=O stretching) (see p. 277).

2. Methyl-8-nonenoate. A 2 liter round bottom flask was charged with benzene (800 ml), pyridine (21 g, 0.26 mole), monomethyl sebacate (50 g, 0.23 mole), cupric acetate (8.2 g, 45 mmole), and lead tetraacetate (160 g, 0.35 mole). The reaction was carried out for 2 hours at reflux under nitrogen. The reaction mixture was worked up, and after distillation, yielded 13 g (32%) of methyl-8-nonenoate (B.P. 67°C/2.5 mm). The infrared spectrum (NaCl plates) showed absorptions centered at  $1742\text{ cm}^{-1}$  (C=O stretching),  $1641\text{ cm}^{-1}$  (C=C stretching), and  $995\text{ cm}^{-1}$  and  $911\text{ cm}^{-1}$  (vinyl C-H bending) (see p. 278). The  $^{13}\text{C}$  NMR spectrum (neat) showed peaks at 25.30 ppm ( $=\text{CH}-\text{CH}_2-\text{CH}_2-$ ,  $-\text{CH}_2-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}$ ), 29.25 ppm ( $-(\text{CH}_2)_2-\text{CH}_2-\text{CH}_2-(\text{CH}_2)_2-$ ), 34.09 ppm ( $=\text{CH}-\text{CH}_2-$ ,  $-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-$ ), 50.92 ppm ( $-\text{O}-\text{CH}_3$ ), 114.50 ppm ( $\text{CH}_2=$ ), 139.04 ppm ( $=\text{CH}-$ ), and 172.90 ppm ( $-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-$ ) (see p. 248).

3. Methyl-8,9-epoxynonanoate. A solution of methyl-8-nonenoate (10 g, 59 mmole) and dichloromethane (31 ml) was added to a solution of m-chloroperoxybenzoic acid

(14 g, 69 mmole) and dichloromethane (80 ml) at 0°C over a 10 minute period. The reaction was carried out for 5 hours at room temperature with stirring under nitrogen. The reaction mixture was worked up, and after distillation, yielded 9.4 g (86%) of methyl-8,9-epoxynonanoate (B.P. 81-2°C/0.5 mm). The infrared spectrum (NaCl plates) showed absorptions centered at  $1739\text{ cm}^{-1}$  (C=O stretching), and at  $915\text{ cm}^{-1}$  and  $836\text{ cm}^{-1}$  (epoxide C-O-C stretching) (see p. 278). The  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ ) showed peaks at 25.28 ppm ( $-\text{CH}_2-\text{CH}_2-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{O}-$ ), 26.33 ppm ( $-\overset{\text{O}}{\text{CH}}-\text{CH}_2-\text{CH}_2-$ ), 29.53 ppm ( $-(\text{CH}_2)_2-\text{CH}_2-\text{CH}_2-(\text{CH}_2)_2-$ ), 32.95 ppm ( $-\overset{\text{O}}{\text{CH}}-\text{CH}_2-$ ), 33.99 ppm ( $-\text{CH}_2-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{O}-$ ), 46.36 ppm ( $\text{CH}_2-\overset{\text{O}}{\text{C}}-$ ), 51.08 ppm ( $-\text{O}-\text{CH}_3$ ), 51.76 ppm ( $-\overset{\text{O}}{\text{CH}}-$ ), and 173.23 ppm ( $-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{O}-$ ) (see p. 252).

#### J. Methyl-9,10-epoxydecanoate.

1. Ethyl-10-undecenoate. A 250 ml single neck round bottom flask was fitted with a condenser and a nitrogen bypass, and the hot glassware was cooled under a dry nitrogen flow. A teflon coated magnetic stir bar was added to the flask, and the flask was charged with 10-undecenoic acid (76 g, 0.41 mole), absolute ethanol (94 g, 2.0 moles), and p-toluenesulfonic acid (0.80 g, 4.2 mmole). The reaction mixture was heated at reflux (78°C) with stirring overnight, then cooled to room temperature. The solution was washed with 250 ml of 5% (wt./vol.) aqueous sodium bicarbonate solution and 200 ml of distilled water, then

dried over anhydrous calcium chloride. Distillation yielded 69 g (79%) of ethyl-10-undecenoate (B.P. 129-30°C/15 mm) as a pale yellow liquid.

2. 1,1-Diphenyl-1,10-undecadiene. This procedure is a modification of that described by Black and Weedon.<sup>151</sup> A 1 liter three-neck round bottom flask was fitted with a pressure equalizer addition funnel, a thermometer, and a condenser and a nitrogen bypass, and the hot glassware was cooled under a dry nitrogen flow. A teflon coated magnetic stir bar was added to the flask, and the flask was charged with phenyl magnesium bromide (300 ml of a 2.4 M solution in diethyl ether, 0.72 mole) using a dry, nitrogen filled syringe under positive nitrogen pressure. The addition funnel was charged with ethyl-10-undecenoate (65 g, 0.31 mole) and anhydrous diethyl ether (330 ml). After cooling to 20°C, the ethyl-10-undecenoate solution was added to the flask dropwise over a 1 hour period while maintaining the temperature at 20°C. The reaction mixture was heated at reflux for 2.5 hours with stirring under nitrogen, after which it was cooled to room temperature and decomposed by slowly adding a saturated ammonium chloride solution (210 ml). The reaction mixture was washed with distilled water to give a clear ethereal solution. Concentration of the ethereal solution gave the crude alcohol, which was then transferred to a 250 ml round bottom flask fitted with a single piece Vigreux column condenser, a

take-off adaptor, and receiver flasks. After flushing the system with nitrogen, the crude alcohol was heated to 200°C for one-half hour, causing the dehydration of the alcohol. Distillation of the product yielded 74 g (79%) of 1,1-diphenyl-1,10-undecadiene (B.P. 200°C/2 mm) as a slightly yellow oil.

3. Methyl-9-decenoate. A 2 liter three-neck round bottom flask was charged with 1,1-diphenyl-1,10-undecadiene (69 g, 0.23 mole) and glacial acetic acid (690 ml). A teflon coated magnetic stir bar was added to the flask, and the flask was fitted with a nitrogen bypass, pressure equalizer addition funnel, and a thermometer. After flushing the system with nitrogen, the addition funnel was charged with a solution of chromium trioxide (52 g, 0.52 mole) and distilled water (55 ml). The flask contents were heated to 35°C, and the chromium trioxide solution was added dropwise with vigorous stirring over a 3 hour period, causing the reaction mixture to take on a greyish-green color. The reaction mixture was kept at 35°C during the reaction and for 0.5 hour after the addition of the chromium trioxide solution was complete. Approximately 200 ml of acetic acid was removed under reduced pressure while maintaining the pot temperature below 40°C. The reaction mixture was then washed with 1.4 liter of 2N aqueous sulfuric acid and extracted with 4 x 75 ml of benzene. The benzene solution was washed with 4 x 100 ml of distilled

water and concentrated. Distillation of the residual solution yielded 16 g (45%) of 9-decenoic acid and benzophenone in equal amounts (B.P. 148-52°C/15 mm).

A 250 ml round bottom flask was fitted with a condenser and nitrogen bypass, and the hot glassware cooled under a dry nitrogen flow. A teflon coated magnetic stir bar was added to the flask, and the flask was charged with the crude 9-decenoic acid (16 g, 95 mmole), anhydrous methanol (16 g, 0.51 mole), and p-toluenesulfonic acid (0.10 g, 1.0 mmole). The reaction mixture was heated at reflux (64°C) overnight with stirring under nitrogen, then cooled to room temperature. After diluting with 75 ml of benzene, the reaction mixture was washed with 125 ml of 5% (wt./vol.) aqueous sodium bicarbonate and 2 x 100 ml of distilled water. Distillation yielded 13 g (75%) of methyl-9-decenoate (B.P. 108-10°C/10 mm). The infrared spectrum (NaCl plates) showed absorptions centered at 1743  $\text{cm}^{-1}$  (C=O stretching), 1641  $\text{cm}^{-1}$  (C=C stretching), and 996  $\text{cm}^{-1}$  and 910  $\text{cm}^{-1}$  (vinyl C-H bending) (see p. 279). The  $^{13}\text{C}$  NMR spectrum (neat) showed peaks at 25.32 ppm ( $=\text{CH}-\text{CH}_2-\text{CH}_2-$ ,  $-\text{CH}_2-\text{CH}_2-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{O}$ ), 29.44 ppm and 29.59 ppm ( $=\text{CH}-(\text{CH}_2)_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-(\text{CH}_2)_2-$ ), 34.03 ppm and 34.20 ppm ( $=\text{CH}-\text{CH}_2-$ ,  $-\text{CH}_2-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{O}$ ), 51.00 ppm ( $-\text{O}-\text{CH}_2$ ), 114.45 ppm ( $\text{CH}_2=$ ), 139.09 ppm ( $=\text{CH}-$ ), and 172.94 ppm ( $-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{O}$ ) (see p. 248).

4. Methyl-9,10-epoxydecanoate. A solution of methyl-9-decenoate (11 g, 60 mmole) and dichloromethane

(34 ml) was added to a solution of m-chloroperoxybenzoic acid (14 g, 70 mmole) and dichloromethane (80 ml) at 0°C over a 10 minute period. The reaction was carried out for 5 hours at room temperature with stirring under nitrogen. The reaction mixture was worked up, and after distillation, yielded 7.8 g (66%) of methyl-9,10-epoxydecanoate (B.P. 87°C/0.4 mm). The infrared spectrum (NaCl plates) showed absorptions centered at  $1740\text{ cm}^{-1}$  (C=O stretching), and  $916\text{ cm}^{-1}$  and  $837\text{ cm}^{-1}$  (epoxide C-O-C stretching) (see p. 279). The  $^{13}\text{C}$  NMR spectrum (neat) showed peaks at 25.33 ppm ( $-\text{CH}_2-\text{CH}_2-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{O}-$ ), 26.44 ppm ( $-\overset{\text{O}}{\text{CH}}-\text{CH}_2-\text{CH}_2-$ ), 29.53 ppm ( $-(\text{CH}_2)_3-\text{CH}_2-(\text{CH}_2)_3-$ ), 29.76 ppm ( $-(\text{CH}_2)_2-\overset{\text{O}}{\text{CH}}_2-\text{CH}_2-\text{CH}_2-(\text{CH}_2)_2-$ ), 33.00 ppm ( $-\overset{\text{O}}{\text{CH}}-\text{CH}_2-$ ), 34.01 ppm ( $-\text{CH}_2-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{O}-$ ), 46.34 ppm ( $\overset{\text{O}}{\text{CH}}_2-$ ), 51.06 ppm ( $-\text{O}-\text{CH}_3$ ), 51.76 ppm ( $-\overset{\text{O}}{\text{CH}}-$ ), and 173.22 ppm ( $-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{O}-$ ) (see p. 252).

K. 1-Hexene oxide. A solution of 1-hexene (13 g, 0.15 mole) and dichloromethane (200 ml) was added to a solution of m-chloroperoxybenzoic acid (33 g, 0.16 mole) and dichloromethane (280 ml) at 0°C over a 30 minute period. The reaction was carried out overnight at room temperature and for 5 hours at 40°C with stirring under nitrogen. The reaction mixture was worked up, and after distillation, yielded 11 g (73%) of 1-hexene oxide (B.P. 121-4°C). The infrared spectrum (NaCl plates) showed absorptions centered at  $917\text{ cm}^{-1}$  and  $836\text{ cm}^{-1}$  (epoxide C-O-C stretching) (see p.

280). The  $^{13}\text{C}$  NMR spectrum (neat) showed peaks at 14.19 ppm ( $-\text{CH}_3$ ), 23.10 ppm ( $-\text{CH}_2-\text{CH}_3$ ), 28.83 ppm ( $-\text{CH}_2-\text{CH}_2-\text{CH}_3$ ), 32.93 ppm ( $-\text{CH}-\text{CH}_2-$ ), 46.27 ppm ( $\text{CH}_2-$ ), and 51.71 ppm ( $-\text{CH}-$ ) (see p. 253).

L. Measurement of the rate of epoxidation of methyl  $\omega$ -alkenoates. The rate of epoxidation of the methyl  $\omega$ -alkenoates was determined by measuring the relative concentrations of the unreacted methyl  $\omega$ -alkenoates and the formed methyl  $\omega$ -epoxyalkanoates by gas chromatography. Samples were withdrawn from the reaction flask at periodic intervals (1 hour), then quenched by chilling to  $-20^\circ\text{C}$  for 5 minutes. The samples were filtered through a coarse sintered filter, then injected into the gas chromatograph. The relative concentrations of starting material and product were determined by cutting out and weighing the gas chromatograph curves. The percent conversion of starting material to product was plotted versus reaction time (see p. 172).

#### IV. Homopolymerizations of the Methyl $\omega$ -Epoxyalkanoates Using the $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$ (1/0.5/1) Initiator System

A. Preparation of the  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$  (1/0.5/1) initiator system. A large Schlenk tube with a side arm and teflon coated magnetic stir bar was fitted with a three way vacuum stopcock, then, alternately, flamed and cooled at

0.005 mm and filled with dry nitrogen three times. The tube was charged with neat triethylaluminum (2.9 g, 25 mmole) under positive nitrogen pressure using a dry, nitrogen filled gas tight syringe. The tube was then cooled to 0°C and fitted with a hot pressure equalizer addition funnel. After cooling the addition funnel under a flow of dry nitrogen (10-15 minutes), the funnel was charged with acetyl acetone (2.5 g, 25 mmole) and freshly distilled anhydrous diethyl ether (18 ml). The acetyl acetone solution was added with stirring under nitrogen dropwise to the chilled triethylaluminum over a 1 hour period, initially causing the evolution of a white vapor. The reaction between the acetyl acetone and the triethylaluminum was completed by stirring an additional 2 hours at 0°C. The flask was then charged with redistilled, deionized water (0.23 ml, 12.5 mmole) over a 10 minute period, causing further gas evolution. The slightly yellow initiator solution (1.02 M in triethylaluminum) was stored under nitrogen at 0°C until use.

B. Polymerization of methyl glycidate. A 25 x 70 mm polymerization tube was fitted with a three-way vacuum stopcock, then alternately, flamed and cooled at 0.005 mm and filled with dry nitrogen three times. The tube was charged under positive nitrogen pressure with benzene (3.0 ml), methyl glycidate (1.0 g, 9.8 mmole), and the triethylaluminum/water/acetyl acetone ( $\text{AlC}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$ ) (1/0.5/1)

initiator solution (0.48 ml, 0.49 mmole, 5 mole% based on monomer) at room temperature using dry, nitrogen filled syringes. The reaction mixture was subjected to three freeze-thaw cycles, after which the tube was sealed under vacuum (0.005 mm). The polymerization was allowed to proceed for 25 days at room temperature, during which time the clear, nearly colorless solution became a pale orange, slightly viscous solution with a small amount of white precipitate. After freezing in liquid nitrogen, the tube was opened, and the contents precipitated by adding them to diethyl ether. The precipitate was collected by filtration on a sintered glass filter funnel as a pale orange, crumbly powder. The material was slurried for 1 day in an isopropanol/water (75/25) solution, then collected as a pure white, tough, elastomeric material. The polymer was dried for 2 days at 61°C and 0.005 mm over  $P_2O_5$  to yield 7.1 mg (0.7%) of material. The infrared spectrum (KBr pellet) showed absorptions centered at  $1745\text{ cm}^{-1}$  (C=O stretching) and  $1135\text{ cm}^{-1}$  (ether C-O-C stretching) (see p. 281).

C. Polymerization of methyl-3,4-epoxybutanoate. A polymerization tube was charged under positive nitrogen pressure with benzene (6.4 ml), methyl-3,4-epoxybutanoate (2.0 g, 17 mmole), and the  $Al(C_2H_5)_3/H_2O/AcAc$  (1/0.5/1) initiator solution (0.85 ml, 0.87 mmole, 5 mole% based on

monomer) at room temperature using dry, nitrogen filled syringes. The reaction mixture was subjected to three freeze-thaw cycles, after which the tube was sealed under vacuum (0.005 mm). The polymerization was allowed to proceed for 25 days at room temperature, during which time the clear, nearly colorless solution became a pale orange, slightly viscous solution with a small amount of white precipitate. After freezing in liquid nitrogen, the tube was opened, and the contents precipitated by slowly adding them to diethyl ether. The precipitate was collected by filtration on a sintered glass filter funnel as an off-white, tough, elastomeric material. The material was slurried for 1 day in isopropanol, collected by filtration, and dried for 2 days at 61°C and 0.005 mm over  $P_2O_5$  to yield 85 mg (4.3%) of very tough, white elastomer. The infrared spectrum (NaCl plates) showed absorptions centered at  $1740\text{ cm}^{-1}$  (C=O stretching),  $1175\text{ cm}^{-1}$  (ester C-O stretching), and  $1125\text{ cm}^{-1}$  (ether C-O-C stretching) (see p. 281). The  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ ) showed peaks at 37.37 ppm ( $-\underline{\text{CH}}_2-$ ), 51.59 ppm ( $-\text{O}-\underline{\text{CH}}_3$ ), 71.62 ppm ( $-\underline{\text{CH}}_2-\text{O}-$ ), 76.05 ppm ( $-\overset{\text{O}}{\text{C}}\text{H}-\text{O}-$ ), and 171.81 ppm ( $-\overset{\text{O}}{\text{C}}-\text{O}$ ) (see p. 253).

D. Polymerization of methyl-4,5-epoxypentanoate. A polymerization tube was charged under positive nitrogen pressure with benzene (6.7 ml), methyl-4,5-epoxypentanoate (2.0 g, 15 mmole), and the  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$  (1/0.5/1)

initiator solution (0.76 ml, 0.78 mmole, 5 mole% based on monomer) at room temperature using dry, nitrogen filled syringes. The reaction mixture was subjected to three freeze-thaw cycles, after which the tube was sealed under vacuum (0.005 mm). The polymerization was allowed to proceed for 25 days at room temperature, during which time the clear, nearly colorless solution became a pale orange, viscous solution with a large amount of white precipitate. After freezing in liquid nitrogen, the tube was opened, and the contents precipitated by slowly adding them to diethyl ether. The precipitate was collected by filtration on a sintered glass filter funnel as a tough, white, elastomeric material. The material was slurried for 1 day in methanol, collected by filtration, and dried for 2 days at 61°C and 0.005 mm over  $P_2O_5$  to yield 0.15 g (7.6%) of tough, white elastomer. The infrared spectrum (NaCl plates) showed absorptions centered at  $1735\text{ cm}^{-1}$  (C=O stretching),  $1170\text{ cm}^{-1}$  (ester C-O stretching), and  $1100\text{ cm}^{-1}$  (ether C-O-C stretching) (see p. 282). The  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ ) showed peaks at 27.29 ppm ( $-\overset{\text{O}}{\text{CH}}-\text{CH}_2-$ ), 29.91 ppm ( $-\text{CH}_2-\overset{\text{O}}{\text{C}}-\text{O}-$ ), 51.49 ppm ( $-\text{O}-\text{CH}_3$ ), 72.36 ppm ( $-\text{CH}_2-\text{O}-$ ), 78.50 ppm ( $-\overset{|}{\text{CH}}-\text{O}-$ ), and 173.87 ppm ( $-\overset{\text{O}}{\text{C}}-\text{O}-$ ) (see p. 254).

E. Polymerization of methyl-5,6-epoxyhexanoate. A polymerization tube was charged under positive nitrogen

pressure with benzene (3.5 ml), methyl-5,6-epoxyhexanoate (1.0 g, 6.9 mmole), and the  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$  (1/0.5/1) initiator solution (0.34 ml, 0.35 mmole, 5 mole% based on monomer) at room temperature using dry, nitrogen filled syringes. The reaction mixture was subjected to three freeze-thaw cycles, after which the tube was sealed under vacuum (0.005 mm). The polymerization was allowed to proceed for 6 days at 65°C, during which time the clear, nearly colorless solution became a clear yellow, very viscous solution. After freezing in liquid nitrogen, the tube was opened, and the polymer dissolved in 200 ml of benzene and 1 ml of acidified methanol (1% hydrochloric acid). The polymer solution was filtered through a sintered glass filter funnel, transferred to a 500 ml separatory funnel, and washed with 2 x 100 ml of 1% (wt./vol.) aqueous hydrochloric acid, 2 x 100 ml of 5% (wt./vol.) aqueous sodium bicarbonate, 2 x 100 ml of distilled water, and 100 ml of saturated aqueous sodium chloride. After concentrating to a volume of 50 ml, the polymer solution was freeze-dried for 2 days at room temperature and 0.005 mm, and yielded 0.33 g (33%) of a tough, off-white elastomer. The infrared spectrum (film on NaCl plates) showed absorptions centered at  $1740\text{ cm}^{-1}$  (ester C=O stretching),  $1170\text{ cm}^{-1}$  (ester C-O stretching), and  $1090\text{ cm}^{-1}$  (ether C-O-C stretching) (see p. 282). The  $^{13}\text{C}$  NMR spectrum (benzene) showed peaks at 21.36 ppm ( $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$ ), 31.89 ppm

$(-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}\text{H}-\text{CH}_2-)$ , 34.18 ppm ( $-\text{CH}_2-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{O}-$ ), 51.06 ppm ( $-\text{O}-\text{CH}_3$ ),  
 72.91 ppm and 73.23 ppm ( $-\text{CH}_2-\text{O}-$ ), 79.60 ppm ( $-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{O}-$ ),  
 and 173.43 ppm ( $-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{O}-$ ) (see p. 254).

F. Polymerization of methyl-6,7-epoxyheptanoate. A polymerization tube was charged under positive nitrogen pressure with benzene (3.6 ml), methyl-6,7-epoxyheptanoate (1.0 g, 6.3 mmole), and the  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$  (1/0.5/1) initiator solution (0.31 ml, 0.32 mmole, 5 mole% based on monomer) at room temperature using dry, nitrogen filled syringes. The reaction mixture was subjected to three freeze-thaw cycles, after which the tube was sealed under vacuum (0.005 mm). The polymerization was allowed to proceed for 25 days at room temperature, during which time the clear, nearly colorless solution became a slightly orange, opaque, solid plug. After freezing in liquid nitrogen, the tube was opened, and the plug dissolved in 100 ml of benzene and 1 ml of acidified methanol (1% hydrochloric acid). The polymer solution was added dropwise to 1 liter of acidified methanol (1% hydrochloric acid), and the precipitated polymer collected by filtration on a sintered glass filter funnel. After rinsing the polymer with methanol, the polymer was redissolved in 100 ml of benzene. The polymer solution was filtered through a sintered glass filter funnel, added dropwise to 1 liter of methanol, and the precipitated polymer collected by filtration on a

sintered glass filter funnel. Drying for 2 days at 61°C and 0.005 mm over  $P_2O_5$  yielded 0.52 g (52%) of a very tough, white elastomer. The infrared spectrum (film on NaCl plates) showed absorptions centered at  $1740\text{ cm}^{-1}$  (C=O stretching),  $1170\text{ cm}^{-1}$  (ester C-O stretching), and  $1100\text{ cm}^{-1}$  (ether C-O-C stretching) (see p. 283). The  $^{13}\text{C}$  NMR spectrum (1,4-dioxane) showed peaks at 25.61 ppm ( $-\overset{\text{O}}{\text{CH}}-\text{CH}_2-$ ), 32.40 ppm ( $-\overset{\text{O}}{\text{CH}}-\text{CH}_2-$ ), 34.14 ppm ( $-\overset{\text{O}}{\text{CH}_2}-\text{C}-\text{O}-$ ), 51.18 ppm ( $-\text{O}-\overset{\text{O}}{\text{CH}_3}$ ), 73.22 ppm ( $-\text{CH}_2-\text{O}-$ ), 79.83 ppm ( $-\overset{\text{O}}{\text{CH}}-\text{O}-$ ), and 173.57 ppm ( $-\overset{\text{O}}{\text{C}}-\text{O}$ ) (see p. 255).

G. Polymerization of methyl-7,8-epoxyoctanoate. A polymerization tube was charged under positive nitrogen pressure with benzene (3.7 ml), methyl-7,8-epoxyoctanoate (1.0 g, 5.8 mmole), and the  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$  (1/0.5/1) initiator solution (0.29 ml, 0.30 mmole, 5 mole% based on monomer) at room temperature using dry, nitrogen filled syringes. The reaction mixture was subjected to three freeze-thaw cycles, after which the tube was sealed under vacuum (0.005 mm). The polymerization was allowed to proceed for 25 days at room temperature, during which time the clear, nearly colorless solution became a clear, slightly orange, solid plug. After freezing in liquid nitrogen, the tube was opened, and the plug dissolved in 100 ml of benzene and 1 ml of acidified methanol (1% hydrochloric acid). The polymer solution was added dropwise to

1 liter of acidified methanol (1% hydrochloric acid), and the precipitated polymer collected by filtration on a sintered glass filter funnel. After rinsing the polymer with methanol, the polymer was redissolved in 100 ml of benzene. The polymer solution was filtered through a sintered glass filter funnel, added dropwise to 1 liter of methanol, and the precipitated polymer collected by filtration on a sintered glass filter funnel. Drying for 2 days at 61°C and 0.005 mm over  $P_2O_5$  yielded 0.63 g (63%) of a very tough, white elastomer. The infrared spectrum (film on NaCl plates) showed absorptions centered at 1740  $cm^{-1}$  (C=O stretching), 1170  $cm^{-1}$  (ester C-O stretching), and 1100  $cm^{-1}$  (ether C-O-C stretching) (see p. 283). The  $^{13}C$  NMR spectrum (1,4-dioxane) showed peaks at 25.45 ppm ( $-\overset{\overset{O}{\parallel}}{CH}-CH_2-\underline{CH_2}-$ ,  $-\underline{CH_2}-CH_2-\overset{\overset{O}{\parallel}}{C}-O$ ), 29.86 ppm ( $-(CH_2)_2-\underline{CH_2}-(CH_2)_2-$ ), 32.60 ppm ( $-\overset{\overset{O}{\parallel}}{CH}-\underline{CH_2}-$ ), 34.08 ppm ( $-\underline{CH_2}-\overset{\overset{O}{\parallel}}{C}-O$ ), 51.12 ppm ( $-O-\underline{CH_3}$ ), 73.44 ppm ( $-\underline{CH_2}-O-$ ), 79.93 ppm ( $-\overset{\overset{|}{CH}}{-}O-$ ), and 173.48 ppm ( $-\overset{\overset{O}{\parallel}}{C}-O$ ) (see p. 255).

H. Polymerization of methyl-8,9-epoxynonanoate. A polymerization tube was charged under positive nitrogen pressure with benzene (3.9 ml), methyl-8,9-epoxynonanoate (1.0 g, 5.4 mmole), and the  $Al(C_2H_5)_3/H_2O/AcAc$  (1/0.5/1) initiator solution (0.26 ml, 0.27 mmole, 5 mole% based on monomer) at room temperature using dry, nitrogen filled syringes. The reaction mixture was subjected to three

freeze-thaw cycles, after which the tube was sealed under vacuum (0.005 mm). The polymerization was allowed to proceed for 25 days at room temperature, during which time the clear, nearly colorless solution became a clear, slightly orange, solid plug. After freezing in liquid nitrogen, the tube was opened, and the plug dissolved in 100 ml of benzene and 1 ml of acidified methanol (1% hydrochloric acid). The polymer solution was added dropwise to 1 liter of acidified methanol (1% hydrochloric acid), and the precipitated polymer collected by filtration on a sintered glass filter funnel. After rinsing the polymer with methanol, the polymer was redissolved in 100 ml of benzene. The polymer solution was filtered through a sintered glass filter funnel, added dropwise to 1 liter of methanol, and the precipitated polymer collected by filtration on a sintered glass filter funnel. Drying for 2 days at 61°C and 0.005 mm over  $P_2O_5$  yielded 0.70 g (70%) of very tough, white elastomer. The infrared spectrum (film on NaCl plates) showed absorptions centered at  $1745\text{ cm}^{-1}$  (C=O stretching),  $1170\text{ cm}^{-1}$  (ester C-O stretching), and  $1100\text{ cm}^{-1}$  (ether C-O-C stretching) (see p. 284). The  $^{13}\text{C}$  NMR spectrum (1,4-dioxane) showed peaks at 25.46 ppm ( $-\text{CH}_2-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{O}-$ ), 25.89 ppm ( $-\overset{\text{O}}{\text{CH}}-\text{CH}_2-\text{CH}_2-$ ), 29.74 ppm ( $-\text{CH}_2-(\text{CH}_2)_2-\overset{\text{O}}{\text{C}}-\text{O}-$ ), 30.08 ppm ( $-\overset{\text{O}}{\text{CH}}-(\text{CH}_2)_2-\text{CH}_2-$ ), 32.76 ppm ( $-\overset{\text{O}}{\text{CH}}-\text{CH}_2-$ ), 34.11 ppm ( $-\text{CH}_2-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{O}-$ ), 51.14 ppm ( $-\text{O}-\text{CH}_3$ ), 73.04 ppm, 73.19 ppm, and 73.46 ppm ( $-\text{CH}_2-\text{O}-$ ), 79.97 ppm ( $-\overset{\text{O}}{\text{CH}}-\text{O}-$ ),

and 173.51 ppm ( $-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{O}-$ ) (see p. 256).

I. Polymerization of methyl-9,10-epoxydecanoate. A polymerization tube was charged under positive nitrogen pressure with benzene (4.0 ml), methyl-9,10-epoxydecanoate (1.0 g, 5.0 mmole), and the  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$  (1/0.5/1) initiator solution (0.25 ml, 0.26 mmole, 5 mole% based on monomer) at room temperature using dry, nitrogen filled syringes. The reaction mixture was subjected to three freeze-thaw cycles, after which the tube was sealed under vacuum (0.005 mm). The polymerization was allowed to proceed for 25 days at room temperature, during which time the clear, nearly colorless solution became a clear, slightly orange, solid plug. After freezing in liquid nitrogen, the tube was opened, and the plug dissolved in 100 ml of benzene and 1 ml of acidified methanol (1% hydrochloric acid). The polymer solution was added dropwise to 1 liter of acidified methanol (1% hydrochloric acid), and the precipitated polymer collected by filtration on a sintered glass filter funnel. After rinsing the polymer with methanol, the polymer was redissolved in 100 ml of benzene. The polymer solution was filtered through a sintered glass filter funnel, added dropwise to 1 liter of methanol, and the precipitated polymer collected by filtration on a sintered glass filter funnel. Drying for 2 days at 61°C and 0.005 mm over  $\text{P}_2\text{O}_5$  yielded 0.79 g (79%)

of very tough, white elastomer. The infrared spectrum (film on NaCl plates) showed absorptions centered at  $1740\text{ cm}^{-1}$  ( $\text{C}=\text{O}$  stretching),  $1170\text{ cm}^{-1}$  (ester  $\text{C}-\text{O}$  stretching), and  $1105\text{ cm}^{-1}$  (ether  $\text{C}-\text{O}-\text{C}$  stretching) (see p. 284). The  $^{13}\text{C}$  NMR spectrum (1,4-dioxane) showed peaks at 25.46 ppm ( $-\text{CH}_2-\text{CH}_2-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{O}-$ ), 25.98 ppm ( $-\overset{\text{O}}{\text{CH}}-\text{CH}_2-\text{CH}_2-$ ), 29.76 ppm ( $-(\text{CH}_2)_3-\text{CH}_2-(\text{CH}_2)_3-$ ), 29.93 ppm ( $-\text{CH}_2-(\text{CH}_2)_2-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{O}-$ ), 30.31 ppm ( $-\overset{\text{O}}{\text{CH}}-(\text{CH}_2)_2-\text{CH}_2-$ ), 32.77 ppm ( $-\overset{\text{O}}{\text{CH}}-\text{CH}_2-$ ), 34.13 ppm ( $-\text{CH}_2-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{O}-$ ), 51.12 ppm ( $-\text{O}-\text{CH}_3$ ), 73.36 ppm and 73.51 ppm ( $-\text{CH}_2-\text{O}-$ ), 80.01 ppm ( $-\overset{\text{O}}{\text{CH}}-\text{O}-$ ), and 173.51 ppm ( $-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{O}-$ ) (see p. 256).

J. Polymerization of propylene oxide. A polymerization tube was charged under positive nitrogen pressure with benzene (9.9 ml), propylene oxide (2.6 g, 52 mmole), and the  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$  (1/0.5/1) initiator solution (2.1 ml, 2.2 mmole, 5 mole% based on monomer) at room temperature using dry, nitrogen filled syringes. The reaction mixture was subjected to three freeze-thaw cycles, after which the tube was sealed under vacuum (0.005 mm). The polymerization was allowed to proceed for 25 days at room temperature, during which time the clear, nearly colorless solution became a clear, slightly orange, solid plug. After freezing in liquid nitrogen, the tube was opened, and the plug dissolved in 200 ml of benzene and 2 ml of acidified methanol (1% hydrochloric acid). The polymer solution

was filtered through a sintered glass filter funnel, transferred to a 1 liter separatory funnel, and washed with 2 x 250 ml of 1% (wt./vol.) aqueous hydrochloric acid, 2 x 250 ml of 5% (wt./vol.) aqueous sodium bicarbonate, and 2 x 250 ml of distilled water. After concentrating to a volume of 50 ml, the polymer solution was freeze-dried for 2 days at room temperature and 0.005 mm, and yielded 2.7 g (90%) of a tough, white elastomer. The infrared spectrum (film on NaCl plates) showed absorptions centered at  $1450\text{ cm}^{-1}$  and  $1375\text{ cm}^{-1}$  (methyl C-H bending), and  $1105\text{ cm}^{-1}$  (ether C-O-C stretching) (see p. 285). The  $^{13}\text{C}$  NMR spectrum (benzene) showed peaks at 17.75 ppm ( $-\underline{\text{CH}}_3$ ), 73.78 ppm ( $-\text{O}-\underline{\text{CH}}_2-$ ), and 75.71 ppm ( $-\overset{|}{\underline{\text{CH}}}-\text{O}-$ ) (see p. 257).

K. Polymerization of 1-hexene oxide. A polymerization tube was charged under positive nitrogen pressure with benzene (3.6 ml), 1-hexene oxide (1.0 g, 10 mmole), and the  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$  (1/0.5/1) initiator solution (0.42 ml), 0.43 mmole, 5 mole% based on monomer) at room temperature using dry, nitrogen filled syringes. The reaction mixture was subjected to three freeze-thaw cycles, after which the tube was sealed under vacuum (0.005 mm). The polymerization was allowed to proceed for 25 days at room temperature, during which time the clear, nearly colorless solution became a clear, slightly orange, solid plug. After freezing in liquid nitrogen, the tube was opened, and

the plug dissolved in 100 ml of benzene and 1 ml of acidified methanol (1% hydrochloric acid). The polymer solution was added dropwise to 1 liter of acidified methanol (1% hydrochloric acid), and the precipitated polymer collected by filtration on a sintered glass filter funnel. After rinsing the polymer with methanol, the polymer was redissolved in 100 ml of benzene. The polymer solution was filtered through a sintered glass filter funnel, added dropwise to 1 liter of methanol, and the precipitated polymer collected by filtration on a sintered glass filter funnel. Drying for 2 days at 61°C and 0.005 mm over  $P_2O_5$  yielded 0.83 g (83%) of tough, white elastomer. The infrared spectrum (film on NaCl plates) showed absorptions centered at 1470  $cm^{-1}$  (methylene C-H bending), and 1110  $cm^{-1}$  (ether C-O-C stretching) (see p. 285). The  $^{13}C$  NMR spectrum (benzene) showed peaks at 14.31 ppm ( $-\underline{CH}_3$ ), 23.29 ppm ( $-\underline{CH}_2-CH_3$ ), 28.10 ppm ( $-\underline{CH}_2-CH_2-CH_3$ ), 32.43 ppm ( $-\overset{O}{\underset{|}{CH}}-\underline{CH}_2-$ ), 73.64 ppm ( $-\underline{CH}_2-O-$ ), and 80.03 ppm ( $-\overset{|}{\underset{O}{CH}}-O-$ ) (see p. 257).

V. Copolymerizations of the Methyl  $\omega$ -Epoxyalkanoates with Several Cyclic Ethers using the  $Al(C_2H_5)_3/H_2O/AcAc$  (1/0.5/1) Initiator System

A. Copolymerization of methyl-3,4-epoxybutanoate.

1. With propylene oxide. A polymerization tube was charged under positive nitrogen pressure with benzene (11 ml), methyl-3,4-epoxybutanoate (1.2 g, 10 mmole, 30

mole% of the monomer feed), propylene oxide (1.4 g, 23 mmole, 70 mole% of the monomer feed), and the  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$  (1/0.5/1) initiator solution (1.6 ml, 1.7 mmole, 5 mole% based on monomer) at room temperature using dry, nitrogen filled syringes. The reaction mixture was subjected to three freeze-thaw cycles, after which the tube was sealed under vacuum (0.025 mm). The polymerization was allowed to proceed for 38 days at room temperature, during which time the clear, nearly colorless solution became a clear, pale yellow, viscous solution. After freezing in liquid nitrogen, the tube was opened, and the contents precipitated by adding them to 800 ml of n-heptane. The precipitate was collected by filtration on a sintered glass filter funnel as a tough, yellow material. The polymer was dissolved in 100 ml of acidified methanol (1% hydrochloric acid); addition of 500 ml of distilled water, in an attempt to precipitate the polymer, failed. After concentrating the solution to dryness, the polymer was redissolved in 95% ethanol, but the addition of distilled water as a precipitant failed again. The solution was concentrated to dryness, and the polymer was redissolved in chloroform. After filtering the polymer solution through a sintered glass filter funnel, it was added to n-heptane. The precipitated polymer was collected by filtration, redissolved in 10 ml of acetone, and precipitated into 1% aqueous hydrochloric acid. After collecting the

polymer by filtration and rinsing with distilled water, it was dried for 3 days at 40°C and 0.025 mm over  $P_2O_5$  to yield 0.6 mg (0.02%) of a pale yellow, tough elastomer. The infrared spectrum (film on NaCl plates) showed absorptions centered at  $1740\text{ cm}^{-1}$  (C=O stretching),  $1440\text{ cm}^{-1}$  and  $1375\text{ cm}^{-1}$  (methyl C-H bending),  $1170\text{ cm}^{-1}$  (ester C-O stretching), and  $1110\text{ cm}^{-1}$  (ether C-O-C stretching) (see p. 286).

2. With 1-butene oxide. A polymerization tube was charged under positive nitrogen pressure with benzene (11 ml), methyl-3,4-epoxybutanoate (1.0 g, 8.8 mmole, 30 mole% of the monomer feed), 1-butene oxide (1.5 g, 21 mmole, 70 mole% of the monomer feed), and the  $Al(C_2H_5)_3/H_2O/AcAc$  (1/0.5/1) initiator solution (1.5 ml, 1.5 mmole, 5 mole% based on monomer) at room temperature using dry, nitrogen filled syringes. The reaction mixture was subjected to three freeze-thaw cycles, after which the tube was sealed under vacuum (0.025 mm). The polymerization was allowed to proceed for 38 days at room temperature, during which time the clear, nearly colorless solution became a clear, pale yellow, viscous solution. After freezing in liquid nitrogen, the tube was opened, and the contents precipitated by adding them to 800 ml of n-heptane. The precipitate was collected by filtration on a sintered glass filter funnel as a tough, yellow material. The polymer was dissolved in 50 ml of acidified methanol (1% hydrochloric

acid); addition of 500 ml of distilled water, in an attempt to precipitate the polymer, failed. After concentrating the solution to dryness, the polymer was redissolved in 95% ethanol, but the addition of distilled water as a precipitant failed again. The solution was concentrated to dryness, and the polymer was redissolved in chloroform. After filtering the polymer solution through a sintered glass filter funnel, it was added to n-heptane. The precipitated polymer was collected by filtration, redissolved in 10 ml of acetone, and precipitated into 1% aqueous hydrochloric acid. After collecting the polymer by filtration and rinsing with distilled water, it was dried for 2 days at 40°C and 0.025 mm over  $P_2O_5$  to yield 11 mg (0.4%) of a pale yellow, tough elastomer. The infrared spectrum (film on NaCl plates) showed absorptions centered at  $1740\text{ cm}^{-1}$  (C=O stretching),  $1440\text{ cm}^{-1}$  and  $1375\text{ cm}^{-1}$  (methyl C-H bending),  $1170\text{ cm}^{-1}$  (ester C-O stretching), and  $1100\text{ cm}^{-1}$  (ether C-O-C stretching) (see p. 286).

3. With 1-hexene oxide. A polymerization tube was charged under positive nitrogen pressure with benzene (12 ml), methyl-3,4-epoxybutanoate (0.93 g, 8.0 mmole, 30 mole % of the monomer feed), 1-hexene oxide (1.9 g, 19 mmole, 70 mole % of the monomer feed), and the  $Al(C_2H_5)_3/H_2O/AcAc$  (1/0.5/1) initiator solution (1.3 ml, 1.3 mmole, 5 mole % based on monomer) at room temperature using dry, nitrogen filled syringes. The reaction mixture was subjected to

three freeze-thaw cycles, after which the tube was sealed under vacuum (0.025 mm). The polymerization was allowed to proceed for 51 days at room temperature, during which time the clear, nearly colorless solution became a clear, pale yellow, viscous solution. After freezing in liquid nitrogen, the tube was opened, and the contents precipitated by adding them to a ten-fold excess of n-heptane. The precipitate was collected by filtration on a sintered glass filter funnel as a tough, yellow material. The polymer was dissolved in a small amount of methanol, and the polymer was precipitated by adding the solution to a twenty-fold excess of 1% aqueous hydrochloric acid. After collecting the precipitate by filtration and rinsing it with distilled water, the polymer was dried for 2 days at 40°C and 0.025 mm over  $P_2O_5$  to yield 1.0 mg (0.04%) of a pale yellow, tough elastomer. The infrared spectrum (film on NaCl plates) showed absorptions centered at 1740  $cm^{-1}$  (C=O stretching), 1470  $cm^{-1}$  (methylene C-H bending), 1170  $cm^{-1}$  (ester C-O stretching), and 1100  $cm^{-1}$  (ether C-O-C stretching) (see p. 287).

4. With epichlorohydrin. A polymerization tube was charged under positive nitrogen pressure with benzene (8.6 ml), methyl-3,4-epoxybutanoate (0.88 g, 7.6 mmole, 30 mole% of the monomer feed), epichlorohydrin (1.6 g, 18 mmole, 70 mole% of the monomer feed), and the  $Al(C_2H_5)_3/H_2O/AcAc$  (1/0.5/1) initiator solution (1.2 ml, 1.3 mmole,

5 mole % based on monomer) at room temperature using dry, nitrogen filled syringes. The reaction mixture was subjected to three freeze-thaw cycles, after which the tube was sealed under vacuum (0.025 mm). The polymerization was allowed to proceed for 55 days at room temperature, during which time the clear, nearly colorless solution became a clear, pale yellow, viscous solution. After freezing in liquid nitrogen, the tube was opened, and the contents precipitated by adding them to a seven-fold excess of n-heptane. The precipitate was collected by filtration on a sintered glass filter funnel as a tough, yellow material. The polymer was dissolved in a small amount of acetone, and the polymer was precipitated by adding the solution to a ten-fold excess of 1% aqueous hydrochloric acid. After collecting the precipitate by filtration and rinsing it with distilled water, it was slurried in methanol for 1 day, collected by filtration, and redissolved in a small amount of acetone. The polymer solution was filtered through a sintered glass filter funnel, then added to a ten-fold excess of distilled water. The precipitated polymer was collected by filtration, then dried for 2 days at 40°C and 0.025 mm over  $P_2O_5$  to yield 15 mg (0.6%) of a tough, white elastomer. The infrared spectrum (film on NaCl plates) showed absorptions centered at  $1740\text{ cm}^{-1}$  (C=O stretching),  $1170\text{ cm}^{-1}$  (ester C-O stretching),  $1115\text{ cm}^{-1}$  (ether C-O-C stretching), and  $745\text{ cm}^{-1}$  (C-Cl stretching).

(see p. 287).

5. With phenyl glycidyl ether. A polymerization tube was charged under positive nitrogen pressure with benzene (11 ml), methyl-3,4-epoxybutanoate (0.74 g, 6.4 mmole, 30 mole% of the monomer feed), phenyl glycidyl ether (2.2 g, 15 mmole, 70 mole% of the monomer feed), and the  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$  (1/0.5/1) initiator solution (1.1 ml, 1.1 mmole, 5 mole% based on monomer) at room temperature using dry, nitrogen filled syringes. The reaction mixture was subjected to three freeze-thaw cycles, after which the tube was sealed under vacuum (0.025 mm). The polymerization was allowed to proceed for 49 days at room temperature, during which time the clear, nearly colorless solution became a viscous, pale yellow solution with some white precipitate. After freezing in liquid nitrogen, the tube was opened, and the polymer solution was filtered through a sintered glass filter funnel. The filtrate was added dropwise to 750 ml of acidified methanol (1% hydrochloric acid), and the fluffy, white precipitate was collected by filtration on a sintered glass filter funnel, rinsed with methanol, then redissolved in a small amount of benzene. The polymer solution was added dropwise to 500 ml of methanol, and the precipitate was collected by filtration. Drying for 2 days at 40°C and 0.025 mm over  $\text{P}_2\text{O}_5$  yielded 15 mg (0.5%) of a tough, white elastomer. The benzene insoluble material was slurried in 200 ml of acidified

methanol (1% hydrochloric acid), collected by filtration, and rinsed with methanol. Attempts to dissolve the polymer in THF and hot xylene (70-90°C) failed. Drying for 2 days at 40°C and 0.025 mm over  $P_2O_5$  yielded 43.5 mg (1.5%) of a white, crumbly polymer. The infrared spectrum (film on NaCl plates) of both the benzene soluble and insoluble fractions showed absorptions centered at  $1740\text{ cm}^{-1}$  (C=O stretching),  $1600\text{ cm}^{-1}$  (aromatic C=C stretching),  $1170\text{ cm}^{-1}$  (ester C-O stretching), and  $1120\text{ cm}^{-1}$  (ether C-O-C stretching) (see p. 288).

6. With oxetane. A polymerization tube was charged under positive nitrogen pressure with benzene (10 ml), methyl-3,4-epoxybutanoate (1.2 g, 10 mmole, 30 mole% of the monomer feed), oxetane (1.3 g, 23 mmole, 70 mole% of the monomer feed), and the  $Al(C_2H_5)_3/H_2O/AcAc$  (1/0.5/1) initiator solution (1.6 ml, 1.7 mmole, 5 mole% based on monomer) at room temperature using dry, nitrogen filled syringes. The reaction mixture was subjected to three freeze-thaw cycles, after which the tube was sealed under vacuum (0.025 mm). The polymerization was allowed to proceed for 55 days at room temperature, during which time the clear, nearly colorless solution became a pale yellow, slightly viscous solution. After freezing in liquid nitrogen, the tube was opened, and the solution was filtered through a sintered glass filter funnel. The filtrate was added dropwise to a seven-fold excess of

n-heptane, and the precipitate was collected by filtration as a yellow material. The polymer was redissolved in a small amount of acetone, then precipitated by adding the solution to an excess of 1% aqueous hydrochloric acid. After collecting the polymer by filtration and rinsing with distilled water, it was slurring in methanol for 3 hours. The polymer was collected by filtration and dried for 2 days at 40°C and 0.025 mm over  $P_2O_5$  to yield 1.1 mg (0.04%) of an off-white elastomer. The infrared spectrum (film on NaCl plates) showed absorptions centered at  $1740\text{ cm}^{-1}$  (C=O stretching),  $1465\text{ cm}^{-1}$  (methylene C-H bending),  $1170\text{ cm}^{-1}$  (ester C-O stretching), and  $1080\text{ cm}^{-1}$  (ether C-O-C stretching) (see p. 288).

7. With THF. A polymerization tube was charged under positive nitrogen pressure with benzene (12 ml), methyl-3,4-epoxybutanoate (1.2 g, 10 mmole, 30 mole% of the monomer feed), tetrahydrofuran (THF) (1.7 g, 23 mmole, 70 mole% of the monomer feed), and the  $Al(C_2H_5)_3/H_2O/AcAc$  (1/0.5/1) initiator solution (1.7 ml, 1.7 mmole, 5 mole% based on monomer) at room temperature using dry, nitrogen filled syringes. The reaction mixture was subjected to three freeze-thaw cycles, after which the tube was sealed under vacuum (0.025 mm). The polymerization was allowed to proceed for 58 days at room temperature, during which time the clear, nearly colorless solution became a pale yellow, slightly viscous solution with a small amount

of white precipitate. After freezing in liquid nitrogen, the tube was opened, and the solution was filtered through a sintered glass filter funnel. The filtrate was added to a seven-fold excess of n-heptane, and the precipitate was collected by filtration as a yellow material. The polymer was slurried in methanol for 1 day, then redissolved in a small amount of 1,4-dioxane. This solution was added to a seven-fold excess of distilled water in an attempt to precipitate the polymer. The solution was dried for 2 days at 40°C and 0.025 mm over  $P_2O_5$  to yield 0.5 mg (0.02%) of a pale yellow, tough elastomer. The infrared spectrum (film on NaCl plates) showed absorptions centered at 1740  $cm^{-1}$  (C=O stretching), 1175  $cm^{-1}$  (ester C-O stretching), and 1125  $cm^{-1}$  (ether C-O-C stretching) (see p. ).

#### B. Copolymerization of methyl-4,5-epoxypentanoate.

1. With propylene oxide. A polymerization tube was charged under positive nitrogen pressure with benzene (10 ml), methyl-4,5-epoxypentanoate (1.2 g, 9.0 mmole, 30 mole% of the monomer feed), propylene oxide (1.2 g, 21 mmole, 70 mole% of the monomer feed), and the  $Al(C_2H_5)_3/H_2O/AcAc$  (1/0.5/1) initiator solution (1.5 ml, 1.5 mmole, 5 mole% based on monomer) at room temperature using dry, nitrogen filled syringes. The reaction mixture was subjected to three freeze-thaw cycles, after which the tube was sealed under vacuum (0.025 mm). The polymeriza-

tion was allowed to proceed for 68 days at room temperature, during which time the clear, nearly colorless solution became a clear, pale yellow, very viscous solution. After freezing in liquid nitrogen, the tube was opened and the polymer was dissolved in 100 ml of 1,4-dioxane. The solution was added dropwise to 1 liter of acidified methanol/water (40/60) (1% hydrochloric acid), and the precipitate was collected by filtration on a sintered glass filter funnel. After rinsing the precipitate with distilled water, the polymer was redissolved in 100 ml of 1,4-dioxane and filtered through a sintered glass filter funnel. The filtrate was added to 1 liter of methanol/water (40/60), and the precipitate collected by filtration. Drying for 3 days at 40°C and 0.025 mm over P<sub>2</sub>O<sub>5</sub> yielded 1.5 g (63%) of a tough, white elastomer. The infrared spectrum (film on NaCl plates) showed absorptions centered at 1740 cm<sup>-1</sup> (C=O stretching), 1440 cm<sup>-1</sup> and 1375 cm<sup>-1</sup> (methyl C-H bending), 1170 cm<sup>-1</sup> (ester C-O stretching), and 1100 cm<sup>-1</sup> (ether C-O-C stretching) (see p. 289). The <sup>13</sup>C NMR spectrum (benzene) showed peaks at 17.73 ppm and 18.62 ppm ( $\overset{\text{O}}{\text{--CH--CH}_3}$ ), 27.76 ppm and 28.34 ppm ( $\overset{\text{O}}{\text{--CH--CH}_2\text{--}}$ ), 30.06 ppm ( $\text{--CH}_2\text{--}\overset{\text{O}}{\underset{\text{O}}{\text{C--O}}}$ ), 51.04 ppm ( $\text{--O--CH}_3$ ), 71.92 ppm and 72.50 ppm (methyl-4,5-epoxypentanoate  $\text{--CH}_2\text{--O--}$ ), 73.09 ppm, 73.53 ppm, 73.80 ppm, 74.45 ppm, and 74.84 ppm (propylene oxide  $\text{--CH}_2\text{--O--}$ ), 75.76 ppm and 76.35 ppm (propylene oxide  $\overset{\text{I}}{\text{--CH--O--}}$ ), 78.58 ppm (methyl-4,5-epoxypentanoate  $\overset{\text{I}}{\text{--CH--O--}}$ ), and 173.50 ppm ( $\text{--}\overset{\text{O}}{\text{C--O--}}$ )

(see p. 258).

2. With 1-butene oxide. A polymerization tube was charged under positive nitrogen pressure with benzene (10 ml), methyl-4,5-epoxypentanoate (1.0 g, 8.0 mmole, 30 mole% of the monomer feed), 1-butene oxide (1.4 g, 19 mmole, 70 mole% of the monomer feed), and the  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$  (1/0.5/1) initiator solution (1.3 ml, 1.3 mmole, 5 mole% based on monomer) at room temperature using dry, nitrogen filled syringes. The reaction mixture was subjected to three freeze-thaw cycles, after which the tube was sealed under vacuum (0.025 mm). The polymerization was allowed to proceed for 69 days at room temperature, during which time the clear, nearly colorless solution became a clear, pale yellow, very viscous solution. After freezing in liquid nitrogen, the tube was opened, and the polymer was dissolved in 80 ml of 1,4-dioxane. The solution was added to 1 liter of acidified methanol/water (1/1) (1% hydrochloric acid), and the precipitate was collected by filtration on a sintered glass filter funnel. After rinsing the precipitate with distilled water, the polymer was redissolved in 80 ml of 1,4-dioxane and filtered through a sintered glass filter funnel. The filtrate was added to 1 liter of methanol/water (1/1), and the precipitate collected by filtration. Drying for 2 days at 40°C and 0.025 mm over  $\text{P}_2\text{O}_5$  yielded 1.2 g (51%) of a very tacky, tough, off-white elastomer. The infrared spectrum (film on NaCl plates) showed

absorptions centered at  $1740\text{ cm}^{-1}$  ( $\text{C}=\text{O}$  stretching),  $1465\text{ cm}^{-1}$  (methylene  $\text{C}-\text{H}$  bending),  $1170\text{ cm}^{-1}$  (ester  $\text{C}-\text{O}$  stretching), and  $1100\text{ cm}^{-1}$  (ether  $\text{C}-\text{O}-\text{C}$  stretching) (see p. 289). The  $^{13}\text{C}$  NMR spectrum (benzene) showed peaks at 9.92 ppm ( $-\text{CH}_2-\text{CH}_3$ ), 25.20 ppm ( $-\text{CH}_2-\text{CH}_3$ ), 27.77 ppm and 28.28 ppm ( $-\overset{\text{O}}{\text{C}}\text{H}-\text{CH}_2-\text{CH}_2-$ ), 30.03 ppm ( $-\text{CH}_2-\overset{\text{O}}{\text{C}}-\text{O}-$ ), 50.99 ppm ( $-\text{O}-\text{CH}_3$ ), 72.13 ppm (methyl-4,5-epoxypentanoate  $-\text{CH}_2-\text{O}-$ ), 72.75 ppm and 74.04 ppm (1-butene oxide  $-\text{CH}_2-\text{O}-$ ), 78.65 ppm (methyl-4,5-epoxypentanoate  $-\overset{\text{O}}{\text{C}}\text{H}-\text{O}-$ ), 81.00 ppm (1-butene oxide  $-\overset{\text{O}}{\text{C}}\text{H}-\text{O}-$ ), and 173.37 ppm ( $-\overset{\text{O}}{\text{C}}-\text{O}-$ ) (see p. 258).

3. With 1-hexene oxide. A polymerization tube was charged under positive nitrogen pressure with benzene (13 ml), methyl-4,5-epoxypentanoate (1.0 g, 7.9 mmole, 30 mole% of the monomer feed), 1-hexene oxide (1.9 g, 19 mmole, 70 mole% of the monomer feed), and the  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$  (1/0.5/1) initiator solution (1.3 ml, 1.3 mmole, 5 mole% based on monomer) at room temperature using dry, nitrogen filled syringes. The reaction mixture was subjected to three freeze-thaw cycles, after which the tube was sealed under vacuum (0.025 mm). The polymerization was allowed to proceed for 70 days at room temperature, during which time the clear, nearly colorless solution became a clear, pale yellow, viscous solution. After freezing in liquid nitrogen, the tube was opened, and the polymer was dissolved in 80 ml of 1,4-dioxane. The solution was added to 1 liter of acidified methanol (1% hydrochloric acid), and the

precipitate was collected by filtration on a sintered glass filter funnel. After rinsing the precipitate with methanol, the polymer was redissolved in 80 ml of 1,4-dioxane and filtered through a sintered glass filter funnel. The filtrate was added to 1 liter of methanol, and the precipitate collected by filtration. Drying for 2 days at 40°C and 0.025 mm over  $P_2O_5$  yielded 0.63 g (22%) of a tacky, tough, off-white elastomer. The infrared spectrum (film on NaCl plates) showed absorptions centered at  $1740\text{ cm}^{-1}$  (C=O stretching),  $1465\text{ cm}^{-1}$  (methylene C-H bending),  $1170\text{ cm}^{-1}$  (ester C-O stretching), and  $1105\text{ cm}^{-1}$  (ether C-O-C stretching) (see p. 290). The  $^{13}\text{C}$  NMR spectrum (benzene) showed peaks at 14.36 ppm ( $-(\text{CH}_2)_3\text{CH}_3$ ), 23.22 ppm ( $-(\text{CH}_2)_2\text{CH}_2\text{CH}_3$ ), 28.11 ppm ( $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$ , methyl-4,5-epoxypentanoate  $-\overset{\text{O}}{\text{C}}\text{H}-\text{CH}_2-$ ), 30.04 ppm ( $-\text{CH}_2-\overset{\text{O}}{\text{C}}-\text{O}-$ ), 32.35 and 33.09 ppm ( $-\overset{\text{O}}{\text{C}}\text{H}-\text{CH}_2-(\text{CH}_2)_2\text{CH}_3$ ), 50.98 ppm ( $\text{O}-\text{CH}_3$ ), 72.54 ppm (methyl-4,5-epoxypentanoate  $-\text{CH}_2-\text{O}-$ ), 72.83 ppm, 73.11 ppm, 73.62 ppm, and 74.43 ppm (1-hexene oxide  $-\text{CH}_2-\text{O}-$ ), 78.75 ppm (methyl-4,5-epoxypentanoate  $-\overset{\text{O}}{\text{C}}\text{H}-\text{O}-$ ), 80.01 ppm (1-hexene oxide  $-\overset{\text{O}}{\text{C}}\text{H}-\text{O}-$ ), and 173.32 ppm ( $-\overset{\text{O}}{\text{C}}-\text{O}-$ ) (see p. 259).

4. With epichlorohydrin. A polymerization tube was charged under positive nitrogen pressure with benzene (11 ml), methyl-4,5-epoxypentanoate (1.1 g, 8.7 mmole, 30 mole% of the monomer feed), epichlorohydrin (1.9 g, 20 mmole, 70 mole% of the monomer feed), and the  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$  (1/0.5/1) initiator solution (1.4 ml, 1.4 mmole,

5 mole% based on monomer) at room temperature using dry, nitrogen filled syringes. The reaction mixture was subjected to three freeze-thaw cycles, after which the tube was sealed under vacuum (0.025 mm). The polymerization was allowed to proceed for 70 days at room temperature, during which time the clear, nearly colorless solution became a dark orange, viscous solution with some white precipitate. After freezing in liquid nitrogen, the tube was opened, and the polymer was dissolved in 120 ml of 1,4-dioxane. The solution was filtered through a sintered glass filter funnel, and the filtrate was added to 1 liter of acidified methanol (1% hydrochloric acid). The precipitate was collected by filtration on a sintered glass filter funnel, rinsed with methanol, then redissolved in 100 ml of 1,4-dioxane. The solution was filtered through a sintered glass filter funnel, and the filtrate was added to 1 liter of methanol. After collecting by filtration, the precipitate was dried for 3 days at 40°C and 0.025 mm over  $P_2O_5$  to yield 0.60 g (20%) of a tough, white elastomer. The benzene and 1,4-dioxane-insoluble material was dried for 3 days at 40°C and 0.025 mm over  $P_2O_5$  to yield 2.0 mg (0.1%) of a tough, white elastomer. The infrared spectrum (film on NaCl plates) of the 1,4-dioxane-soluble polymer showed absorptions centered at  $1735\text{ cm}^{-1}$  (C=O stretching),  $1170\text{ cm}^{-1}$  (ester C-O stretching),  $1120\text{ cm}^{-1}$  (ether-O-C stretching), and  $745\text{ cm}^{-1}$  (C-Cl stretching) (see p. 290). The  $^{13}\text{C}$

NMR spectrum (benzene) showed peaks at 27.35 ppm ( $-\overset{\text{O}}{\text{CH}}-\text{CH}_2-$   
 $\text{CH}_2-$ ), 29.95 ppm ( $-\text{CH}_2-\overset{\text{O}}{\text{C}}-\text{O}-$ ), 43.97 ppm ( $-\text{CH}_2-\text{Cl}$ ), 51.18 ppm  
 $(-\text{O}-\text{CH}_3)$ , 69.98 ppm (epichlorohydrin  $-\text{CH}_2-\text{O}-$ ), 72.56 ppm  
 (methyl-4,5-epoxypentanoate  $-\text{CH}_2-\text{O}-$ ), 78.56 ppm (methyl-  
 4,5-epoxypentanoate  $-\overset{|}{\text{CH}}-\text{O}-$ ), 79.24 ppm (epichlorohydrin  
 $-\overset{|}{\text{CH}}-\text{O}-$ ), and 173.39 ppm ( $-\overset{\text{O}}{\text{C}}-\text{O}-$ ) (see p. 259).

5. With phenyl glycidyl ether. A polymerization tube was charged under positive nitrogen pressure with benzene (11 ml), methyl-4,5-epoxypentanoate (0.8 g, 6.2 mmole, 30 mole% of the monomer feed), phenyl glycidyl ether (2.2 g, 15 mmole, 70 mole% of the monomer feed), and the  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$  (1/0.5/1) initiator solution (1.0 ml, 1.0 mmole, 5 mole% based on monomer) at room temperature using dry, nitrogen filled syringes. The reaction mixture was subjected to three freeze-thaw cycles, after which the tube was sealed under vacuum (0.025 mm). The polymerization was allowed to proceed for 70 days at room temperature, during which time the clear, nearly colorless solution became an opaque, orange, solid gel. After freezing in liquid nitrogen, the tube was opened, and the polymer was dissolved in 170 ml of 1,4-dioxane. The solution was filtered through a sintered glass filter funnel, and the filtrate was added to 1 liter of acidified methanol (1% hydrochloric acid). The precipitate was collected by filtration on a sintered glass filter funnel, rinsed with methanol, then redissolved in 100 ml of 1,4-dioxane. The

solution was filtered through a sintered glass filter funnel, and the filtrate was added to 1 liter of methanol. After collecting by filtration, the precipitate was dried for 2 days at 40°C and 0.025 mm over  $P_2O_5$  to yield 0.51 g (17%) of a tough, white elastomer. The benzene and 1,4-dioxane-insoluble material was slurried in 500 ml of acidified methanol (1% hydrochloric acid) for 2 hours, collected by filtration and rinsed with methanol, and dried for 2 days at 40°C and 0.025 mm over  $P_2O_5$  to yield 0.84 g (28%) of a flaky, white polymer. The infrared spectrum (film on NaCl plates) of the 1,4-dioxane-soluble material showed absorptions centered at  $1740\text{ cm}^{-1}$  (C=O stretching),  $1600\text{ cm}^{-1}$  (aromatic C=C stretching),  $1170\text{ cm}^{-1}$  (ester C-O stretching), and  $1100\text{ cm}^{-1}$  (ether C-O-C stretching) (see p. 291). The  $^{13}\text{C}$  NMR spectrum (benzene) showed peaks at 27.44 ppm ( $-\overset{\text{O}}{\text{CH}}-\text{CH}_2-\text{CH}_2-$ ), 29.96 ppm ( $-\text{CH}_2-\overset{\text{O}}{\text{C}}-\text{O}-$ ), 51.06 ppm ( $-\text{O}-\text{CH}_3$ ), 68.35 ppm ( $-\overset{\text{O}}{\text{CH}}-\text{CH}_2-\text{O}-$ ), 70.27 ppm (phenyl glycidyl ether  $-\text{CH}_2-\text{O}-$ ), 72.15 ppm, 72.55 ppm and 72.90 ppm (methyl-4,5-epoxypentanoate  $-\text{CH}_2-\text{O}-$ ), 78.63 ppm ( $-\overset{\text{I}}{\text{CH}}-\text{O}-$ ), 114.96 ppm ( $-\text{O}-\text{C}_6\text{H}_4^*$ ), 121.08 ppm ( $-\text{O}-\text{C}_6\text{H}_4^*$ ), 129.73 ppm ( $-\text{O}-\text{C}_6\text{H}_4^*$ ), 159.31 ppm ( $-\text{O}-\text{C}_6\text{H}_4^*$ ), and 173.43 ppm ( $-\overset{\text{O}}{\text{C}}-\text{O}-$ ) (see p. 260).

6. With oxetane. A polymerization tube was charged under positive nitrogen pressure with benzene (10 ml), methyl-4,5-epoxypentanoate (1.2 g, 9.4 mmole, 30 mole% of the monomer feed), oxetane (1.3 g, 22 mmole, 70 mole%

of the monomer feed), and the  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$  (1/0.5/1) initiator solution (1.5 ml, 1.6 mmole, 5 mole% based on monomer) at room temperature using dry, nitrogen filled syringes. The reaction mixture was subjected to three freeze-thaw cycles, after which the tube was sealed under vacuum (0.025 mm). The polymerization was allowed to proceed for 77 days at room temperature, during which time the clear, nearly colorless solution became an opaque, orange, solid plug. After freezing in liquid nitrogen, the tube was opened, and the polymer was dissolved in 120 ml of 1,4-dioxane. The solution was filtered through a sintered glass filter funnel, and the filtrate was added to 1 liter of n-pentane. The precipitate was collected by filtration on a sintered glass filter funnel and slurried for 12 hours in acidified methanol (1% hydrochloric acid). After filtration, the polymer was rinsed with methanol, then redissolved in 200 ml of benzene. The solution was filtered through a sintered glass filter funnel and added to 1 liter of methanol. The precipitate was collected by filtration and dried for 3 days at 40°C and 0.025 mm over  $\text{P}_2\text{O}_5$  to yield 0.16 g (6%) of a tacky, tough, white elastomer. The benzene and 1,4-dioxane-insoluble material was slurried in 200 ml of methanol for 2 hours, collected by filtration, and dried for 3 days at 40°C and 0.025 mm over  $\text{P}_2\text{O}_5$  to yield 0.12 g (5%) of a tough, white elastomer. The infrared spectra (film

on NaCl plates) of the 1,4-dioxane-soluble and insoluble materials showed absorptions centered at  $1740\text{ cm}^{-1}$  (C=O stretching),  $1460\text{ cm}^{-1}$  (methylene C-H bending),  $1170\text{ cm}^{-1}$  (ester C-O stretching), and  $1110\text{ cm}^{-1}$  (ether C-O-C stretching) (see pp. 291, 292).

7. With THF. A polymerization tube was charged under positive nitrogen pressure with benzene (12 ml), methyl-4,5-epoxypentanoate (1.2 g, 9.4 mmole, 30 mole% of the monomer feed), THF (1.6 g, 22 mmole, 70 mole% of the monomer feed), and the  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$  (1/0.5/1) initiator solution (1.5 ml, 1.6 mmole, 5 mole% based on monomer) at room temperature using dry, nitrogen filled syringes. The reaction mixture was subjected to three freeze-thaw cycles, after which the tube was sealed under vacuum (0.025 mm). The polymerization was allowed to proceed for 77 days at room temperature, during which time the clear, nearly colorless solution became a clear, orange, viscous solution with a small amount of white precipitate. After freezing in liquid nitrogen, the tube was opened, and the polymer was dissolved in 80 ml of 1,4-dioxane. The solution was filtered through a sintered glass filter funnel, and the filtrate added to 1 liter of acidified methanol (1% hydrochloric acid). The precipitate was collected by filtration on a sintered glass filter funnel, rinsed with methanol, and redissolved in 40 ml of benzene. The solution was filtered through a sintered glass

filter funnel and added to 500 ml of methanol. The precipitate was collected by filtration and dried for 3 days at 40°C and 0.025 mm over  $P_2O_5$  to yield 30 mg (1%) of a slightly tacky, tough, white elastomer. The benzene and 1,4-dioxane-insoluble material was slurried in methanol for 2 hours, collected by filtration, and dried for 3 days at 40°C and 0.025 mm over  $P_2O_5$  to yield 64 mg (2%) of a powdery, white polymer. The infrared spectrum (film on NaCl plates) of the insoluble material showed absorptions centered at  $1740\text{ cm}^{-1}$  (C=O stretching),  $1170\text{ cm}^{-1}$  (ester C-O stretching), and  $1100\text{ cm}^{-1}$  (ether C-O-C stretching) (see p. 292).

### C. Copolymerization of methyl-7,8-epoxyoctanoate.

1. With propylene oxide. A polymerization tube was charged under positive nitrogen pressure with benzene (13 ml), methyl-7,8-epoxyoctanoate (1.7 g, 9.8 mmole, 30 mole% of the monomer feed), propylene oxide (1.3 g, 23 mmole, 70 mole% of the monomer feed), and the  $Al(C_2H_5)_3/H_2O/AcAc$  (1/0.5/1) initiator solution (1.6 ml, 1.6 mmole, 5 mole% based on monomer) at room temperature using dry, nitrogen filled syringes. The reaction mixture was subjected to three freeze-thaw cycles, after which the tube was sealed under vacuum (0.005 mm). The polymerization was allowed to proceed for 28 weeks at room temperature, during which time the clear, nearly colorless

solution became a slightly opaque, amber, solid plug. After freezing in liquid nitrogen, the tube was opened, and the polymer was dissolved in a mixture of 200 ml of 1,4-dioxane and 4 ml of methanol. The solution was added dropwise to 1400 ml of acidified methanol (1% hydrochloric acid), diluted with 200 ml of distilled water, and the precipitate was collected by filtration on a sintered glass filter funnel. After rinsing with distilled water, the polymer was redissolved in 100 ml of 1,4-dioxane. The solution was filtered through a sintered glass filter funnel, added dropwise to 1 liter of 1,4-dioxane/water (1/3), and the precipitated polymer collected by filtration. The polymer was dried for 3 days at 77°C and 0.005 mm over  $P_2O_5$  to yield 1.0 g (64%) of a tacky, tough, orangish elastomer. The infrared spectrum (film on NaCl plates) showed absorptions centered at  $1745\text{ cm}^{-1}$  (C=O stretching),  $1440\text{ cm}^{-1}$  and  $1375\text{ cm}^{-1}$  (methyl C-H bending),  $1165\text{ cm}^{-1}$  (ester C-O stretching), and  $1110\text{ cm}^{-1}$  (ether C-O-C stretching) (see p. 293). The  $^{13}C$  NMR spectrum (benzene) showed peaks at 17.75 ppm and 18.70 ppm ( $-\overset{\text{O}}{\text{C}}\text{H}-\text{CH}_3$ ), 25.31 ppm ( $-\overset{\text{O}}{\text{C}}\text{H}-\text{CH}_2-\text{CH}_2-$ ,  $-\text{CH}_2-\text{CH}_2-\overset{\text{O}}{\text{C}}-\text{O}$ ), 29.64 ppm ( $-(\text{CH}_2)_2-\text{CH}_2-(\text{CH}_2)_2-$ ), 32.43 ppm ( $-\overset{\text{O}}{\text{C}}\text{H}-\text{CH}_2-$ ), 34.05 ppm ( $-\text{CH}_2-\overset{\text{O}}{\text{C}}-\text{O}$ ), 50.90 ppm ( $-\text{O}-\text{CH}_3$ ), 72.67 ppm (methyl-7,8-epoxyoctanoate  $-\text{CH}_2-\text{O}-$ ), 73.73 ppm (propylene oxide  $-\text{CH}_2-\text{O}-$ ), 75.71 ppm (propylene oxide  $-\overset{\text{I}}{\text{C}}\text{H}-\text{O}-$ ), 79.69 ppm (methyl-7,8-epoxyoctanoate  $-\overset{\text{I}}{\text{C}}\text{H}-\text{O}-$ ), and 173.09 ppm ( $-\overset{\text{O}}{\text{C}}-\text{O}-$ ) (see p. 260).

2. With 1-butene oxide. A polymerization tube was charged under positive nitrogen pressure with benzene (13 ml), methyl-7,8-epoxyoctanoate (1.5 g, 8.7 mmole, 30 mole% of the monomer feed), 1-butene oxide (1.5 g, 21 mmole, 70 mole% of the monomer feed), and the  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$  (1/0.5/1) initiator solution (1.4 ml, 1.5 mmole, 5 mole% based on monomer) at room temperature using dry, nitrogen filled syringes. The reaction mixture was subjected to three freeze-thaw cycles, after which the tube was sealed under vacuum (0.005 mm). The polymerization was allowed to proceed for 28 weeks at room temperature, during which time the clear, nearly colorless solution became a clear, amber, solid plug. After freezing in liquid nitrogen, the tube was opened, and the polymer was dissolved in a mixture of 200 ml of 1,4-dioxane and 6 ml of methanol. The solution was added dropwise to 1 liter of acidified methanol (1% hydrochloric acid), and the precipitate was collected by filtration on a sintered glass filter funnel. After rinsing with methanol, the polymer was redissolved in 100 ml of 1,4-dioxane, and the solution was filtered through a sintered glass filter funnel. The solution was added dropwise to 1 liter of methanol, and after concentrating, the precipitate was collected by filtration. Drying for 2 days at 77°C and 0.005 mm over  $\text{P}_2\text{O}_5$  yielded 2.2 g (75%) of a tough, pale yellow elastomer. The infrared spectrum (film on NaCl plates) showed absorptions centered

at  $1745\text{ cm}^{-1}$  (C=O stretching),  $1465\text{ cm}^{-1}$  (methylene C-H bending),  $1170\text{ cm}^{-1}$  (ester C-O stretching), and  $1100\text{ cm}^{-1}$  (ether C-O-C stretching) (see p. 294). The  $^{13}\text{C}$  NMR spectrum (benzene) showed peaks at 9.93 ppm ( $-\text{CH}_2-\text{CH}_3$ ), 24.23 ppm, 24.67 ppm, 25.26 ppm, 26.15 ppm, and 26.23 ppm ( $-\overset{\text{O}}{\text{CH}}-\text{CH}_2-\text{CH}_3$ ,  $-\overset{\text{O}}{\text{CH}}-\text{CH}_2-\text{CH}_2$ ,  $-\text{CH}_2-\text{CH}_2-\overset{\text{O}}{\text{C}}-\text{O}-$ ), 29.63 ppm ( $-(\text{CH}_2)_2-\text{CH}_2-(\text{CH}_2)_2-$ ), 32.42 ppm and 32.97 ppm ( $-\overset{\text{O}}{\text{CH}}-\text{CH}_2-(\text{CH}_2)_4-$ ), 34.02 ppm ( $-\text{CH}_2-\overset{\text{O}}{\text{C}}-\text{O}-$ ), 50.88 ppm ( $-\text{O}-\text{CH}_3$ ), 72.77 ppm and 72.83 ppm (1-butene oxide  $-\text{CH}_2-\text{O}-$ ), 73.25 ppm, 73.91 ppm, 74.00 ppm, and 74.28 ppm (methyl-7,8-epoxyoctanoate  $-\text{CH}_2-\text{O}-$ ), 78.53 ppm, 78.95 ppm, and 79.79 ppm (methyl-7,8-epoxyoctanoate  $-\overset{\text{I}}{\text{CH}}-\text{O}-$ ), 81.01 ppm and 81.98 ppm (1-butene oxide  $-\overset{\text{I}}{\text{CH}}-\text{O}-$ ), and 173.12 ppm ( $-\overset{\text{O}}{\text{C}}-\text{O}-$ ) (see p. 261).

3. With 1-hexene oxide. A polymerization tube was charged under positive nitrogen pressure with benzene (13 ml), methyl-7,8-epoxyoctanoate (1.3 g, 7.4 mmole, 30 mole% of the monomer feed), 1-hexene oxide (1.7 g, 17 mmole, 70 mole% of the monomer feed), and the  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$  (1/0.5/1) initiator solution (1.2 ml, 1.2 mmole, 5 mole% based on monomer) at room temperature using dry, nitrogen filled syringes. The reaction mixture was subjected to three freeze-thaw cycles, after which the tube was sealed under vacuum (0.005 mm). The polymerization was allowed to proceed for 28 weeks at room temperature, during which time the clear, nearly colorless solution became a clear, amber,

solid plug. After freezing in liquid nitrogen, the tube was opened, and the polymer was dissolved in a mixture of 200 ml of 1,4-dioxane and 6 ml of methanol. The solution was added dropwise to 1 liter of acidified methanol (1% hydrochloric acid), and the precipitate was collected by filtration on a sintered glass filter funnel. After rinsing with methanol, the polymer was redissolved in 80 ml of 1,4-dioxane, and the solution was filtered through a sintered glass filter funnel. The solution was added dropwise to 1 liter of methanol, and after concentrating, the precipitate was collected by filtration. Drying for 3 days at 77°C and 0.005 mm over  $P_2O_5$  yielded 2.8 g (93%) of a tough, pale yellow elastomer. The infrared spectrum (film on NaCl plates) showed absorptions centered at  $1745\text{ cm}^{-1}$  (C=O stretching),  $1465\text{ cm}^{-1}$  (methylene C-H bending),  $1170\text{ cm}^{-1}$  (ester C-O stretching), and  $1110\text{ cm}^{-1}$  (ether C-O stretching) (see p. 294). The  $^{13}\text{C}$  NMR spectrum (benzene) showed peaks at 14.35 ppm ( $-(\text{CH}_2)_3\text{CH}_3$ ), 23.31 ppm ( $-(\text{CH}_2)_2\text{CH}_2\text{CH}_3$ ), 25.29 ppm ( $-\overset{\text{O}}{\text{CH}}-\text{CH}_2-\text{CH}_2-$ ,  $-\text{CH}_2-\text{CH}_2-\overset{\text{O}}{\text{C}}-\text{O}-$ ), 28.12 ppm ( $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$ ), 29.68 ppm ( $-(\text{CH}_2)_2\text{CH}_2-(\text{CH}_2)_2-$ ), 32.45 ppm (methyl-7,8-epoxyoctanoate and 1-hexene oxide  $-\overset{\text{O}}{\text{CH}}-\text{CH}_2-$ ), 34.04 ppm ( $-\text{CH}_2-\overset{\text{O}}{\text{C}}-\text{O}-$ ), 50.87 ppm ( $-\text{O}-\text{CH}_3$ ), 72.51 ppm, 72.74 ppm, 73.62 ppm, and 74.55 ppm (methyl-7,8-epoxyoctanoate and 1-hexene oxide  $-\text{CH}_2-\text{O}-$ ), 77.38 ppm, 77.83 ppm, and 79.99 ppm (methyl-7,8-epoxyoctanoate and 1-hexene oxide  $-\overset{\text{O}}{\text{CH}}-\text{O}-$ ), and 173.06 ppm ( $-\overset{\text{O}}{\text{C}}-\text{O}-$ ) (see p. 261).

4. With epichlorohydrin. A polymerization tube was charged under positive nitrogen pressure with benzene (11 ml), methyl-7,8-epoxyoctanoate (1.3 g, 7.7 mmole, 30 mole% of the monomer feed), epichlorohydrin (1.7 g, 18 mmole, 70 mole% of the monomer feed), and the  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$  (1/0.5/1) initiator solution (1.3 ml, 1.3 mmole, 5 mole% based on monomer) at room temperature using dry, nitrogen filled syringes. The reaction mixture was subjected to three freeze-thaw cycles, after which the tube was sealed under vacuum (0.005 mm). The polymerization was allowed to proceed for 28 weeks at room temperature, during which time the clear, nearly colorless solution became an opaque, pale orange, solid plug. After freezing in liquid nitrogen, the tube was opened, and the polymer dissolved in a mixture of 200 ml of 1,4-dioxane and 6 ml of methanol. The solution was added dropwise to 1 liter of acidified methanol (1% hydrochloric acid), and the precipitate was collected by filtration on a sintered glass filter funnel. After rinsing with methanol, the polymer was redissolved in 200 ml of 1,4-dioxane, and the solution was filtered through a sintered glass filter funnel. The solution was added dropwise to 1 liter of methanol, and after concentrating, the precipitate was collected by filtration. Drying for 2 days at 77°C and 0.005 mm over  $\text{P}_2\text{O}_5$  yielded 2.7 g (89%) of a tough, pale yellow elastomer. The infrared spectrum (film on NaCl plates) showed absorptions

centered at  $1745\text{ cm}^{-1}$  (C=O stretching),  $1165\text{ cm}^{-1}$  (ester C-O stretching),  $1110\text{ cm}^{-1}$  (ether C-O-C stretching), and  $745\text{ cm}^{-1}$  (C-Cl stretching) (see p. 295). The  $^{13}\text{C}$  NMR spectrum (1,4-dioxane) showed peaks at 25.36 ppm ( $-\overset{\text{O}}{\text{CH}}-\text{CH}_2-\text{CH}_2-$ ,  $-\text{CH}_2-\text{CH}_2-\overset{\text{O}}{\text{C}}-\text{O}-$ ), 29.71 ppm ( $-(\text{CH}_2)_2-\text{CH}_2-(\text{CH}_2)_2-$ ), 32.19 ppm ( $-\overset{\text{O}}{\text{CH}}-\text{CH}_2-$ ), 34.02 ppm ( $-\text{CH}_2-\overset{\text{O}}{\text{C}}-\text{O}-$ ), 44.26 ppm ( $-\text{CH}_2-\text{Cl}$ ), 51.19 ppm ( $-\text{O}-\text{CH}_3$ ), 70.02 ppm and 70.72 ppm (epichlorohydrin  $-\text{CH}_2-\text{O}-$ ), 73.25 ppm (methyl-7,8-epoxyoctanoate  $-\text{CH}_2-\text{O}-$ ), 79.42 ppm (methyl-7,8-epoxyoctanoate  $-\overset{|}{\text{CH}}-\text{O}-$ ), 79.64 ppm (epichlorohydrin  $-\overset{|}{\text{CH}}-\text{O}-$ ), and 173.59 ppm ( $-\overset{\text{O}}{\text{C}}-\text{O}-$ ) (see p. 262).

5. With phenyl glycidyl ether. A polymerization tube was charged under positive nitrogen pressure with benzene (11 ml), methyl-7,8-epoxyoctanoate (1.0 g, 5.8 mmole, 30 mole% of the monomer feed), phenyl glycidyl ether (2.0 g, 13 mmole, 70 mole% of the monomer feed), and the  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$  (1/0.5/1) initiator solution (0.9 ml, 1.0 mmole, 5 mole% based on monomer) at room temperature using dry, nitrogen filled syringes. The reaction mixture was subjected to three freeze-thaw cycles, after which the tube was sealed under vacuum (0.005 mm). The polymerization was allowed to proceed for 28 weeks at room temperature, during which time the clear, nearly colorless solution became an opaque, milky yellow, solid plug. After freezing in liquid nitrogen, the tube was opened, and the polymer was dissolved in a mixture of 200 ml of 1,4-dioxane

and 6 ml of acidified methanol (1% hydrochloric acid). The solution was added dropwise to 1 liter of acidified methanol (1% hydrochloric acid), and the precipitate was collected by filtration on a sintered glass filter funnel. After rinsing with methanol, the polymer was redissolved in 200 ml of 1,4-dioxane. The solution was centrifuged until the solid material had completely settled to the bottom, the supernatant liquid removed, and the solid resuspended in 1,4-dioxane. After centrifuging the suspension and removing the supernatant liquid, the combined supernatants were added dropwise to 1.5 liter of methanol, and after concentration, the precipitate was collected by filtration. Drying for 3 days at 77°C and 0.005 mm over  $P_2O_5$  yielded 1.9 g (62%) of a tough, slightly yellow elastomer. The insoluble polymer was slurried in 200 ml of methanol for 2 hours, collected by filtration, and dried for 3 days at 77°C and 0.005 mm over  $P_2O_5$  to yield 0.25 g (9%) of a white, powdery polymer. The infrared spectra (film on NaCl plates) of both the soluble and insoluble polymer showed absorptions centered at  $1740\text{ cm}^{-1}$  ( $C=O$  stretching),  $1600\text{ cm}^{-1}$  (aromatic  $C=C$  stretching),  $1170\text{ cm}^{-1}$  (ester  $C-O$  stretching), and  $1100\text{ cm}^{-1}$  (ether  $C-O-C$  stretching) (see p. 295). The  $^{13}C$  NMR spectrum (benzene) of the soluble polymer showed peaks at 25.33 ppm ( $-\overset{\overset{O}{\parallel}}{CH}-CH_2-\underline{CH_2}-$ ,  $-\overset{\overset{O}{\parallel}}{CH_2}-CH_2-$ ,  $\overset{\overset{O}{\parallel}}{C}-O-$ ), 29.59 ppm ( $-(CH_2)_{\frac{1}{2}}-\overset{\overset{O}{\parallel}}{CH_2}-(CH_2)_{\frac{1}{2}}-$ ), 32.15 ppm ( $-\overset{\overset{O}{\parallel}}{CH}-CH_2-$ ,  $-(CH_2)_{\frac{1}{4}}-$ ), 34.08 ppm ( $-\underline{CH_2}-\overset{\overset{O}{\parallel}}{C}-O-$ ), 50.99 ppm ( $-O-\underline{CH_3}$ ), 68.58

ppm ( $-\overset{\text{O}}{\text{C}}\text{H}-\text{CH}_2-\text{O}-$ ), 70.36 ppm (phenyl glycidyl ether  $-\text{CH}_2-\text{O}-$ ), 73.47 ppm (methyl-7,8-epoxyoctanoate  $-\text{CH}_2-\text{O}-$ ), 78.78 ppm (phenyl glycidyl ether  $-\overset{|}{\text{C}}\text{H}-\text{O}-$ ), 79.88 ppm (methyl-7,8-epoxyoctanoate  $-\overset{|}{\text{C}}\text{H}-\text{O}-$ ), 115.10 ppm ( $-\text{O}-\text{C}_6\text{H}_5^*$ ), 121.16 ppm ( $-\text{O}-\text{C}_6\text{H}_5^*$ ), 129.76 ppm ( $-\text{O}-\text{C}_6\text{H}_5^*$ ), 159.44 ppm ( $-\text{O}-\text{C}_6\text{H}_5^*$ ), and 173.19 ppm ( $-\overset{\text{O}}{\text{C}}-\text{O}-$ ) (see p. 262).

6. With oxetane. A polymerization tube was charged under positive nitrogen pressure with benzene (13 ml), methyl-7,8-epoxyoctanoate (1.7 g, 9.8 mmole, 30 mole% of the monomer feed), oxetane (1.3 g, 23 mmole, 70 mole% of the monomer feed), and the  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$  (1/0.5/1) initiator solution (1.6 ml, 1.6 mmole, 5 mole% based on monomer) at room temperature using dry, nitrogen filled syringes. The reaction mixture was subjected to three freeze-thaw cycles, after which the tube was sealed under vacuum (0.005 mm). The polymerization was allowed to proceed for 28 weeks at room temperature, during which time the clear, nearly colorless solution became a slightly opaque, orange, solid plug. After freezing in liquid nitrogen, the tube was opened, and the polymer was dissolved in a mixture of 200 ml of 1,4-dioxane and 8 ml of acidified methanol (1% hydrochloric acid). The solution was added dropwise to 1 liter of acidified methanol (1% hydrochloric acid), and the precipitate was collected by filtration on a sintered glass filter funnel. After rinsing with methanol, the polymer was redissolved in 100 ml of

1,4-dioxane, and the solution was filtered through a sintered glass filter funnel. The solution was added dropwise to 1 liter of methanol, and the precipitate was collected by filtration. Drying for 2 days at 77°C and 0.005 mm over  $P_2O_5$  yielded 1.5 g (51%) of a tough, off-white elastomer. The infrared spectrum (film on NaCl plates) showed absorptions centered at  $1740\text{ cm}^{-1}$  (C=O stretching),  $1460\text{ cm}^{-1}$  (methylene C-H bending),  $1170\text{ cm}^{-1}$  (ester C=O stretching), and  $1110\text{ cm}^{-1}$  (ether C-O-C stretching) (see p. 296). The  $^{13}C$  NMR spectrum (benzene) showed peaks at 25.28 ppm ( $-\overset{\text{O}}{\underset{|}{\text{CH}}}-\text{CH}_2-\text{CH}_2-$ ,  $-\text{CH}_2-\text{CH}_2-\overset{\text{O}}{\underset{|}{\text{C}}}-\text{O}-$ ), 29.64 ppm ( $-(\text{CH}_2)_2-\text{CH}_2-$ ,  $-(\text{CH}_2)_2-$ ), 30.78 ppm (oxetane  $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O}-$ ), 32.40 ppm ( $-\text{CH}-\text{CH}_2-(\text{CH}_2)_4-$ ), 34.03 ppm ( $-\text{CH}_2-\overset{\text{O}}{\underset{|}{\text{C}}}-\text{O}-$ ), 50.89 ppm ( $-\text{O}-\text{CH}_3$ ), 67.25 ppm and 68.05 ppm (oxetane  $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O}-$ ), 73.51 ppm and 73.93 ppm ( $-\text{CH}_2-\text{O}-$ ), 79.35 ppm and 79.89 ppm ( $-\overset{\text{O}}{\underset{|}{\text{CH}}}-\text{O}-$ ), and 173.21 ppm ( $-\overset{\text{O}}{\underset{|}{\text{C}}}-\text{O}-$ ) (see p. 263).

7. With THF. A polymerization tube was charged under positive nitrogen pressure with benzene (10 ml), methyl-7,8-epoxyoctanoate (1.5 g, 8.8 mmole, 30 mole% of the monomer feed), THF (1.5 g, 21 mmole, 70 mole% of the monomer feed), and the  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$  (1/0.5/1) initiator solution (1.4 ml, 1.5 mmole, 5 mole% based on monomer) at room temperature using dry, nitrogen filled syringes. The reaction mixture was subjected to three freeze-thaw cycles, after which the tube was sealed under vacuum (0.005 mm). The polymerization was allowed to proceed for

28 weeks at room temperature, during which time the clear, nearly colorless solution became a clear, amber, solid plug. After freezing in liquid nitrogen, the tube was opened, and the polymer was dissolved in a mixture of 200 ml of 1,4-dioxane and 6 ml of acidified methanol (1% hydrochloric acid). The solution was added dropwise to 1 liter of acidified methanol (1% hydrochloric acid), and the precipitate was collected by filtration on a sintered glass filter funnel. After rinsing with methanol, the polymer was redissolved in 80 ml of 1,4-dioxane, and the solution was filtered through a sintered glass filter funnel. The solution was added dropwise to 1 liter of methanol, and after concentrating, the precipitate was collected by filtration. Drying for 3 days at 77°C and 0.005 mm over  $P_2O_5$  yielded 1.3 g (43%) of a tough, off-white elastomer. The infrared spectrum (film on NaCl plates) showed absorptions centered at  $1740\text{ cm}^{-1}$  (C=O stretching),  $1170\text{ cm}^{-1}$  (ester C-O stretching), and  $1100\text{ cm}^{-1}$  (ether C-O-C stretching) (see p. 297). The  $^{13}C$  NMR spectrum (benzene) showed peaks at 25.32 ppm ( $-\underline{CH}_2-\underline{CH}_2-\overset{\text{O}}{\parallel}{C}-O-$ ), 25.52 ppm ( $-\overset{\text{O}}{\parallel}{CH}-CH_2-\underline{CH}_2-$ ), 29.70 ppm ( $-(CH_2)_2-\underline{CH}_2-(CH_2)-$ ), 32.52 ppm and 33.23 ppm ( $-\overset{\text{O}}{\parallel}{CH}-\underline{CH}_2-$ ), 34.07 ppm ( $-\underline{CH}_2-\overset{\text{O}}{\parallel}{C}-O-$ ), 50.93 ppm ( $-O-\underline{CH}_3$ ), 72.62 ppm, 72.91 ppm, 73.54 ppm and 74.44 ppm ( $-\underline{CH}_2-O-$ ), 79.92 ppm ( $-\overset{\text{O}}{\parallel}{CH}-O-$ ), and 173.21 ppm ( $-\overset{\text{O}}{\parallel}{C}-O-$ ) (see p. 263).

VI. Homopolymerizations of the Methyl  $\omega$ -  
Epoxyalkanoates Using  
Cationic Initiators

A. Methyl-3,4-epoxybutanoate.

1. Boron trifluoride etherate as initiator. A flat bottom polymerization tube with a teflon coated magnetic stir bar was capped with a rubber septum while hot and cooled under a dry nitrogen flow. The tube was immersed in a dry ice/isopropanol bath and charged under positive nitrogen pressure with dichloromethane (1.1 ml), methyl-3,4-epoxybutanoate (1.0 g, 8.6 mmole) and boron trifluoride etherate (61 mg, 0.43 mmole, 5 mole% based on monomer) with stirring using dry, nitrogen filled syringes. The polymerization was allowed to proceed for 5 hours at  $-78^{\circ}\text{C}$ , during which time the clear, colorless solution became a clear, colorless, viscous solution. The polymerization was terminated by the addition of methanol (0.03 ml, 0.86 mmole) at  $-78^{\circ}\text{C}$  and pyridine (0.02 ml, 0.21 mmole) at room temperature, causing the formation of a white precipitate. After diluting with 10 ml of dichloromethane, the reaction mixture was washed with 2 x 25 ml of 1% aqueous hydrochloric acid, 2 x 25 ml of 5% aqueous sodium bicarbonate, and 25 ml of distilled water. The product was concentrated, and dried at  $100^{\circ}\text{C}$  and 1 mm for 1 hour to yield 0.67 g (67%) of a light tan, viscous oil. The infrared spectrum (smear on NaCl plates) showed absorptions

centered at  $3480\text{ cm}^{-1}$  (alcohol O-H stretching),  $1740\text{ cm}^{-1}$  (C=O stretching),  $1175\text{ cm}^{-1}$  (ester C-O stretching), and  $1120\text{ cm}^{-1}$  (ether C-O-C stretching) (see p. 297). The  $^{13}\text{C}$  NMR spectrum (benzene) showed peaks centered at 37.35 ppm ( $-\text{CH}_2-$ ), 51.27 ppm ( $-\text{O}-\text{CH}_3$ ), 67.49 ppm ( $-\text{CH}_2-\text{O}-$ ), 71.78 ppm, 73.14 ppm and 74.36 ppm ( $-\text{CH}_2-\text{O}-$ ), 75.23 ppm and 76.45 ppm ( $-\text{CH}-\text{O}-$ ), and 171.69 ppm ( $-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{O}-$ ) (see p. 264).

## 2. $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}$ (1/0.5) as initiator system.

Preparation of the  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}$  (1/0.5) initiator system--A large Schlenk tube with a side arm and teflon coated magnetic stir bar was fitted with a three-way vacuum stopcock, then alternately flamed and cooled at  $0.005\text{ mm}$  and filled with dry nitrogen three times. The tube was charged with neat triethylaluminum (2.9 g, 25 mmole) under positive nitrogen pressure using a dry, nitrogen filled gas tight syringe. The tube was then cooled to  $0^\circ\text{C}$  and fitted with a hot pressure equalizer addition funnel. After cooling the addition funnel under a flow of dry nitrogen (10-15 minutes), the funnel was charged with a diethyl ether (19 ml, 180 mmole) and distilled water (0.23 ml, 12.5 mmole) azeotrope using a dry, nitrogen filled syringe. The azeotrope was added dropwise over a 1.5 hour period to the well stirred  $0^\circ\text{C}$  triethylaluminum. The clear, colorless initiator solution (1.10 M in triethylaluminum) was stored under nitrogen at  $0^\circ\text{C}$  until use.

## Polymerization of methyl-3,4-epoxybutanoate--A

polymerization tube was charged under positive nitrogen pressure with benzene (3.2 ml), methyl-3,4-epoxybutanoate (1.0 g, 8.6 mmole), and the  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}$  (1/0.5) initiator solution (0.39 ml, 0.43 mmole, 5 mole% based on monomer) at room temperature using dry, nitrogen filled syringes. The reaction mixture was subjected to three freeze-thaw cycles, after which the tube was sealed under vacuum (0.005 mm). The polymerization was allowed to proceed for 10 days at 50°C, during which time the clear, colorless solution became a clear, pale yellow, viscous solution with a large amount of white precipitate. After freezing in liquid nitrogen, the tube was opened, and the contents precipitated by dropwise addition to 70 ml of diethyl ether. The precipitate was collected by filtration on a sintered glass filter funnel, then slurried in 70 ml of methanol/water (1/1). After collecting by filtration and rinsing with distilled water and diethyl ether, the polymer was dried for 2 days at 40°C and 0.005 mm over  $\text{P}_2\text{O}_5$  to yield 42 mg (4%) of a powdery, off-white material. The infrared spectrum (KBr disc) showed absorptions centered at  $1740\text{ cm}^{-1}$  (C=O stretching),  $1175\text{ cm}^{-1}$  (ester C-O stretching), and  $1120\text{ cm}^{-1}$  (ether C-O-C stretching) (see p. 299).

#### B. Methyl-4,5-epoxypentanoate.

1. Boron trifluoride etherate as initiator. A flat bottom polymerization tube with a teflon coated

magnetic stir bar was capped with a rubber septum while hot and cooled under a dry nitrogen flow. The tube was immersed in a dry ice/isopropanol bath and charged under positive nitrogen pressure with dichloromethane (0.9 ml), methyl-4,5-epoxypentanoate (1.0 g, 7.7 mmole), and boron trifluoride etherate (54 mg, 0.38 mmole, 5 mole% based on monomer) with stirring using dry, nitrogen filled syringes. The polymerization was allowed to proceed for 5 hours at  $-78^{\circ}\text{C}$ , during which time the clear, colorless solution became a clear, colorless, viscous solution. The polymerization was terminated by the addition of methanol (0.03 ml, 0.76 mmole) at  $-78^{\circ}\text{C}$  and pyridine (0.02 ml, 0.19 mmole) at room temperature, causing the formation of a white precipitate. After diluting with 10 ml of dichloromethane, the reaction mixture was washed with 2 x 25 ml of 1% aqueous hydrochloric acid, 2 x 25 ml of 5% aqueous sodium bicarbonate, and 25 ml of distilled water. The product was concentrated, and dried at  $100^{\circ}\text{C}$  and 1 mm for 1 hour to yield 0.25 g (25%) of a light brown, paste-like polymer. The infrared spectrum (smear on NaCl plates) showed absorptions centered at  $3450\text{ cm}^{-1}$  (alcohol O-H stretching),  $1735\text{ cm}^{-1}$  (C=O stretching),  $1170\text{ cm}^{-1}$  (ester C-O stretching), and  $1080\text{ cm}^{-1}$  (ether C-O-C stretching) (see p. 299).

2.  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}$  (1/0.5) as the initiator system.

A polymerization tube was charged under positive nitrogen pressure with benzene (3.4 ml), methyl-4,5-epoxypentanoate

(1.0 g, 7.7 mmole), and the  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}$  (1/0.5) initiator solution (0.35 ml, 0.38 mmole, 5 mole% based on monomer) at room temperature using dry, nitrogen filled syringes. The reaction mixture was subjected to three freeze-thaw cycles, after which the tube was sealed under vacuum (0.005 mm). The polymerization was allowed to proceed for 10 days at  $50^\circ\text{C}$ , during which time the clear, colorless solution became a clear, bright yellow solution. After freezing in liquid nitrogen, the tube was opened, and after diluting with 100 ml of benzene, the solution was washed with 3 x 100 ml of 1% aqueous hydrochloric acid, 3 x 100 ml of 5% aqueous sodium bicarbonate, and 2 x 100 ml of distilled water. The benzene solution was concentrated to 25 ml and freeze-dried for 2 days at room temperature and 0.005 mm to yield 41 mg (4%) of a light brown, paste-like material. The infrared spectrum (smear on NaCl plates) showed absorptions centered at  $3450\text{ cm}^{-1}$  (alcohol O-H stretching),  $1735\text{ cm}^{-1}$  (C=O stretching),  $1170\text{ cm}^{-1}$  (ester C-O stretching), and  $1080\text{ cm}^{-1}$  (ether C-O-C stretching) (see p. 299).

### C. Methyl-7,8-epoxyoctanoate.

1. Boron trifluoride etherate as initiator. A flat bottom polymerization tube with a teflon coated magnetic stir bar was capped with a rubber septum while hot and cooled under a dry nitrogen flow. The tube was immersed in a dry ice/isopropanol bath and charged under

positive nitrogen pressure with dichloromethane (0.4 ml), methyl-7,8-epoxyoctanoate (1.0 g, 5.8 mmole), and boron trifluoride etherate (42 mg, 0.29 mmole, 5 mole% based on monomer) with stirring using dry, nitrogen filled syringes. The polymerization was allowed to proceed for 5 hours at  $-78^{\circ}\text{C}$ , during which time the clear, colorless solution became a clear, colorless, viscous solution. The polymerization was terminated by the addition of methanol (0.02 ml, 0.58 mmole) at  $-78^{\circ}\text{C}$  and pyridine (0.01 ml, 0.15 mmole) at room temperature, causing the formation of a white precipitate. After diluting with 10 ml of dichloromethane, the reaction mixture was washed with 2 x 25 ml of 1% aqueous hydrochloric acid, 2 x 25 ml of 5% aqueous sodium bicarbonate, and 25 ml of distilled water. The product was concentrated, and dried at  $100^{\circ}\text{C}$  and 1 mm for 1 hour to yield 0.99 g (100%) of a light tan, paste-like material. The infrared spectrum (smear on NaCl plates) showed absorptions centered at  $3460\text{ cm}^{-1}$  (alcohol O-H stretching),  $1740\text{ cm}^{-1}$  (C=O stretching),  $1170\text{ cm}^{-1}$  (ester C-O stretching), and  $1100\text{ cm}^{-1}$  (ether C-O-C stretching) (see p. 298). The  $^{13}\text{C}$  NMR spectrum (benzene) showed peaks centered at 25.18 ppm ( $-\overset{\text{O}}{\text{CH}}-\text{CH}_2-\text{CH}_2-$ ,  $-\overset{\text{O}}{\text{CH}_2}-\text{CH}_2-\overset{\text{O}}{\text{C}}-\text{O}-$ ), 29.53 ppm ( $-(\text{CH}_2)_2-\text{CH}_2-$ ,  $-(\text{CH}_2)-$ ), 32.23 ppm ( $-\overset{\text{O}}{\text{CH}}-\text{CH}_2-$ ), 33.94 ppm ( $-\overset{\text{O}}{\text{CH}_2}-\text{C}-\text{O}-$ ), 51.02 ppm ( $-\text{O}-\text{CH}_3$ ), 67.27 ppm ( $-\text{CH}_2-\text{O}-$ ), 70.12 ppm, 73.11 ppm, and 74.48 ppm ( $-\text{CH}_2-\text{O}-$ ), 77.79 ppm, 78.97 ppm, and 79.63 ppm ( $-\overset{\text{O}}{\text{CH}}-\text{O}-$ ), and 173.25 ppm ( $-\overset{\text{O}}{\text{C}}-\text{O}-$ ) (see p. 264).

2.  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}$  (1/0.5) as the initiator system.

A polymerization tube was charged under positive nitrogen pressure with benzene (3.7 ml), methyl-7,8-epoxyoctanoate (1.0 g, 5.8 mmole), and the  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}$  (1/0.5) initiator solution (0.26 ml, 0.29 mmole, 5 mole% based on monomer) at room temperature using dry, nitrogen filled syringes. The reaction mixture was subjected to three freeze-thaw cycles, after which the tube was sealed under vacuum (0.005 mm). The polymerization was allowed to proceed for 10 days at 50°C, during which time the clear, colorless solution became a clear, colorless, solid plug. After freezing in liquid nitrogen, the tube was opened, and the polymer was dissolved in a mixture of 50 ml of 1,4-dioxane and 5 ml of acidified methanol (1% hydrochloric acid). The solution was added dropwise to 500 ml of acidic methanol (1% hydrochloric acid), and the precipitate was collected by filtration on a sintered glass filter funnel. After rinsing with methanol, the polymer was redissolved in 50 ml of 1,4-dioxane, and the solution was filtered through a sintered glass filter funnel. The solution was added dropwise to 500 ml of methanol, and the precipitate collected by filtration. Drying for 2 days at 40°C and 0.005 mm over  $\text{P}_2\text{O}_5$  yielded 0.74 g (74%) of a tough, white elastomer. The infrared spectrum (film on NaCl plates) showed absorptions centered at  $1740\text{ cm}^{-1}$  (C=O stretching),  $1170\text{ cm}^{-1}$  (ester C-O stretching), and  $1100\text{ cm}^{-1}$  (ether C-O-C

stretching) (see p. 300). The  $^{13}\text{C}$  NMR spectrum (1,4-dioxane) showed peaks centered at 25.50 ppm ( $-\overset{\text{O}}{\text{CH}}-\text{CH}_2-\text{CH}_2-$ ,  $-\text{CH}_2-\text{CH}_2-\overset{\text{O}}{\text{C}}-\text{O}-$ ), 29.89 ppm ( $-(\text{CH}_2)_2-\text{CH}_2-(\text{CH}_2)_2-$ ), 32.59 ppm ( $-\overset{\text{O}}{\text{CH}}-\text{CH}_2-$ ), 34.12 ppm ( $-\text{CH}_2-\overset{\text{O}}{\text{C}}-\text{O}-$ ), 51.19 ppm ( $-\text{O}-\text{CH}_3$ ), 73.33 ppm ( $-\text{CH}_2-\text{O}-$ ), 79.83 ppm ( $-\overset{|}{\text{CH}}-\text{O}-$ ), and 173.59 ppm ( $-\overset{\text{O}}{\text{C}}-\text{O}-$ ) (see p. 265).

#### D. Propylene oxide.

1. Boron trifluoride etherate as initiator. A flat bottom polymerization tube with a teflon coated magnetic stir bar was capped with a rubber septum while hot and cooled under a dry nitrogen flow. The tube was immersed in a dry ice/isopropanol bath and charged under positive nitrogen pressure with dichloromethane (4.2 ml), propylene oxide (1.5 g, 26 mmole), and boron trifluoride etherate (0.16 g, 1.3 mmole, 5 mole% based on monomer) with stirring using dry, nitrogen filled syringes. The polymerization was allowed to proceed for 5 hours at  $-78^\circ\text{C}$ , during which time the clear, colorless solution became a clear, deep brown, slightly viscous solution. The polymerization was terminated by the addition of methanol (0.10 ml, 2.6 mmole) at  $-78^\circ\text{C}$  and pyridine (0.10 ml, 1.3 mmole) at room temperature, causing the formation of a white precipitate. After diluting with 15 ml of dichloromethane, the reaction mixture was washed with 2 x 25 ml of 1% aqueous hydrochloric acid, 2 x 25 ml of 5% aqueous

sodium bicarbonate, and 25 ml of distilled water. The product was concentrated, and dried at 100°C and 1 mm for 1 hour to yield 1.2 g (81%) of a brown, viscous oil. The infrared spectrum (smear on NaCl plates) showed absorptions centered at 3465  $\text{cm}^{-1}$  (alcoholic O-H stretching), 1450  $\text{cm}^{-1}$  and 1375  $\text{cm}^{-1}$  (methyl C-H bending), and 1110  $\text{cm}^{-1}$  (C-O-C stretching) (see p. 298). The  $^{13}\text{C}$  NMR spectrum (benzene) showed peaks centered at 17.49 ppm ( $-\overset{\text{O}}{\text{CH}}-\text{CH}_3$ ), 66.12 ppm ( $-\text{CH}_2-\text{O}-$ ), 73.38 ppm ( $-\text{CH}_2-\text{O}-$ ), and 75.50 ppm ( $-\overset{|}{\text{CH}}-\text{O}-$ ) (see p. 265).

2.  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}$  (1/0.5) as the initiator system.

A polymerization tube was charged under positive nitrogen pressure with benzene (4.4 ml), propylene oxide (1.0 g, 17 mmole) and the  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}$  (1/0.5) initiator solution (0.78 ml, 0.86 mmole, 5 mole% based on monomer) at room temperature using dry, nitrogen filled syringes. The reaction mixture was subjected to three freeze-thaw cycles, after which the tube was sealed under vacuum (0.005 mm). The polymerization was allowed to proceed for 10 days at 50°C, during which time the clear, colorless solution became a slightly opaque, pale yellow, solid plug. After freezing in liquid nitrogen, the tube was opened, and the polymer was dissolved in 50 ml of benzene. After diluting with 150 ml of benzene, the solution was washed with 3 x 100 ml of 1% aqueous hydrochloric acid, 3 x 100 ml of 5% aqueous sodium bicarbonate, and 2 x 100 ml of distilled

water. The solution was concentrated to 50 ml and freeze-dried for 3 days at room temperature and 0.005 mm to yield 0.91 g (91%) of a tough, white elastomer. The infrared spectrum (film on NaCl plates) showed absorptions centered at  $1450\text{ cm}^{-1}$  and  $1375\text{ cm}^{-1}$  (methyl C-H bending), and  $1100\text{ cm}^{-1}$  (ether C-O-C stretching) (see p. 300). The  $^{13}\text{C}$  NMR spectrum (1,4-dioxane) showed peaks centered at 17.66 ppm ( $-\overset{\text{O}}{\underset{|}{\text{CH}}}-\text{CH}_3$ ), 73.72 ppm ( $-\text{CH}_2-\text{O}-$ ), and 75.81 ppm ( $-\overset{|}{\text{CH}}-\text{O}-$ ) (see p. 266).

VII. Anionic Homopolymerizations of Methyl  
 $\omega$ -Epoxyalkanoates using Potassium  
Hydroxide as Initiator

A. Methyl-3,4-epoxybutanoate. A 10 ml round bottom flask with a teflon coated magnetic stir bar was transferred while hot to a glove bag and cooled under dry nitrogen. The flask was charged with powdered potassium hydroxide (24 mg, 0.43 mmole, 4 mole% based on monomer) and capped with a rubber septum. The flask was then charged under positive nitrogen pressure with 1,4-dioxane (1.1 ml) and methyl-3,4-epoxybutanoate (1.0 g, 8.6 mmole) at room temperature using dry, nitrogen filled syringes. Immediately upon addition of the monomer, the solution became deep orangish yellow. The polymerization was allowed to proceed for 3 days at room temperature, during which time no further change was noted. The reaction mixture was diluted to 20 ml with benzene, and neutralized with a mixture

of 4 ml of 1% aqueous hydrochloric acid and 6 ml of distilled water. The benzene solution was concentrated and yielded 0.57 g (57%) of a light brown liquid. The infrared spectrum (smear on NaCl plates) showed absorptions centered at  $3460\text{ cm}^{-1}$  (alcohol O-H stretching),  $1730\text{ cm}^{-1}$  (C=O stretching),  $1660\text{ cm}^{-1}$  (C=C stretching),  $1170\text{ cm}^{-1}$  (ester C-O stretching), and  $960\text{ cm}^{-1}$  (trans olefin C-H bending) (see p. 301). The  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ ) showed peaks at 37.89 ppm ( $-\text{CH}-\text{CH}_2-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{O}-$ ), 46.71 ppm ( $\text{CH}_2-\overset{\text{O}}{\text{C}}-$ ), 48.08 ppm ( $-\text{CH}-$ ), 51.48 ppm (olefin  $-\text{O}-\text{CH}_3$ ), 51.95 ppm (epoxide  $-\text{O}-\text{CH}_3$ ), 61.61 ppm ( $\text{HO}-\text{CH}_2-\text{CH}=\text{}$ ), 119.52 ppm ( $-\text{CH}_2-\text{CH}=\text{}$ ), 147.99 ppm ( $=\text{CH}-\overset{\text{O}}{\text{C}}-\text{O}-$ ), 167.18 ppm (olefin  $-\overset{\text{O}}{\text{C}}-\text{O}-$ ), and 171.01 ppm (epoxide  $-\overset{\text{O}}{\text{C}}-\text{O}-$ ) (see p. 266).

B. Methyl-4,5-epoxypentanoate. A 10 ml round bottom flask with a teflon coated magnetic stir bar was transferred while hot to a glove bag and cooled under dry nitrogen. The flask was charged with powdered potassium hydroxide (21 mg, 0.38 mmole, 4 mole% based on monomer) and capped with a rubber septum. The flask was then charged under positive nitrogen pressure with 1,4-dioxane (0.9 ml) and methyl-4,5-epoxypentanoate (1.0 g, 7.7 mmole) at room temperature using dry, nitrogen filled syringes. The polymerization was allowed to proceed for 3 days at room temperature, during which time the cloudy, colorless solution became somewhat cloudier and pale yellow. The

reaction mixture was diluted to 20 ml with benzene, and neutralized with a mixture of 3 ml of 1% aqueous hydrochloric acid and 7 ml of distilled water. The benzene solution was concentrated, and yielded 0.93 g (93%) of an almost water-white liquid. The infrared spectrum (smear on NaCl plates) showed absorptions centered at  $1740\text{ cm}^{-1}$  (C=O stretching), and  $920\text{ cm}^{-1}$  and  $840\text{ cm}^{-1}$  (epoxide C-O-C stretching) (see p. 301). The  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ ) showed peaks at 27.77 ppm ( $-\text{CH}-\text{CH}_2-$ ), 30.21 ppm ( $-\text{CH}_2-\text{C}(=\text{O})-$ ), 46.92 ppm ( $\text{CH}_2-\text{O}$ ), 51.16 ppm ( $-\text{O}-\text{CH}_3$ ), 51.62 ppm ( $-\text{CH}-\text{O}$ ), and 173.23 ppm ( $-\text{C}(=\text{O})-\text{O}-$ ) (see p. 267).

C. Methyl-7,8-epoxyoctanoate. A 10 ml round bottom flask with a teflon coated magnetic stir bar was transferred while hot to a glove bag and cooled under dry nitrogen. The flask was charged with powdered potassium hydroxide (13 mg, 0.24 mmole, 4 mole% based on monomer) and capped with a rubber septum. The flask was then charged under positive nitrogen pressure with 1,4-dioxane (0.4 ml) and methyl-7,8-epoxyoctanoate (1.0 g, 5.8 mmole) at room temperature using dry, nitrogen filled syringes. The polymerization was allowed to proceed for 3 days at room temperature, during which time the cloudy, colorless solution became somewhat cloudier. The reaction mixture was diluted to 20 ml with benzene, and neutralized with a mixture of 3 ml of 1% aqueous hydrochloric acid and 7 ml of

distilled water. The benzene solution was concentrated, and yielded 1.0 g (100%) of a colorless liquid. The infrared spectrum (smear on NaCl plates) showed absorptions centered at  $1740\text{ cm}^{-1}$  (C=O stretching), and  $910\text{ cm}^{-1}$  and  $830\text{ cm}^{-1}$  (epoxide C-O-C stretching) (see p. 302). The  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ ) showed peaks at 24.91 ppm ( $-\text{CH}_2-\text{CH}_2-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{O}-$ ), 25.77 ppm ( $-\overset{\text{O}}{\text{CH}}-\text{CH}_2-\text{CH}_2-$ ), 29.00 ppm ( $-(\text{CH}_2)_2-\text{CH}_2-(\text{CH}_2)_2-$ ), 32.38 ppm ( $-\overset{\text{O}}{\text{CH}}-\text{CH}_2-$ ), 33.92 ppm ( $-\text{CH}_2-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{O}-$ ), 46.84 ppm ( $\text{CH}_2-$ ), 51.33 ppm ( $-\text{O}-\text{CH}_3$ ), 52.06 ppm ( $-\overset{\text{O}}{\text{CH}}-$ ), and 173.87 ppm ( $-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{O}-$ ) (see p. 267).

D. Propylene oxide. A 15 ml round bottom flask with a teflon coated magnetic stir bar was transferred while hot to a glove bag and cooled under dry nitrogen. The flask was charged with powdered potassium hydroxide (82 mg, 1.5 mmole, 4 mole% based on monomer) and capped with a rubber septum. The flask was then charged under positive nitrogen pressure with 1,4-dioxane (5.6 ml) and propylene oxide (2.0 g, 34 mmole) at room temperature using dry, nitrogen filled syringes. The polymerization was allowed to proceed for 3 days at room temperature, during which time the cloudy, colorless solution became somewhat cloudier. The reaction mixture was diluted to 30 ml with benzene, and neutralized with a mixture of 1.5 ml of 10% aqueous hydrochloric acid and 8.5 ml of distilled water. The benzene solution was concentrated, and yielded 0.26 g (13%) of a

light brown, viscous oil. The infrared spectrum (smear on NaCl plates) showed absorptions centered at  $3480\text{ cm}^{-1}$  (alcohol O-H stretching),  $1450\text{ cm}^{-1}$  and  $1375\text{ cm}^{-1}$  (methyl C-H bending), and  $1110\text{ cm}^{-1}$  (ether C-O-C stretching) (see p. 302). The  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ ) showed peaks at 17.40 ppm and 17.51 ppm ( $-\overset{\text{O}}{\text{C}}\text{H}-\text{CH}_3$ ), 73.13 ppm and 73.53 ppm ( $-\text{CH}_2-\text{O}-$ ), and 75.29 ppm, 75.49 ppm, and 75.62 ppm ( $-\overset{\text{O}}{\text{C}}\text{H}-\text{O}-$ ) (see p. 268).

### VIII. Measurements

Infrared spectra were recorded either on a Perkin-Elmer Model 283 Spectrophotometer or a Nicolet 7199 FTIR System. Solid samples were measured as KBr pellets, and liquid samples were measured between NaCl plates. The infrared spectra of most of the polymer samples were measured as films cast directly onto a NaCl plate from THF solutions. The peak assignments for the polymers were made to the nearest  $5\text{ cm}^{-1}$ .

The  $^{13}\text{C}$  NMR spectra were recorded on a 22.6 MHz Varian CFT-20 Spectrometer. Common instrument parameters used were a pulse width of 15-19 microseconds, a pulse delay of 0-5 seconds, an acquisition time of 1.023 seconds, and 8184 data points. Solutions were generally 20-30% in benzene, 1,4-dioxane, or deuterated chloroform. An external  $\text{D}_2\text{O}$  lock was used in the case of non-deuterated solvents.

Inherent viscosity measurements were made using an Ubbelohde viscometer at 30°C. Solutions were approximately 0.5 wt.% in benzene or 1,4-dioxane.

The gel permeation chromatograph (GPC) results were obtained on a Waters Associates GPC with 500 Å,  $10^3$  Å (2),  $10^4$  Å, and  $10^5$  Å Styragel polystyrene columns. The solutions were approximately 0.2 wt.% in THF.

The thermal properties of the polymers were examined on a Perkin-Elmer DSC-2 Differential Scanning Calorimeter (DSC) at a heating rate of 20°C/min. The instrument was calibrated against a cyclohexane standard for low temperature experiments, and against indium and lead standards for high temperature experiments.

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

## CHAPTER III

### RESULTS AND DISCUSSION

#### I. Objectives

The objectives of this research were three-fold:

(1) to synthesize several novel ester substituted poly(alkylene oxide) homo- and copolymers, where the ester groups were separated from the polymer backbone by a well defined number of methylene spacer groups; (2) to determine the proximity effect of the ester groups on the epoxide reactivity towards polymerization; and (3) to carry out basic characterization of the resultant polymers. In order to reach these objectives, a series of methyl  $\omega$ -epoxy-alkanoates with 0 to 7 methylene spacer groups were synthesized from their corresponding methyl  $\omega$ -alkenoates, and were homo- and copolymerized with several common cyclic ether comonomers using a coordinate initiator. Homopolymerizations of selected monomers were also carried out using cationic initiators. The polymers were characterized by their yields, relative molecular weights, spectroscopic and thermal properties, and in the case of the copolymers, by their copolymer compositions.<sup>152,153</sup>

## II. Preparation of Monomers

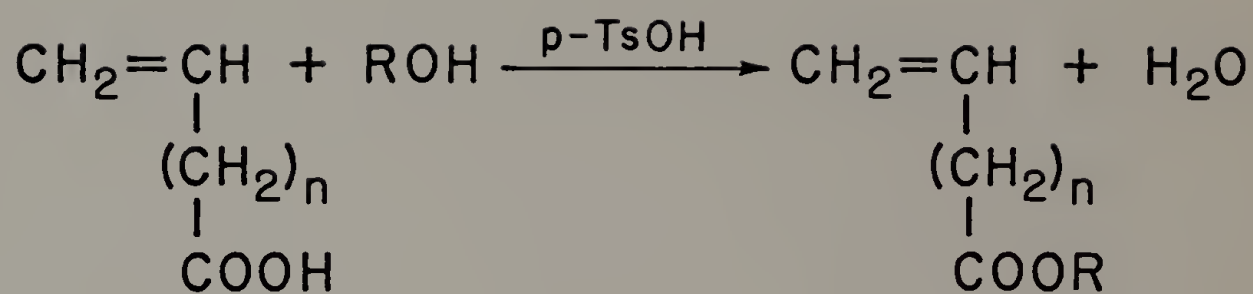
A. Preparation of methyl  $\omega$ -alkenoates. Several synthetic routes were employed to prepare the series of methyl  $\omega$ -alkenoates which served as the immediate precursors to the corresponding epoxide monomers. These will be discussed in this section.

1. Methyl acrylate. Methyl acrylate was purchased from Aldrich Chemical Co.

2. Esterification of  $\omega$ -alkenoic acids. The reaction of an acid with an appropriate alcohol using an acid catalyst is the simplest, and therefore most desirable, route for preparing esters.<sup>154</sup> A general reaction mechanism is shown in Figure 1. While an esterification can be carried out without the aid of an acid catalyst, the rate of reaction and conversion are both increased when acid catalysts are used.. The acid catalyst can serve as a dehydrating agent, effectively removing water from the reaction system and displacing the reaction equilibrium in favor of product formation.<sup>155</sup>

The use of an acid catalyst, while desirable from the point of view of rate of reaction and conversion, can produce undesirable side effects when working with  $\omega$ -alkenoic acids. The acid could protonate the terminal alkene group and lead to rearrangement products with internal alkenes. This possibility could become a serious

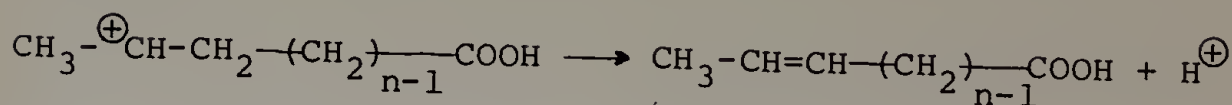
Figure 1. Esterification of  $\omega$ -alkenoic acids.



$$n = 1, 2, 8$$

$$R = \text{CH}_3, \text{C}_2\text{H}_5$$

Figure 1.



problem, especially if the rearrangement product is more stable than the starting material. This would be the case where one methylene group separated the alkene and acid groups in the starting material; the final product would be a conjugated alkenoic acid. Following protonation, addition of the acid counterion could also occur. Acids with nucleophilic counterions, such as sulfuric or hydrochloric acids, are therefore normally not used. Acids with relatively weak nucleophilic counterions, such as p-toluenesulfonic acid, are more suitable and are normally used.

Methyl-3-butenate: 3-Butenoic acid was allowed to react with an excess of methanol using a p-toluenesulfonic acid catalyst to give methyl-3-butenate in a 63% yield after distillation. Because the ester is slightly soluble in water, ice cold aqueous wash solutions should be used during workup.

Methyl-4-pentenoate: 4-Pentenoic acid was allowed to react with an excess of methanol using a p-toluenesulfonic acid catalyst to give methyl-4-pentenoate in a 66% yield after distillation. As in the case of methyl-3-butenate, methyl-4-pentenoate is slightly soluble in water,

and ice cold aqueous wash solution should be used during workup.

### 3. General method for the preparation of $\omega$ -alkenoates by oxidative decarboxylation of half-esters.

While direct esterification of an  $\omega$ -alkenoic acid is the most desirable way to produce methyl- $\omega$ -alkenoates, the  $\omega$ -alkenoic acids are not always readily available. The synthesis of methyl  $\omega$ -alkenoates with three, four, five, and six methylene groups between the vinyl and carbomethoxy groups is described in this section.

Monoesters of dicarboxylic acids can be readily converted to  $\omega$ -alkenoic acid esters by oxidative decarboxylation using lead(IV) tetraacetate and a copper(II) acetate-pyridine catalyst. The overall transformation can be illustrated as in Figure 2. When terminal carboxylic acids are used, the products formed are vinyl compounds, and when secondary carboxylic acids are used, vinylene compounds are formed. Using the lead tetraacetate-copper acetate-pyridine system, the reaction with terminal carboxylic acids produces the following products:

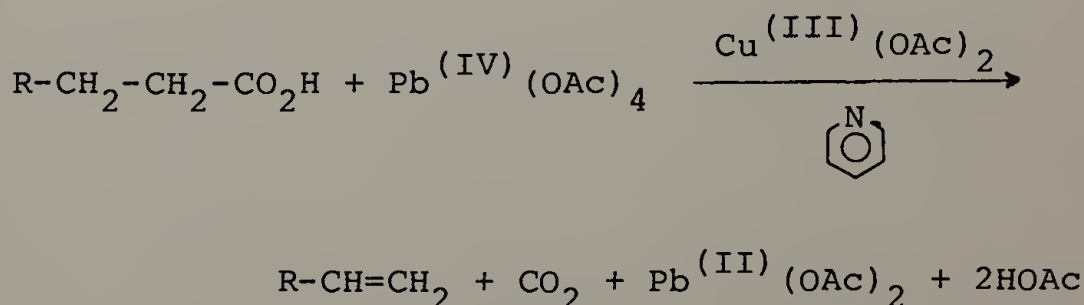
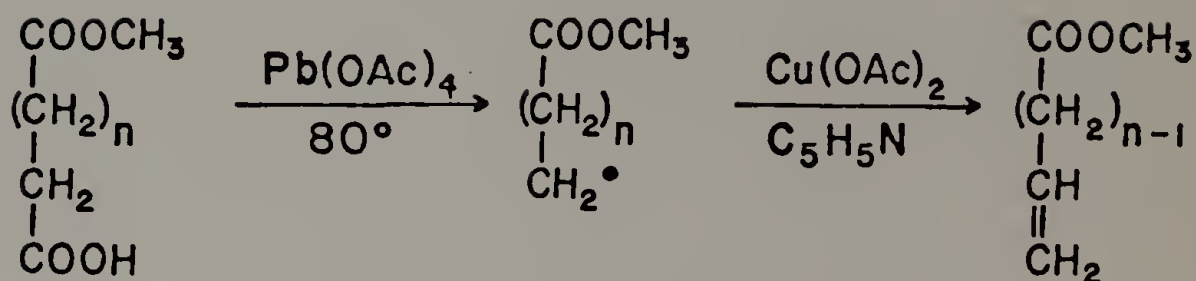


Figure 2. Oxidative decarboxylation of monoesters of dicarboxylic acids.

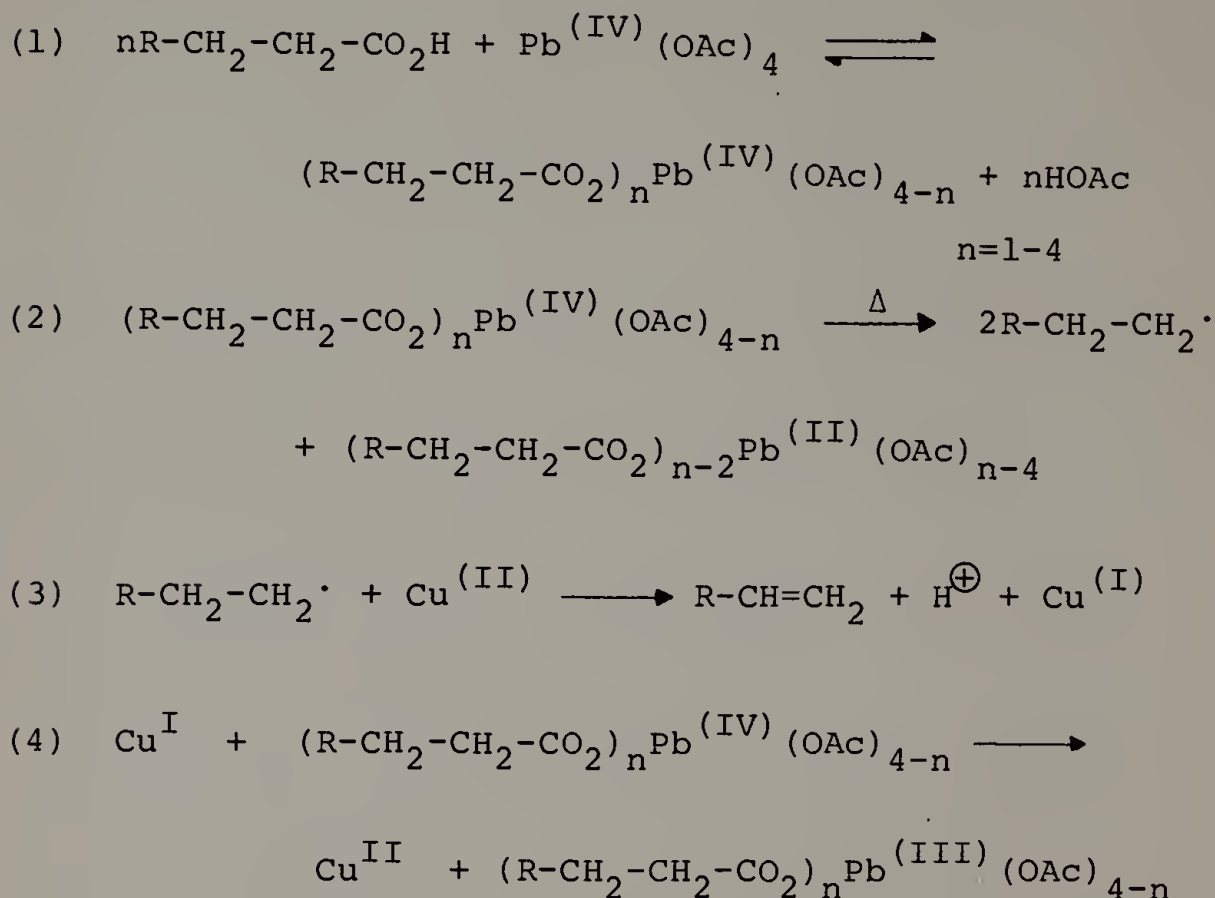
## FUNCTIONAL OLEFIN SYNTHESIS



$$n = 4 - 7$$

Figure 2.

The reaction may occur thermolytically or photolytically, the former being favored for larger scale reactions. The overall reaction proceeds by a chain mechanism, as shown below.<sup>156</sup>

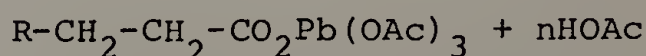


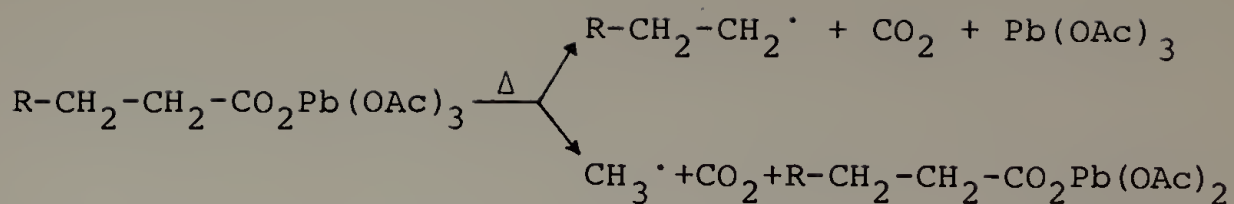
In reaction (1), lead tetraacetate reacts with the terminal carboxylic acid to yield a variety of carboxylate substituted lead(IV) salts. When these salts are heated, as shown in (2), decarboxylation occurs, resulting in the formation of a terminal methylene radical and a reduced lead salt. The copper(II) acetate·pyridine complex, represented as  $\text{Cu}^{\text{II}}$  in (3), then oxidizes the terminal methylene radical to form the alkene and a proton, which

subsequently forms a pyridine acetate salt. The reduced copper salt, represented by  $\text{Cu}^{(\text{I})}$  in (4), in turn reduces a lead(IV) salt, which then undergoes further reaction. The copper(II) salt is thus catalytically regenerated.

In the absence of copper(II) acetate, the decarboxylation of terminal and secondary carboxylic acids with lead(IV) tetraacetate is very slow, and alkenes are produced only in poor yields. In the presence of copper(II) acetate, decarboxylation occurs much more rapidly, and alkenes are formed in excellent yields. The mechanism of the catalysis by copper(II) acetate pertaining to the increase in decarboxylation rate is not known. In the reaction system described on the following pages, pyridine also serves two functions; as a catalyst and as a proton acceptor. It is not necessary to use these particular reagents; other copper salts and amines can successfully be used.

The yields of alkenes from terminal carboxylic acids in these reaction systems are normally below 50%, and use of excess lead tetraacetate does not significantly alter these yields. Competitive decarboxylation of the acetoxy groups of lead(IV) tetraacetate can also occur, as shown below.





The formation of a methyl radical is almost as favorable as that of a higher primary alkyl radical, resulting in a lower ultimate conversion of the desired product.

Methyl-5-hexenoate: Pimelic acid, dimethyl pimelate, and methanol were reacted in a di-n-butyl ether solution using a hydrochloric acid catalyst to give 68% of monomethyl pimelate. The infrared spectrum showed two carbonyl absorptions, an ester carbonyl at  $1745\text{ cm}^{-1}$  and an acid carbonyl at  $1715\text{ cm}^{-1}$ , and a strong acid hydroxyl absorption centered near  $3200\text{ cm}^{-1}$ . Monomethyl pimelate was allowed to react with lead tetraacetate in a benzene solution using a copper acetate-pyridine catalyst to give a 22% yield of methyl-5-hexenoate after distillation.

Methyl-6-heptenoate: Suberic acid, dimethyl suberate, and methanol were reacted in a di-n-butyl ether solution using a hydrochloric acid catalyst to give a 60% yield of monomethyl suberate after distillation. Monomethyl suberate was reacted with lead tetraacetate in a benzene solution using a copper acetate-pyridine catalyst to give a 32% yield of methyl-6-heptenoate after distillation.

Methyl-7-octenoate: Azelaic acid, dimethyl azelate,

and methanol were reacted in a di-n-butyl ether solution using a hydrochloric acid catalyst to give a 68% yield of monomethyl azelate after distillation. Monomethyl azelate was reacted with lead tetraacetate in a benzene solution using a copper acetate-pyridine catalyst to give a 41% yield of methyl-7-octenoate after distillation.

Methyl-8-nonenoate: Sebacic acid, dimethyl sebacate, and methanol were reacted in a di-n-butyl ether solution using a hydrochloric acid catalyst to give a 51% yield of monomethyl sebacate after distillation. Monomethyl sebacate was reacted with lead tetraacetate in a benzene solution using a cupric acetate-pyridine catalyst to give a 32% yield of methyl-8-nonenoate after distillation.

4. Methyl-9-decenoate. Rather than utilize the oxidative decarboxylation route for preparing the final methyl  $\omega$ -alkenoate in the series, the Barbier-Wieland degradation route was chosen.<sup>157,158</sup> The oxidative decarboxylation of the appropriate monoester of a dicarboxylic acid was not used due to a combination of high cost for the dicarboxylic acid and the overall low yield for the oxidative decarboxylation reaction. The Barbier-Wieland degradation is a stepwise carboxylic acid degradation of aliphatic acids to the next lower homolog, as shown in Figure 3. In the first step, ethyl-10-undecenoate, prepared by esterification of 10-undecenoic acid, was reduced to 1,1-

Figure 3. Barbier-Wieland degradation.

## FUNCTIONAL OLEFIN SYNTHESIS

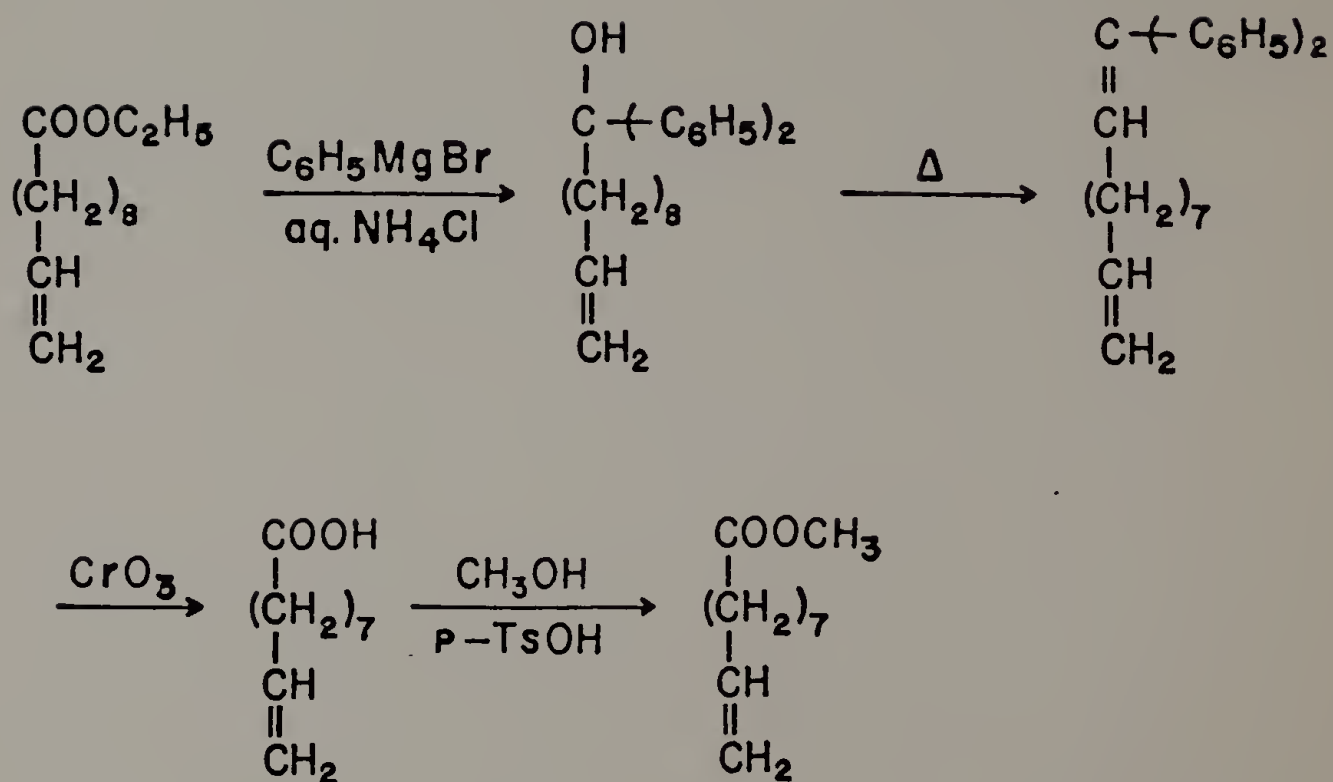


Figure 3.

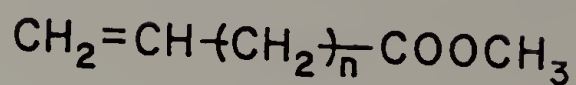
diphenyl-10-undecenol in a 79% yield by reaction with phenyl magnesium bromide and subsequent destruction of the Grignard complex by treatment with aqueous ammonium chloride. The crude alcohol was dehydrated by heating to give 1,1-diphenyl-1,10-undecadiene in a 79% yield. After purification of the diene, it was oxidized with chromic acid to yield 9-decenoic acid and benzophenone in equal proportions (45% yield). The reaction was carried out under mild conditions to assure formation of the desired oxidation product as the primary product. 9-Decenoic acid was esterified with excess methanol using a p-toluene-sulfonic acid catalyst to give methyl-9-decenoate in a 75% yield after distillation.

5. Characterization of methyl  $\omega$ -alkenoates. The results of the methyl  $\omega$ -alkenoate preparations are shown in Table 5. The column headed by n corresponds to the number of methylene spacer groups.

The infrared spectra of the methyl  $\omega$ -alkenoates all showed the expected carbonyl stretching band near  $1740\text{ cm}^{-1}$ , the alkene stretching band near  $1640\text{ cm}^{-1}$ , and the vinyl C-H bending bands near  $990\text{ cm}^{-1}$  and  $910\text{ cm}^{-1}$ , as shown in Table 6. The frequency of the lower vinyl C-H bending band was found to decrease initially as the number of methylene spacer groups, n, increased from zero to three, after which essentially no change was noted. This was attributed to the vinyl groups of methyl acrylate, methyl-3-

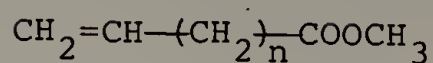
TABLE 5

## PREPARATION OF METHYL ALKENOATES



	$\frac{n}{1}$	<u>B.P. (°C/mmHg)</u>	<u>YIELD (%)</u>
METHYL-3-BUTENOATE	1	108-9/760	65
METHYL-4-PENTENOATE	2	129-30/760	70
METHYL-5-HEXENOATE	3	60/20	22
METHYL-6-HEPTENOATE	4	80/30	30
METHYL-7-OCTENOATE	5	74/10	41
METHYL-8-NONENOATE	6	67/2.5	32
METHYL-9-DECENOATE	7	109-10/10	27

TABLE 6

INFRARED DATA OF METHYL  $\omega$ -ALKENOATES<sup>1</sup>

Compound	n	$\nu_{\text{C=O}}, \text{cm}^{-1}$	$\nu_{\text{C=C}}, \text{cm}^{-1}$	$\nu_{=\text{C-H}}, \text{cm}^{-1}$	
Methyl acrylate	0	1732	1634	988	972
Methyl-3-butenolate	1	1743	1644	995	924
Methyl-4-pentenoate	2	1742	1643	991	917
Methyl-5-hexenoate	3	1742	1641	995	913
Methyl-6-heptenoate	4	1742	1641	995	912
Methyl-7-octenoate	5	1742	1641	994	911
Methyl-8-nonenoate	6	1741	1641	995	911
Methyl-9-decenoate	7	1743	1641	996	910

<sup>1</sup>neat

butenoate, and methyl-4-pentenoate being somewhat electron deficient compared to the methyl  $\omega$ -alkenoates with three or more methylene spacer groups. Thus, methyl acrylate would possess the most electron deficient vinyl group, followed by methyl-3-butenate and methyl-4-pentenoate.

Analysis of the  $^{13}\text{C}$  NMR spectra of the methyl  $\omega$ -alkenoates showed that the vinyl and carbonyl carbon resonances were also affected by the number of methylene spacer groups (Table 7). The chemical shift of the vinyl methylene carbon resonance has been correlated with the electron density of the vinyl group; the farther downfield the resonance peak lies, the more electron deficient the vinyl group. From these results,<sup>159</sup> the vinyl group of methyl acrylate was found to be considerably more electron deficient than the rest of the methyl  $\omega$ -alkenoate series. The vinyl group of methyl-3-butenate was found to be electron rich in comparison to methyl acrylate, but relatively electron poor compared to the methyl  $\omega$ -alkenoates with two or more methylene spacer groups. The shift upfield of the vinyl methylene carbon resonance for the rest of the methyl  $\omega$ -alkenoates was found to be much more gradual, as the number of methylene spacer groups increased from two to seven, indicating a much smaller increase in the vinyl group electron densities occurred. These results were similar to those found by infrared analysis of the same compounds.

TABLE 7  
<sup>13</sup>C NMR CHEMICAL SHIFT DATA OF METHYL  $\omega$ -ALKENOATES <sup>1</sup>

COMPOUND	n	CH <sub>2</sub> =CH-(CH <sub>2</sub> ) <sub>n</sub> -COOCH <sub>3</sub>				CARBON ATOMS OF SPACER GROUP <sup>2</sup>						
		CH <sub>2</sub> =CH-	CH <sub>2</sub> =CH-	C=O	OCH <sub>3</sub>	1	2	3	4	5	6	7
METHYL ACRYLATE	0	129.22	130.63	166.58	51.60							
METHYL-3-BUTENOATE	1	131.60	118.14	171.60	51.69	39.12						
METHYL-4-PENTENOATE	2	137.66	115.47	172.92	51.37	29.44	33.59					
METHYL-5-HEXENOATE	3	138.28	115.32	172.99	51.04	33.53	24.69	33.53				
METHYL-6-HEPTENOATE	4	138.89	114.83	173.18	51.11	33.88	24.93	28.95	34.00			
METHYL-7-OCTENOATE	5	139.04	114.60	173.08	51.03	34.06	25.23	29.10	25.23	34.06		
METHYL-8-NONENOATE	6	139.04	114.50	172.90	50.92	34.09	25.30	29.25	29.25	25.30	34.09	
METHYL-9-DECENOATE	7	139.09	114.45	172.94	51.00	34.03	25.32	29.44	29.59	29.44	25.32	34.20

<sup>1</sup> IN ppm DOWNFIELD FROM TMS (14.4AT)

<sup>2</sup> CARBON ATOM NEAREST OLEFIN DESIGNATED ATOM 1 OF SPACER GROUP

## B. Preparation of methyl $\omega$ -epoxyalkanoates (MEA).

1. General procedure for the epoxidation of alkenes with m-chloroperoxybenzoic acid. The reaction between m-chloroperoxybenzoic acid and an alkene to form the corresponding epoxide is normally very facile.<sup>160</sup> Epoxidation occurs by attack of an electropositive oxygen atom from the peracid on the electronegative alkene, as illustrated in Figure 4. The activity of a peracid towards epoxidation is strongly influenced by the structure of the group attached to the peracid. As the group attached to the peracid becomes more electronegative, the peracid oxygen atom becomes more electropositive and more reactive.<sup>161</sup> Thus, m-chloroperoxybenzoic acid is a stronger epoxidation agent than peroxybenzoic acid due to the presence of the electron withdrawing chlorine atom on the former. Along with the increase in epoxidation activity of the peracid comes an increase in the acidity of the corresponding acid by-product. This can cause unwanted side reactions, such as ring opening of the formed epoxide. These side reactions can be avoided by carrying out the epoxidations in the presence of a buffer,<sup>160</sup> or in a solvent in which the acid is insoluble.<sup>161</sup>

The effect of reaction solvent on the epoxidation of several olefins by m-chloroperoxybenzoic acid has been studied.<sup>161</sup> Non-hydrogen bonding polar solvents, such as dichloromethane and chloroform, were found to be most

Figure 4. Monomer synthesis.

## MONOMER SYNTHESIS

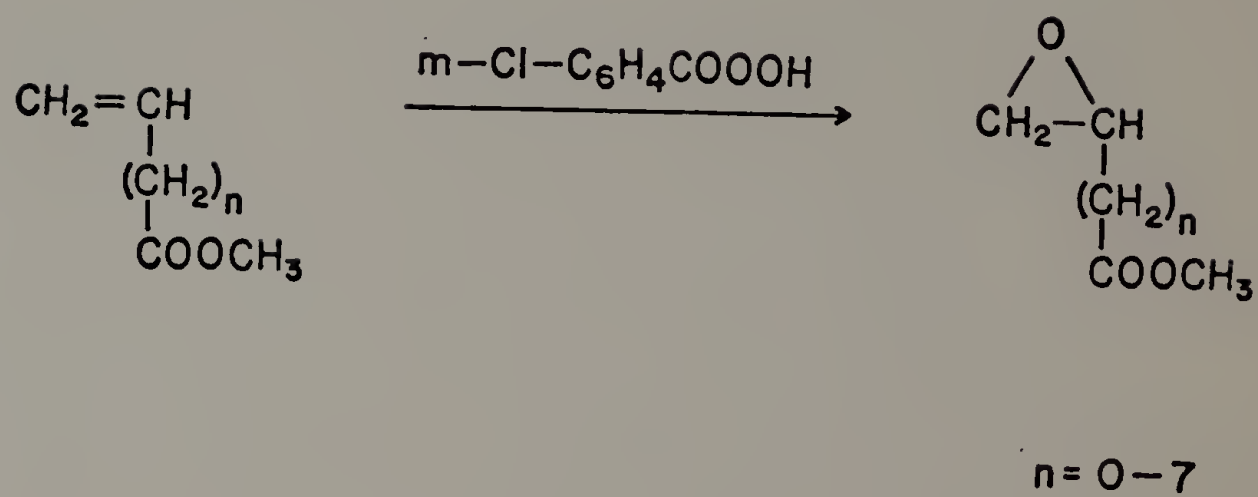


Figure 4.

suitable for producing epoxides under very mild reaction conditions. In these solvents, the by-product m-chlorobenzoic acid is essentially insoluble. Temperatures for these reactions were normally relatively low, i.e.,  $\leq 40^{\circ}\text{C}$ , and reaction times necessary to achieve high conversions rarely needed to be greater than 12 hours.

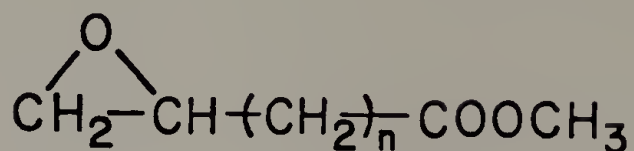
The structure of the alkene starting material is also an important factor in these reactions. The reactivity of an alkene towards epoxidation is related to its electron density. Electron withdrawing groups or atoms such as esters or halogens decrease the electron density of an alkene, which in turn decreases the reactivity of the alkene, while adjacent alkyl groups increase the alkene reactivity.

## 2. Preparation of methyl $\omega$ -epoxyalkanoates (MEA).

The results of the methyl  $\omega$ -epoxyalkanoate preparations are shown in Table 8. The column headed by n corresponds to the number of methylene spacer groups. A slight excess (10%) of m-chloroperoxybenzoic acid relative to the methyl  $\omega$ -alkenoate was used in these reactions. Two methods were employed for preparing methyl glycidate (MG). The first involved reacting equimolar portions of methyl acrylate and m-chloroperoxybenzoic acid in a dichloromethane solution for 17 hours at room temperature and 96 hours at  $40^{\circ}\text{C}$ . The final conversion to product was 24%. Attempts to isolate and purify the product were unsuccessful. The second

TABLE 8

## PREPARATION OF MEA



MEA	n	B.P. (°C/mm Hg)	YIELD (%)
MG <sup>1</sup>	0	88/90	31
MEB <sup>2</sup>	1	60/13	60
MEP <sup>3</sup>	2	72/9	71
MEH <sub>x</sub> <sup>3</sup>	3	85/8	55
MEH <sub>p</sub> <sup>3</sup>	4	85-6/3	77
MEO <sup>3</sup>	5	89/2	65
MEN <sup>3</sup>	6	81/0.5	86
MED <sup>3</sup>	7	87/0.4	66

<sup>1</sup> 14 HOURS AT 83°C IN 1,2-DICHLOROETHANE

<sup>2</sup> 22 HOURS AT 25°C, 4 HOURS AT 40°C IN  
DICHLOROMETHANE

<sup>3</sup> 5-12 HOURS AT 25°C IN DICHLOROMETHANE

method involved reacting methyl acrylate with a slight excess of m-chloroperoxybenzoic acid in a 1,2-dichloroethane solution for 14 hours at 83°C in the presence of 4,4-thiobis (6-tert-butyl-m-cresol). The results of this preparation are shown in Table 8. This same procedure has been used for the epoxidation of methyl methacrylate to give a complete conversion to the epoxide in 1 hour.<sup>162</sup> The electron donating  $\alpha$ -methyl group of methyl methacrylate was responsible for the difference in reactivity of the two acrylates.

In the course of the homo- and copolymerization studies of the methyl  $\omega$ -epoxyalkanoates, the polymerization of non-ester substituted epoxide monomers as qualitative references was desired. Two alkyl substituted epoxides were chosen as the reference materials, propylene oxide (PO) and 1-hexene oxide (HO). PO is commercially available, but HO is not. HO was synthesized in the same manner as the MEA monomers in a 73% yield after distillation.

The infrared spectra of the methyl  $\omega$ -epoxyalkanoates all showed the expected carbonyl stretching band near 1740  $\text{cm}^{-1}$  and the epoxide asymmetric ring stretching bands near 920  $\text{cm}^{-1}$  and 830  $\text{cm}^{-1}$ . The alkene stretching band and vinyl C-H bending bands of the methyl  $\omega$ -alkenoates had completely disappeared. There was some ambiguity in assigning the latter band to the epoxide ring. There did not appear to be a discernable change in the frequency of either of the epoxide bands as a function of the methylene group

spacer length.

The  $^{13}\text{C}$  NMR chemical shift data for the methyl  $\omega$ -epoxyalkanoates is shown in Table 9. In contrast to the corresponding methyl  $\omega$ -alkenoates, the methylene carbon resonance of the epoxide group remained essentially constant as a function of the number of methylene spacer groups. Thus, it does not appear that a correlation between the epoxide methylene carbon chemical shift and the epoxide electron density can be readily made. This may be due to the epoxide oxygen providing the major electronic effect felt by the epoxide carbons, overwhelming the effect of the ester group. The  $^{13}\text{C}$  NMR spectrum of MG has been described in the literature,<sup>163</sup> and chemical shifts determined for MG in this research agreed well with the published values except in the case of the carbonyl carbons. The chemical shift for the carbonyl carbon was reported to be 166.5 ppm, while the chemical shift for the same carbon found in this research was 170.51 ppm.

C. Measurement of the rate of epoxidation of methyl  $\omega$ -alkenoates. Because the reactivity of an alkene toward epoxidation is directly related to its electron density, it was believed that determining the relative rates of epoxidation of the methyl  $\omega$ -alkenoate series would yield useful information concerning the relative effect of the ester groups on the chemical reactivity of the vinyl, and,

TABLE 9

<sup>13</sup>C NMR CHEMICAL SHIFT DATA OF METHYL ω-EPOXYALKANOATES <sup>1</sup>

COMPOUND	n	$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{CH}_2-\text{CH}-\text{CH}_2-\text{CH}-\text{COOCH}_3 \\ \diagdown \quad \diagup \\ \text{O} \end{array}$				CARBON ATOMS OF SPACER GROUP <sup>2</sup>						
		CH <sub>2</sub>	CH	C=O	OCH <sub>3</sub>	1	2	3	4	5	6	7
MG	0	47.71	46.57	170.51	52.63							
ME8	1	48.01	46.54	170.91	51.80	37.94						
MEP	2	51.54	46.78	173.23	51.12	27.94	30.22					
MEHx	3	51.70	46.68	173.56	51.42	31.94	21.57	33.65				
MEHp	4	51.75	46.43	173.42	51.20	32.69	26.05	25.23	33.99			
ME0	5	51.88	46.60	173.60	51.19	32.54	25.89	29.14	25.04	33.91		
MEN	6	51.76	46.36	173.23	51.08	32.95	26.23	29.53	29.53	25.28	33.99	
ME0	7	51.76	46.34	173.22	51.06	33.00	26.44	29.53	29.76	29.53	25.33	34.01

<sup>1</sup> IN ppm DOWNFIELD FROM TMS (CDCl<sub>3</sub> SOLUTIONS)<sup>2</sup> CARBON ATOM NEAREST EPOXIDE RING DESIGNATED ATOM 1 OF SPACER GROUP

subsequently, the epoxide groups. It would be desirable and convenient to be able to predict the reactivity of a series of monomers, such as the MEA monomers, in polymerizations by determining the rate of their formation in simple, well characterized chemical reactions. The conversion of methyl  $\omega$ -alkenoates to the MEA monomers as a function of time is shown in Figure 5.

As expected from the infrared and  $^{13}\text{C}$  NMR spectroscopic results, the rates of epoxidation of the methyl  $\omega$ -alkenoates were found to vary depending on the methylene spacer length,  $n$ . The epoxidation of methyl acrylate, shown on the smaller scale, was carried out in a dichloromethane solution, as were the epoxidations of the other methyl  $\omega$ -alkenoates, at  $40^\circ\text{C}$ . Time zero was actually after 17 hours at room temperature. As expected, the epoxidation of methyl acrylate was very slow under the mild reaction conditions employed. In contrast, conversions greater than 82% were achieved for the remainder of the methyl  $\omega$ -alkenoate series within 12 hours at room temperature. From these results, it was easy to see that the vinyl groups of the methyl  $\omega$ -alkenoates were only slightly affected, if at all, by the ester groups in those methyl  $\omega$ -alkenoates with two or more methylene spacer groups. However, methyl-3-butenate, with one methylene spacer group, was more slowly epoxidized, indicating the ester group reduced the electron density of the vinyl group. These results corresponded

Figure 5. Epoxidation of methyl alkenoates.

EPOXIDATION OF METHYL ALKENOATES

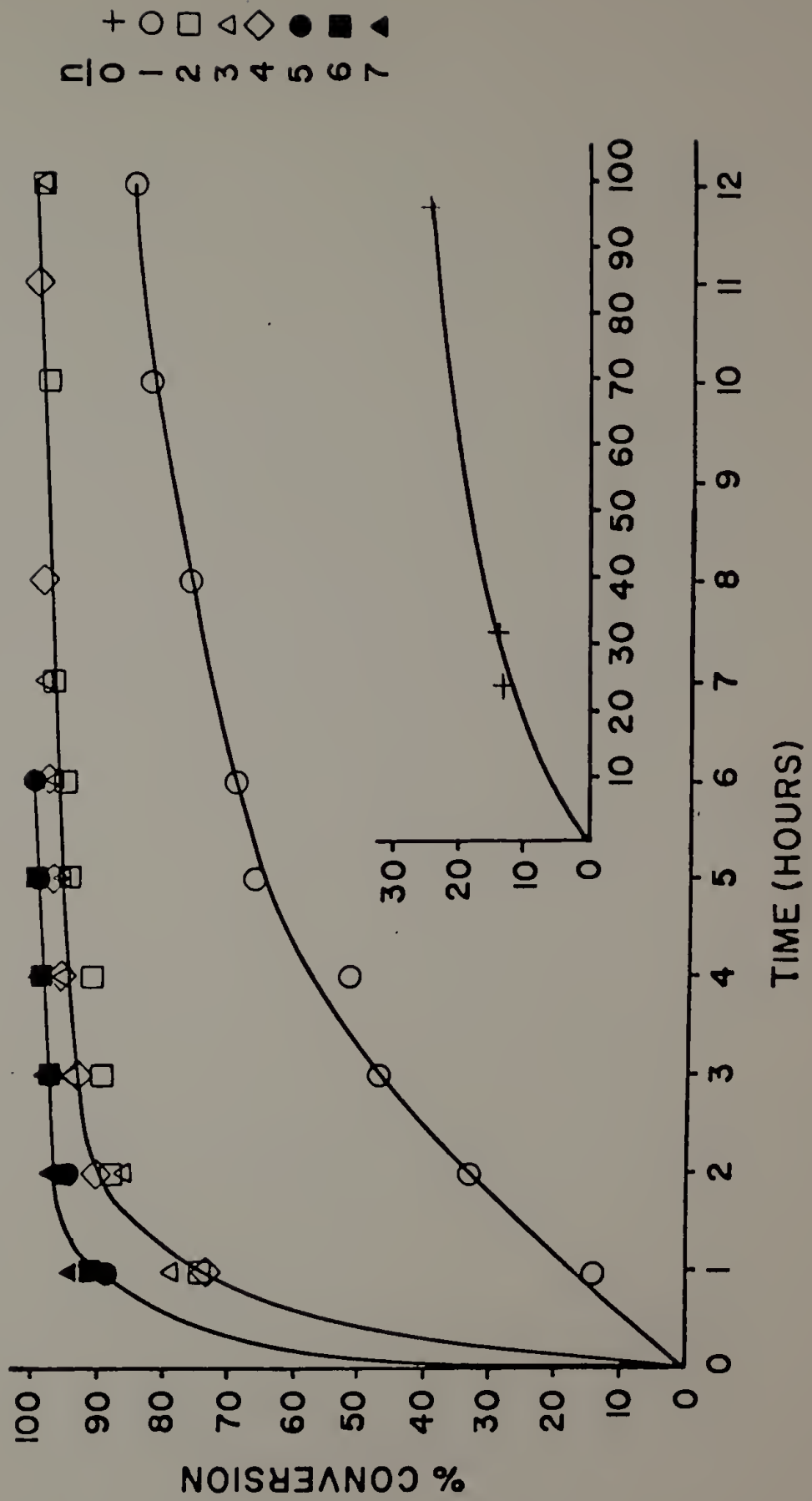


Figure 5.

well with the change of the  $^{13}\text{C}$  NMR chemical shifts of the vinyl methylene carbon atoms of the methyl  $\omega$ -alkenoates as a function of the number of methylene spacer groups.

### III. Homopolymerization of Methyl $\omega$ -Epoxy-alkanoates using the $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$ (1/0.5/1) Initiator System

A. Preparation of the  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$  (1/0.5/1) initiator system. The family of partially hydrolyzed aluminum alkyls and their reaction products with various electron donating (chelating) compounds are very active initiators for preparing high molecular weight polymers from epoxide monomers.<sup>34,44</sup> Relatively high initiator concentrations (several mole% based on monomer) are normally used in these polymerizations. This indicates one of two possibilities; either only a small fraction of the aluminum atoms are active polymerization sites,<sup>164</sup> or several aluminum atoms are involved in each polymerization center.<sup>44</sup> As yet, the structure of the active initiator is unknown. A proposed initiator structure and the mechanism for its formation are shown in Figure 6.<sup>44</sup> The particular composition used in this research was chosen because it has been successfully used in polymerizations of several different substituted epoxides.<sup>80,83</sup>

B. Polymerization of methyl  $\omega$ -epoxyalkanoates. The entire series of methyl  $\omega$ -epoxyalkanoates with 0 to 7 methylene

Figure 6. Schematic illustration of preparation of the  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$  (1/0.5/1) initiator system.

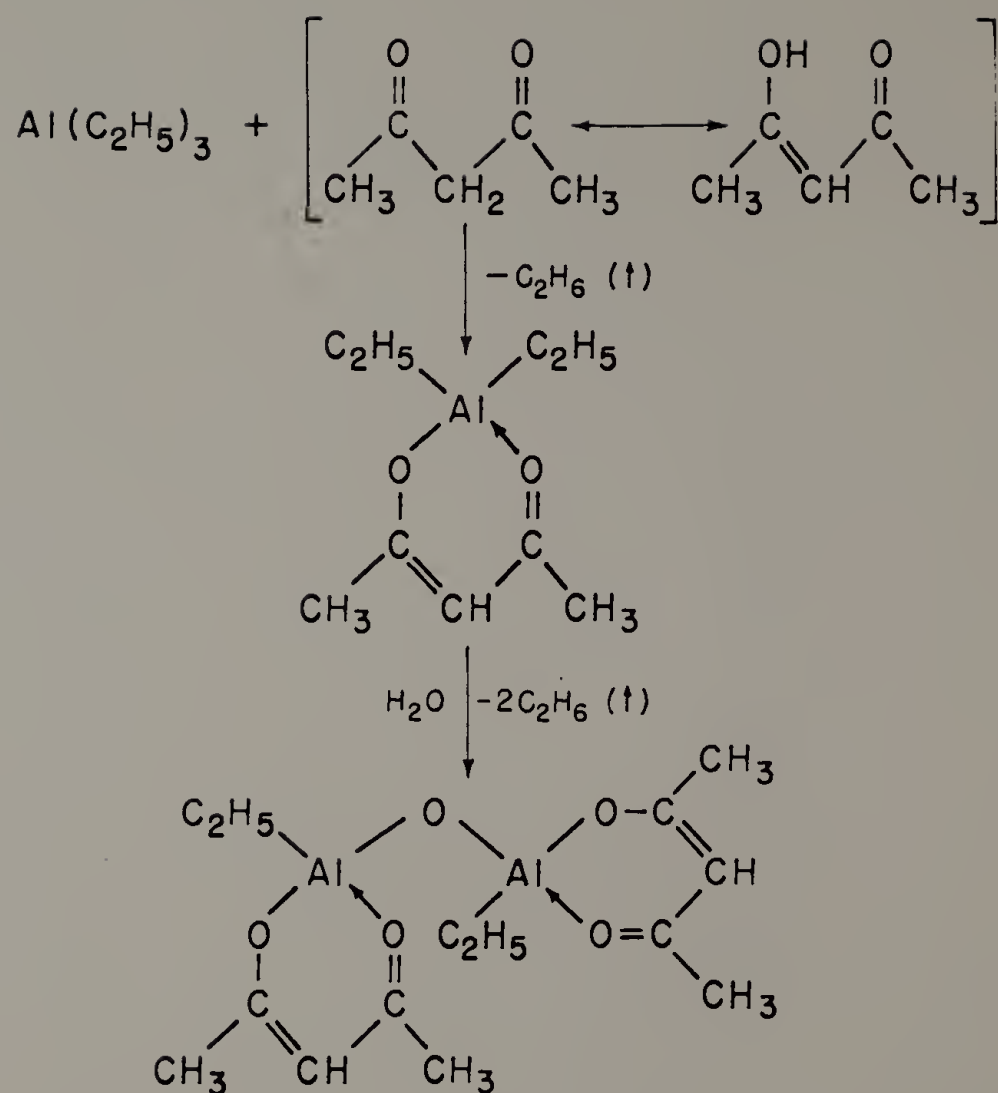


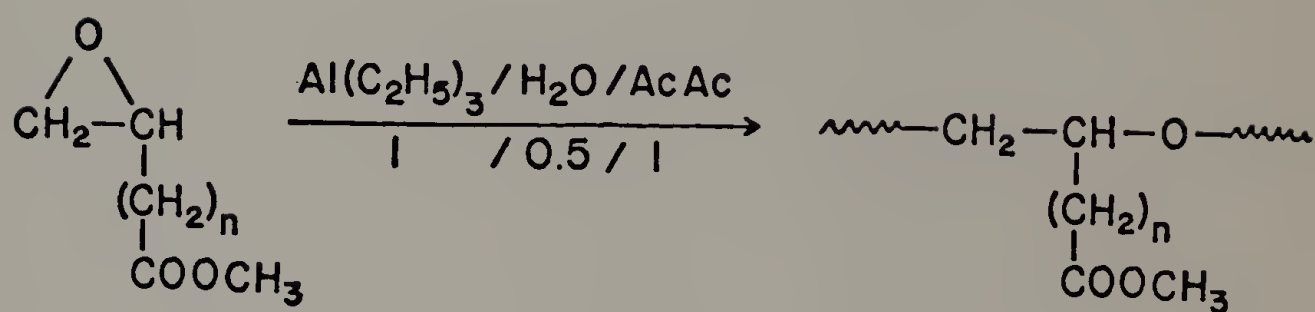
Figure 6.

spacer groups were homopolymerized in a benzene solution using the  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$  (1/0.5/1) initiator system. The reaction scheme is shown in Figure 7. All of the polymerizations were carried out under identical conditions (room temperature for 25 days) except for MEHx, which was polymerized at a higher temperature over a shorter period of time (65°C for 6 days). Polymerizations of MEB and MEP were also carried out at the higher temperature. Homopolymerizations of PO and HO were carried out as references. The isolated yields for these polymerizations are shown in Table 10, and are plotted as a function of the methylene spacer length in Figure 8.

The isolated yields from the room temperature polymerizations were found to lie along two distinct lines as a function of the methylene spacer length  $n$ . The isolated yields from the MG, MEB, and MEP ( $n = 0, 1$ , and  $2$ ) polymerizations were found to lie along a line with a small slope, while those from the MEHp, MEO, MEN, and MED ( $n = 4, 5, 6$ , and  $7$ ) were found to lie along a line with a larger slope. The polymerization of MEHx ( $n = 3$ ) was not carried out at room temperature. Polymerizations of MEB, MEP, and MEHx were carried out at 65°C, and the isolated yields from these polymerizations were found to lie along a straight line. Assuming MEHx would behave in a similar way relative to MEB and MEP at room temperature, a hypothetical yield for the polymerization of MEHx at room temperature

Figure 7. Homopolymerization of MEA.

## HOMOPOLYMERIZATION OF MEA



$n = 0 - 7$

Figure 7.

TABLE 10  
HOMOPOLYMERIZATION OF MEA USING  
 $\text{Al}(\text{C}_2\text{H}_5)_3 / \text{H}_2\text{O} / \text{AcAc}$  (1/0.5/1) INITIATOR<sup>(1)</sup>

<u>MEA</u>	<u>n</u>	<u>ISOLATED YIELD, in %</u>
MG	0	0.7
MEB	1	4.3, 3.6 <sup>(2)</sup>
MEP	2	7.6, 19 <sup>(2)</sup>
MEHx	3	33 <sup>(2)</sup>
MEHp	4	52
MEO	5	63
MEN	6	70
MED	7	79
PO	—	90
HO	—	96

<sup>1</sup> INITIATOR CONC. 5 mole %; ROOM TEMP. IN BENZENE; 25 DAYS

<sup>2</sup> INITIATOR CONC. 5 mole %; 65 °C IN BENZENE; 6 DAYS

Figure 8. Isolated yields of MEA homopolymers as a function of  $n$ , methylene space length.

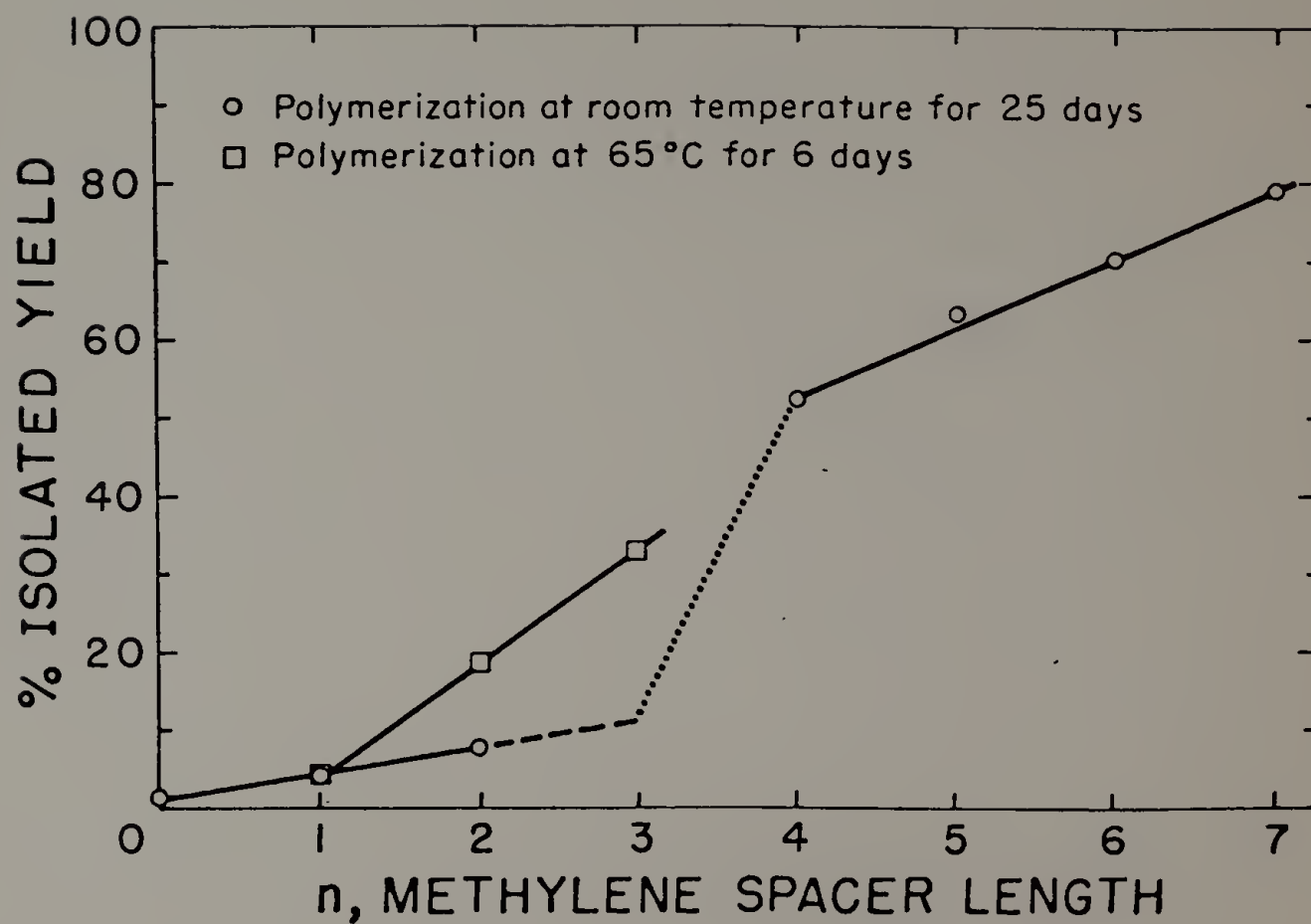


Figure 8.

was determined. These results demonstrated a discontinuity in the isolated yield as a function of the methylene spacer length on going from three to four methylene spacer groups. The reason for this sudden increase in monomer reactivity upon changing from 3 to 4 methylene spacer groups is not clear.

During the course of the polymerizations, obvious differences in the appearance of the systems were seen. White precipitates, which later proved to be crystalline polymer fractions, were formed in the MG, MEB, and MEP polymerizations, the amount of precipitate increasing from MG to MEP. Along with the precipitate formation, the solutions became somewhat viscous and pale orange. The color formation was a characteristic of all of the polymerizations. Polymerization of MEHx resulted in the formation of a clear, yellow, very viscous solution rather than a white precipitate. The rest of the series, MEHp to MED, polymerized to yield solid, slightly orange, opaque or clear plugs. These results were very encouraging because it was thought that the high concentration of ester groups in the reaction medium could seriously affect the polymerization of all of the monomers. The polymerizations of PO and HO proceeded to give clear, slightly orange, solid plugs. PO was polymerized more quickly than any of the MEA or HO; the originally non-viscous solution gelled to a solid plug within a few hours. HO, on the other hand, took

1 day to become a solid plug. All of the MEA were polymerized more slowly, requiring from 2 days to 2 weeks before no further visual changes in the polymerization systems could be detected.

During the course of purifying the MEA polymers, an interaction between the ester groups and the initiator was seen. When the polymerizations proceeded to the point where solid polymer plugs were obtained, attempts to dissolve the plugs in benzene failed; rather, the plugs would swell to several times their original volume. However, if a small quantity of acidified methanol was added, the gel became a homogeneous solution within a few hours. This was attributed to a disruption of intermolecular bonding between ester groups of the polymer and aluminum atoms of the initiator. On the other hand, homopolymers of PO and HO dissolved readily in benzene, without acidified methanol.

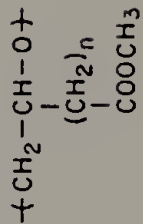
The final appearance of the polymers varied as a function of methylene spacer length also. The polymers from MG, MEB, and MEP were very tough elastomers, almost powdery in appearance. The polymers from MEHx, MEHp, MEO, MEN, and MED were tough elastomers, becoming more rubbery as the number of methylene spacer groups increased. The PO and HO polymers were also elastomeric, although less tough than the MEA polymers.

The infrared spectra of the polymers all showed the expected carbonyl stretching band of the ester groups near

1740  $\text{cm}^{-1}$  and the ether stretching band of the poly(alkylene oxide) backbone near 1100  $\text{cm}^{-1}$ , and other bands characteristic for substituted poly(alkylene oxides).<sup>153</sup> The  $^{13}\text{C}$  NMR spectra also showed resonances characteristic of substituted poly(alkylene oxides) (Table 11). There were multiple resonances for the backbone methylene and methine carbon atoms for most of the polymers, and in these cases the major resonances were underlined. These results were attributed to the presence of head-to-head, as well as head-to-tail, linkages in the polymer backbone and different stereochemical configurations of the polymer repeat unit.<sup>153</sup>

Analysis of the MEA polymers by determining their inherent viscosities and GPC molecular weights (relative to polystyrene standards) showed that they were high molecular weight materials (Table 12). Choosing a single suitable solvent for determining the inherent viscosities of all of the MEA homopolymers proved difficult; 1,4-dioxane was found to be useful for these measurements. The inherent viscosities ranged from 0.30 to 1.53 dL/g for the MEA homopolymers. The lowest viscosities were measured for the MEB, MEP, and MEHx polymers. The inherent viscosities for PPO and PHO were 4.34 and 0.39 dL/g, respectively. GPC analysis of the MEA homopolymers showed a similar wide range of  $\bar{M}_n$  and  $\bar{M}_w$  values. The values for  $\bar{M}_n$  ranged from 10,000 to 1,200,000, and the values for  $\bar{M}_w$  ranged from

TABLE 11  
<sup>13</sup>C NMR CHEMICAL SHIFT DATA OF MEA HOMOPOLYMERS <sup>1</sup>



MONOMER	n	<sup>1</sup> -CH-O	-CH <sub>2</sub> -O	C=O	OCH <sub>3</sub>	CARBON ATOMS OF SPACER GROUP <sup>2</sup>						
						1	2	3	4	5	6	7
MEB	1	75.10, 75.40 75.56, 76.05	71.06, 71.29 71.62	171.81	51.59	37.37						
MEP	2	78.50	71.40, 71.67 72.36	173.87	51.49	27.29	29.91					
MEHx	3	79.10, 79.60	72.27, 72.91 73.23	173.43	51.06	31.89	21.36	34.18				
MEHp	4	79.80	73.22	173.54	51.17	32.38	25.58	25.58	34.12			
MEo	5	79.44, 79.93	73.44, 74.30	173.48	51.12	32.60	25.45	29.86	25.45	34.08		
MEN	6	79.50, 79.97	72.68, 72.93 73.04, 73.19 73.46	173.51	51.14	32.76	25.89	30.08	29.74	25.46	34.11	
MED	7	79.61, 79.72 79.82, 80.01	73.01, 73.36 73.51	173.51	51.12	32.77	25.98	30.01	29.76	29.93	25.46	34.13

<sup>1</sup> IN ppm DOWNFIELD FROM TMS (CDCl<sub>3</sub>, BENZENE, OR 1,4-DIOXANE SOLUTION)  
<sup>2</sup> CARBON ATOM NEAREST POLYMER BACKBONE DESIGNATED ATOM 1 OF SPACER GROUP

TABLE 12

## RELATIVE MOLECULAR WEIGHTS OF MEA HOMOPOLYMERS

MEA	n	$\eta_{inh}^{(1)}$ in dL/g	$\bar{M}_n \times 10^{-5}^{(2)}$	$\bar{M}_w \times 10^{-5}^{(2)}$	MWD
MEB	1	0.30	0.1	0.2	2.0
MEP	2	0.30	0.4	3.8	9.8
MEHx	3	0.37	0.7	4.5	6.6
MEHp	4	1.53	12.0	19	1.7
MEO	5	0.77	7.1	14	1.9
MEN	6	1.44	7.5	13	1.7
MED	7	0.57	6.5	13	2.1
PO	—	4.34	8.1	12	1.5
HO	—	0.39	6.6	11	1.7

<sup>1</sup> 0.5 % IN 1,4-DIOXANE<sup>2</sup> GPC

20,000 to 1,900,000. The lowest values for  $\bar{M}_n$  and  $\bar{M}_w$  were measured for the MEB, MEP, and MEHx polymers, as in the case of the inherent viscosities. The molecular weight distributions, MWD ( $\bar{M}_w/\bar{M}_n$ ), were all narrow (MWD of approximately 2 or less) except for PMEP and PMEHx (MWD = 9.8 and 6.5, respectively). The  $\bar{M}_n$  values for PPO and PHO were 810,000 and 660,000, respectively, and the  $\bar{M}_w$  values were 1,200,000 and 1,100,000. The MWD values for PPO and PHO were 1.5 and 1.7, respectively. PMG was not examined because it was found to be insoluble in 1,4-dioxane and THF. Many of the MEA homopolymers were largely insoluble in THF. Therefore, the GPC results may not accurately reflect the molecular weights of the bulk polymers.

The MEA homopolymers were also characterized by differential scanning calorimetry (DSC). The glass transition temperatures, melting temperatures, and melting ranges are shown in Table 13. The glass transition temperatures ( $T_g$ ) were found to decrease as the number of methylene spacer groups increased, ranging from  $-26^\circ\text{C}$  for PMEB to  $-56^\circ\text{C}$  for PMEN. PMG was not analyzed due to insufficient sample. PMED did not exhibit a distinct  $T_g$ , even after several scans. The glass transition temperatures for PPO and PHO were found to be  $-63$  and  $-62^\circ\text{C}$ , respectively. The MEA homopolymers were all found to be semicrystalline materials, with multiple melting peaks evident for many of the samples. The  $T_m$  and melting range values reported were

TABLE 13  
TRANSITION TEMPERATURES OF MEA HOMOPOLYMERS

MEA	n	T <sub>g</sub> in °C	T <sub>m</sub> in °C	MELTING RANGE in °C
MEB	1	-26	119	102 to 132
MEP	2	-35	89,119	84 to 127
MEH <sup>x</sup>	3	-48	41 86	35 to 53 66 to 91
MEH <sup>p</sup>	4	-50	45 83,112	35 to 53 72 to 120
MEO	5	-53	51,70	33 to 87
MEN	6	-56	44,73,90 117	33 to 103 111 to 127
MED	7	—	40,86	31 to 108 <sup>(1)</sup>
PO	—	-63	57	31 to 64 <sup>(2)</sup>
HO	—	-62	59,68	31 to 85

<sup>1</sup> INFLECTION AT 96°C  
<sup>2</sup> INFLECTION AT 44°C

from the first heating scan. Two additional heating scans were performed, and normally showed the same melting peak temperatures seen in the first scan. The melting ranges were also very similar on reheating. However, the shape of the melting endotherms were found to be different on reheating in most cases. It is not clear whether these melting endotherms correspond to side chain or main chain melting, or a combination thereof.<sup>153</sup> However, it seems likely that the melting behavior observed for the MEA polymers with short methylene spacer lengths is main chain melting.

#### IV. Copolymerization of the Methyl $\omega$ -Epoxy- alkanoates with Cyclic Ethers Using the $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$ (1/0.5/1) Initiator System

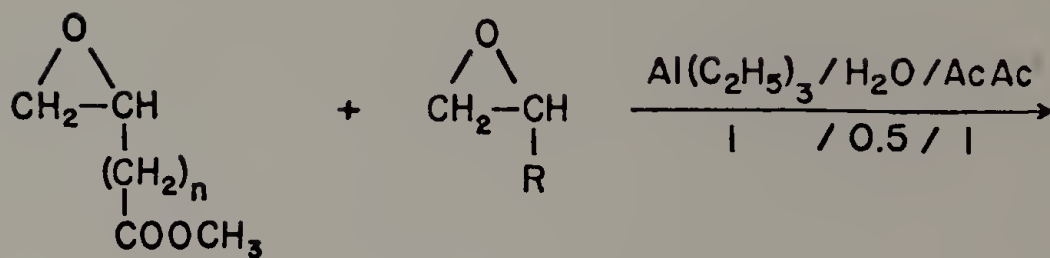
Three MEA monomers, MEB, MEP, and MEO, with 1, 2, and 5 methylene spacer groups, respectively, were chosen for the copolymerization studies described in this section, and for the cationic and anionic homopolymerizations described in the following sections. These monomers were chosen as representative of the least and most reactive of the MEA monomers.

##### A. Copolymerization of methyl-3,4-epoxybutanoate (MEB).

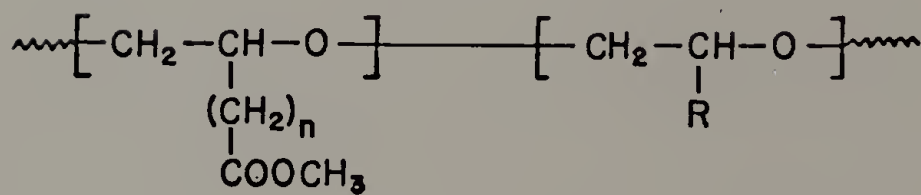
MEB was copolymerized with several substituted epoxides, oxetane, and THF using the  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$  (1/0.5/1) initiator system; the general schemes are shown in Figures

Figure 9. Copolymerization of MEA with oxiranes.

## COPOLYMERIZATION WITH OXIRANES



$n = 1, 2, 5$



$\text{R} = \text{CH}_3$   
 $\text{C}_2\text{H}_5$   
 $\text{C}_4\text{H}_9$   
 $\text{CH}_2\text{Cl}$   
 $\text{CH}_2 - \text{O} - \text{C}_6\text{H}_5$

Figure 9.

Figure 10. Copolymerization of MEA with cyclic ethers.

# COPOLYMERIZATION OF MEA WITH CYCLIC ETHERS

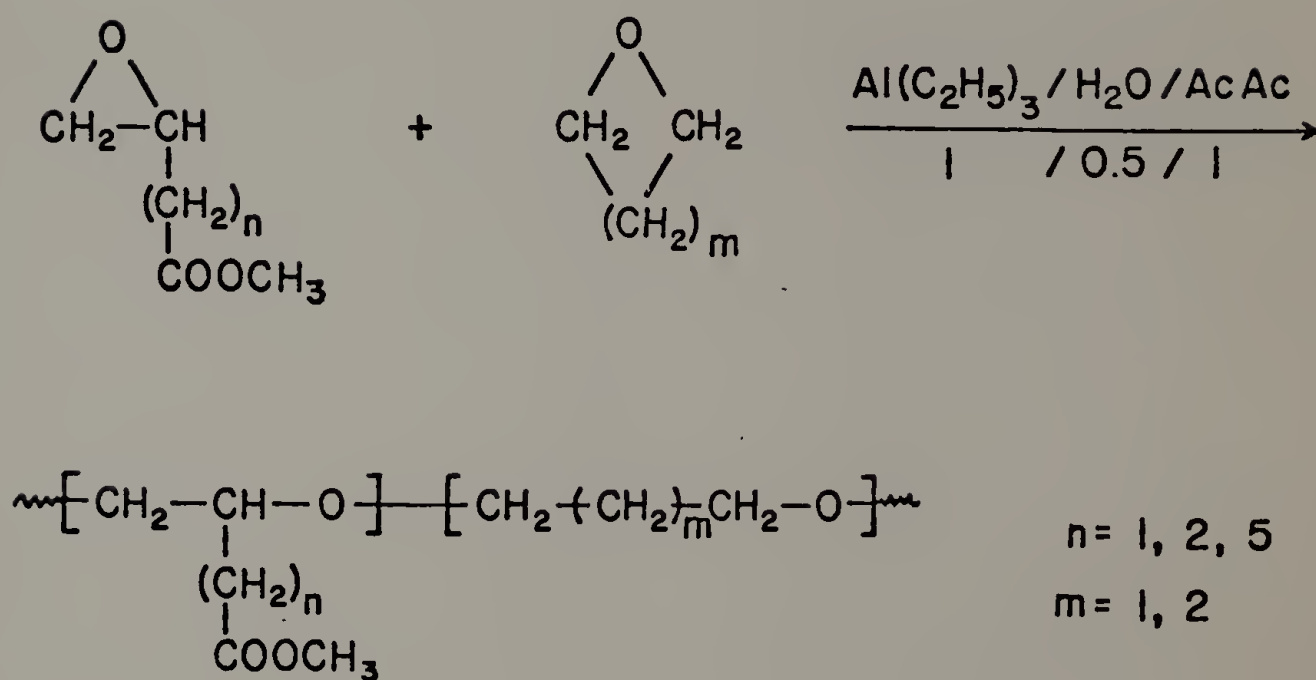


Figure 10.

9 and 10. The comonomers were mixed in a 70 mole%:30 mole% feed ratio of comonomer to MEB. Two homopolymerizations of MEB were also carried out, and in one of these, epichlorohydrin was used as a promoter. The results of the homo- and copolymerizations are shown in Table 14. The homo- and copolymers were all produced in very low yields. Polymerizations of PO and BO were carried out using the same initiator solution used for the MEB polymerizations, and good yields (80 to 90%) of high molecular weight polymers were obtained. This showed that the initiator solution was indeed active. The low yields could be attributed to an unknown monomer impurity, or to a stable initiator: MEB complex. Experimental evidence was not determined for either possibility.

The infrared spectra of the copolymers showed absorption bands characteristic of both comonomers, which in the case of MEB were the ester carbonyl and ester ether bands near  $1740\text{ cm}^{-1}$  and  $1170\text{ cm}^{-1}$ , respectively, and the ether stretching band of the poly(alkylene oxide) backbone near  $1100\text{ cm}^{-1}$ . The formation of two homopolymers, rather than true copolymers, can not be ruled out by infrared analysis alone.

#### B. Copolymerization of methyl-4,5-epoxypentanoate (MEP).

MEP was copolymerized with the same series of cyclic ether comonomers described in the MEB copolymerizations using the

TABLE 14  
COPOLYMERIZATION OF MEB WITH CYCLIC ETHERS

No.	Comonomer	Yield, in %
1	--	-- <sup>9</sup>
2	-- <sup>1</sup>	-- <sup>9</sup>
3	PO <sup>2</sup>	-- <sup>9</sup>
4	BO <sup>3</sup>	0.4
5	HO <sup>4</sup>	-- <sup>9</sup>
6	ECH <sup>5</sup>	0.6
7	PGE <sup>6</sup>	2.0
8	OX <sup>7</sup>	-- <sup>9</sup>
9	THF <sup>8</sup>	-- <sup>9</sup>

<sup>1</sup>2 mole% of epichlorohydrin (based on MEB) used as a promoter.

<sup>2</sup>PO = propylene oxide; <sup>3</sup>BO = 1-butene oxide;

<sup>4</sup>HO = 1-hexene oxide; <sup>5</sup>ECH = epichlorohydrin;

<sup>6</sup>PGE = phenyl glycidyl ether; <sup>7</sup>OX = oxetane;

<sup>8</sup>THF = tetrahydrofuran

<sup>9</sup>Yield less than 0.1%.

$\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$  (1/0.5/1) initiator system. As in the case of the MEB copolymerizations, the comonomers were mixed in a 70 mole%:30 mole% feed ratio of comonomer to MEP.

The yields from the MEP homo- and copolymerizations and the amount of MEP in the copolymers are shown in Table 15. The yields from the MEP homo- and copolymerizations were substantially higher than the MEB homo- and copolymerizations. This was attributed to the greater separation of the epoxide and ester groups in MEP than in MEB. The yields from the MEP copolymerizations with epoxide comonomers were higher in every instance than those from the MEP homopolymerizations. The amount of MEP in these copolymers ranged from 25 to 30 mole%, which indicated that the final copolymer composition was very similar to the initial comonomer composition. These results also indicated that MEP had a lower reactivity than the epoxide comonomers in these polymerization systems. In contrast, the yields from the MEP copolymerizations with oxetane and THF were lower than those from the MEP homopolymerizations. The amount of MEP in the oxetane copolymer was found to be 17 mole%, considerably less than the 30 mole% of MEP in the monomer feed. The low yield was attributed to low reactivity of both MEP and oxetane using this coordinate initiator system. The copolymer composition could be due to the difference in oxetane and epoxide oxygen nucleophilicities, or due to

TABLE 15  
COPOLYMERIZATION OF MEP WITH CYCLIC ETHERS

No.	Comonomer	Yield, in %	Mole % of MEP in copolymers
1	--	13 <sup>9</sup>	100
2	-- <sup>1</sup>	14 <sup>9</sup>	98
3	PO <sup>2</sup>	63	27
4	BO <sup>3</sup>	51	25
5	HO <sup>4</sup>	22	25
6	ECH <sup>5</sup>	20 <sup>10</sup>	30
7	PGE <sup>6</sup>	45 <sup>11</sup>	25
8	OX <sup>7</sup>	11 <sup>12</sup>	17
9	THF <sup>8</sup>	3 <sup>13</sup>	100

<sup>1</sup>2 mole% of epichlorohydrin (based on MEB) used as a promoter.

<sup>2</sup>PO = propylene oxide; <sup>3</sup>BO = 1-butene oxide;

<sup>4</sup>HO = 1-hexene oxide; <sup>5</sup>ECH = epichlorohydrin;

<sup>6</sup>PGE = phenyl glycidyl ether; <sup>7</sup>OX = oxetane;

<sup>8</sup>THF = tetrahydrofuran

<sup>9</sup>8% benzene insoluble; <sup>10</sup>0.1% 1,4-dioxane insoluble;

<sup>11</sup>28% 1,4-dioxane insoluble; <sup>12</sup>5% benzene insoluble;

<sup>13</sup>2% benzene insoluble

steric hindrance. MEP homopolymer was isolated from the attempted polymerization of MEP with THF. Attempted homopolymerizations of THF using the same initiator system also failed, indicating THF was not a suitable monomer in these systems.

The infrared spectra of the MEP homo- and copolymers all showed absorption bands characteristic of the monomers present in the monomer feed, and the ether stretching band of the poly(alkylene oxide) backbone near  $1100\text{ cm}^{-1}$ . The characteristic bands for MEP were the ester carbonyl and ester ether bands near  $1740\text{ cm}^{-1}$  and  $1170\text{ cm}^{-1}$ , respectively. The  $^{13}\text{C}$  NMR spectra also showed resonances characteristic of the substituted poly(alkylene oxide) copolymers (Table 16). As was found in the MEA homopolymers, multiple resonances for the backbone methylene and methine carbon atoms for most of the copolymers were seen, and in these cases the major resonances were underlined. The presence of multiple resonance for the backbone carbon atoms could arise from the junctions of different comonomer units, head-to-head linkages, or different stereochemical configurations of the polymer repeat unit.<sup>153</sup> The major resonances of the copolymer backbone carbon atoms had similar chemical shifts to the same carbon atoms of the corresponding homopolymers.

The MEP homo- and copolymers were analyzed by determining their inherent viscosities and GPC molecular

TABLE 16

 $^{13}\text{C}$  NMR CHEMICAL SHIFT DATA OF MEP COPOLYMERS<sup>1</sup>

Comonomer	Comonomer <sup>2</sup>		MEP <sup>2</sup>	
	$-\overset{ }{\text{CH}}-\text{O}$	$-\text{CH}_2-\text{O}$	$-\overset{ }{\text{CH}}-\text{O}$	$-\text{CH}_2-\text{O}$
--	--	--	76.34, 76.56, 78.62	72.54, 73.94
PO	75.76, 76.35	73.09, 73.53, 73.80, 74.45, 74.84	78.58	71.92, 72.50
BO	81.00	72.75, 74.04	78.65	72.13
HO	80.01	72.83, 73.11, 73.62, 74.43	78.75	72.54
ECH	79.24	69.68	78.56	72.56
PGE	78.63	70.27	78.63	72.15, 72.55, 72.90

<sup>1</sup>In ppm downfield from TMS (benzene solution).<sup>2</sup>Polymer backbone carbon atoms.

weights, and the results are shown in Table 17. The MEP homopolymers were insoluble in benzene and THF, and were not analyzed. The inherent viscosities ranged from 0.83 to 1.29 dL/g. Under similar conditions, an intrinsic viscosity of 1.3 dL/g was found to correspond to a molecular weight for PPO of 190,000. The copolymers probably exhibited molecular weights ranging from 100,000 to 200,000. GPC analysis showed the copolymers had a wide range of MWD values. The values for  $\bar{M}_n$  ranged from 20,000 to 130,000, and the values for  $\bar{M}_w$  ranged from 110,000 to 410,000. The MWD values ranged from approximately 2 to 16. Those copolymers with MWD values of approximately 3 or less exhibited fairly symmetrical elution curves, while those with MWD values of approximately 5 or greater showed elution curves with significant tailing in the low molecular weight region. It is not clear what the cause, or causes, of the wide range of MWD values are

The glass transition and melting temperatures for the MEP homo- and copolymers are shown in Table 18. Those polymers which were separated into benzene or 1,4-dioxane soluble and insoluble fractions were measured separately. The glass transition temperatures for the copolymers were found to lie in a wide range depending on the comonomer and copolymer composition. The copolymers were semicrystalline materials which exhibited less complicated melting behavior than the MEA homopolymers. The propylene oxide:MEP and

TABLE 17  
RELATIVE MOLECULAR WEIGHTS OF MEP COPOLYMERS

No.	Comonomer	$\eta_{inh},^9$ in dL/g	$\bar{M}_n \times 10^{-5}^{10}$	$\bar{M}_w \times 10^{-5}^{10}$	MWD <sup>11</sup>
1		--11	--12	--12	--12
2	--1	--11	--12	--12	--12
3	PO <sup>2</sup>	1.29	0.6	3.2	5.8
4	BO <sup>3</sup>	1.06	0.2	3.0	16
5	HO <sup>4</sup>	1.08	1.3	3.9	3.1
6	ECH <sup>5</sup>	0.93	0.9	4.7	5.2
7	PGE <sup>6</sup>	0.83	0.3	3.4	13
8	OX <sup>7</sup>	0.92	0.5	1.1	2.1
9	THF <sup>8</sup>	--11	--12	--12	--12

<sup>1</sup> 2 mole% of epichlorohydrin (based on MEP) used as a promoter.

<sup>2</sup> PO = propylene oxide; <sup>3</sup> BO = 1-butene oxide; <sup>4</sup> HO = 1-hexene oxide;

<sup>5</sup> ECH = epichlorohydrin; <sup>6</sup> PGE = phenyl glycidyl ether; <sup>7</sup> OX = oxetane;

<sup>8</sup> THF = tetrahydrofuran; <sup>9</sup> 0.5% (wt/vol) solution in benzene, 30°C

<sup>10</sup> GPC; <sup>11</sup> Insoluble in benzene (after drying); <sup>12</sup> Insoluble in THF

TABLE 18  
TRANSITION TEMPERATURES OF MEP COPOLYMERS

No.	Comonomer	T <sub>g</sub> in °C	T <sub>m</sub> in °C	Melting Range in °C
1	--	-23	115	114 to 128
	-- <sup>9</sup>	-20	146	125 to 151
2	-- <sup>1</sup>	-23	105	72 to 131
	-- <sup>1,9</sup>	-23	139	101 to 145
3	PO <sup>2</sup>	-54	amorphous	
4	BO <sup>3</sup>	-58	amorphous	
5	HO <sup>4</sup>	-46	64	33 to 71
6	ECH <sup>5</sup>	-17	amorphous	
	ECH <sup>5,10</sup>	-15	114	97 to 120
7	PGE <sup>6</sup>	12	amorphous	
	PGE <sup>6,10</sup>	18	122	122 to >177
8	OX <sup>7</sup>	-61	28	12 to 30
			101	99 to 121
	OX <sup>7,9</sup>	-40	24	12 to 35
			67,77	62 to 83
			142	108 to 147
9	THF <sup>8</sup>	-- <sup>11</sup>	-- <sup>11</sup>	

<sup>1</sup>2 mole% of epichlorohydrin (based on MEP) used as a promoter.

<sup>2</sup>PO = propylene oxide; <sup>3</sup>BO = 1-butene oxide;

<sup>4</sup>HO = 1-hexene oxide; <sup>5</sup>ECH = epichlorohydrin;

<sup>6</sup>PGE = phenyl glycidyl ether; <sup>7</sup>OX = oxetane;

<sup>8</sup>THF = tetrahydrofuran

<sup>9</sup>Benzene insoluble fraction; <sup>10</sup>1,4-dioxane insoluble fraction

<sup>11</sup>Not measured

1-butene oxide:MEP copolymers were found to be completely amorphous. Completely amorphous 1,4-dioxane soluble fractions of the epichlorohydrin:MEP and phenyl glycidyl ether:MEP copolymers were also isolated. The semicrystalline copolymers were found to be less crystalline than the MEA homopolymers, although no attempts to measure the percent crystallinity were made.

A comparison of the glass transition temperatures measured for the copolymers and those calculated for the copolymers using the Fox equation<sup>165</sup> was made. The glass transition temperatures for the homopolymers of the comonomers, the calculated copolymer glass transition temperatures, and the measured copolymer glass transition temperatures are shown in Table 19. The Fox equation can

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}}$$

be used to calculate glass transition temperatures for compatible copolymers if the weight fractions of the individual components,  $W_1$  and  $W_2$ , and the glass transition temperatures of the homopolymers of both components,  $T_{g1}$  and  $T_{g2}$ , are known. The calculated and measured glass transition temperatures were found to deviate by 1 to 8°C. The reason for the larger deviations was not clear.

#### C. Copolymerization of methyl-7,8-epoxyoctanoate (MEO).

Copolymerizations of MEO with the same cyclic ether

TABLE 19

MEASURED AND PREDICTED GLASS TRANSITION TEMPERATURES (Tg) FOR THE MEP COPOLYMERS

No.	Comonomer	Tg of Comonomer Homopolymer, in °C	Tg of Copolymer Calculated, <sup>8</sup> in °C	Tg of Copolymer Measured, in °C
1	--	--	-23	-23
2	PO <sup>1</sup>	-67	-49	-54
3	BO <sup>2</sup>	-63	-50	-58
4	HO <sup>3</sup>	-63	-52	-46
5	ECH <sup>4</sup>	-24	-24	-20
6	PGE <sup>5</sup>	29	16	13
7	OX <sup>6</sup>	-73	-60	-61
8	THF <sup>7</sup>	-- <sup>9</sup>	-- <sup>9</sup>	-- <sup>9</sup>

<sup>1</sup>PO = propylene oxide; <sup>2</sup>BO = 1-butene oxide; <sup>3</sup>HO = 1-hexene oxide;<sup>4</sup>ECH = epichlorohydrin; <sup>5</sup>PGE = phenyl glycidyl ether; <sup>6</sup>OX = oxetane;<sup>7</sup>THF = tetrahydrofuran<sup>8</sup>Determined using the Fox equation,  $1/Tg = W_1/Tg_1 + W_2/Tg_2$ <sup>9</sup>Not measured

comonomers described for MEB and MEP were carried out using the  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$  (1/0.5/1) initiator system. The yields for the polymerizations and the copolymer compositions are shown in Table 20.

In comparison to the copolymerizations involving MEB and MEP, the yields of the MEO homo- and copolymers were quite high. The presence of the ester functional group in MEO did not adversely affect either the homo- or copolymerizations of MEO with respect to the polymer yields or composition. The MEO homo- and copolymerizations proceeded qualitatively at the same rate as the HO homopolymerization. The polymerizations were allowed to proceed for 28 weeks. The amount of MEO in all of the copolymers was found to be 30 mole%. The polymer isolated from the attempted copolymerization of MEO with THF was found to be MEO homopolymer, the same result found in the attempted copolymerization of MEP with THF. These results showed that the final copolymer compositions were the same as the initial comonomer compositions, but do not show the pattern of comonomer incorporation into the copolymers.

The infrared spectra of the MEO homo- and copolymers, as was found for the MEB and MEP copolymers, all showed absorption bands characteristic of the monomers present in the monomer feed, and the ether stretching band of the poly(alkylene oxide) backbone near  $1100\text{ cm}^{-1}$ . The characteristic ester carbonyl and ester ether bands of MEO

TABLE 20  
COPOLYMERIZATION OF MEO WITH CYCLIC ETHERS

No.	Comonomer	Yield, in %	Mole% of MEO in copolymers
1	--	88	100
2	PO <sup>1</sup>	64	30
3	BO <sup>2</sup>	75	30
4	HO <sup>3</sup>	93	30
5	ECH <sup>4</sup>	89	30
6	PGE <sup>5</sup>	71 <sup>8</sup>	30
7	OX <sup>6</sup>	51	30
8	THF <sup>7</sup>	43	100

<sup>1</sup>PO = propylene oxide;    <sup>2</sup>BO = 1-butene oxide;

<sup>3</sup>HO = 1-hexene oxide;    <sup>4</sup>ECH = epichlorohydrin;

<sup>5</sup>PGE = phenyl glycidyl ether;    <sup>6</sup>OX = oxetane;

<sup>7</sup>THF = tetrahydrofuran

<sup>8</sup>12% 1,4-dioxane insoluble

were seen. The  $^{13}\text{C}$  NMR spectra also showed resonances characteristic of the substituted poly(alkylene oxide) homo- and copolymers (Table 21). Multiple resonances for the backbone methylene and methine carbon atoms for most of the homo- and copolymers were seen, and in these cases the major resonances were underlined. The presence of the multiple resonances for the backbone carbon atoms could be explained in the same way as the MEP polymers.<sup>153</sup>

Analysis of the MEO homo- and copolymers by determining their inherent viscosities and GPC molecular weights was carried out, and the results are shown in Table 22. Unlike the MEP homopolymers, the MEO homopolymers were found to be soluble in both benzene and THF. The inherent viscosities of the homo- and copolymers ranged from 0.80 to 1.77 dL/g. The GPC molecular weights fell in a smaller range than found in the MEA homopolymers or the MEP copolymers. The values for  $\bar{M}_n$  ranged from 100,000 to 430,000, and the values for  $\bar{M}_w$  ranged from 300,000 to 1,100,000. The MWD values were found to range from 2.4 to 4.8, a considerably smaller range than found for the MEP copolymers. These results indicated that high molecular copolymers of MEO with a variety of cyclic ether comonomers could be readily prepared.

Glass transition and melting temperatures for the MEO homo- and copolymers were measured, and the results are shown in Table 23. The phenyl glycidyl ether:MEO copolymer

TABLE 21

 $^{13}\text{C}$  NMR CHEMICAL SHIFT DATA OF MEO COPOLYMERS<sup>1</sup>

Comonomer	Comonomer <sup>2</sup>		MEO <sup>2</sup>	
	$-\overset{ }{\text{CH}}-\text{O}$	$-\text{CH}_2-\text{O}$	$-\overset{ }{\text{CH}}-\text{O}$	$-\text{CH}_2-\text{O}$
--			77.49, 77.65, 77.86, <u>79.80</u>	72.05, 72.44, <u>73.51</u>
PO	<u>75.71</u> , 76.99	73.73	77.23, 77.47, 77.58, 77.72, <u>79.69</u>	72.67
BO	<u>81.01</u> , 81.98	72.27, 72.83	78.53, 78.95, <u>79.79</u>	73.25, <u>73.91</u> , 74.00, 74.28
HO	77.38, 77.83, <u>79.99</u>	72.51, 72.74, <u>73.62</u> , 74.55	77.38, 77.83, <u>79.99</u>	72.51, 72.74, <u>73.62</u> , 74.55
ECH	79.42	<u>70.02</u> , 70.72	79.64	73.25
PGE	78.78	70.36	79.88	73.47
OX		67.25, <u>68.05</u>	79.35, <u>79.89</u>	<u>73.51</u> , <u>73.93</u>
THF		--	79.92	72.62, 72.91, <u>73.54</u> , 74.44

<sup>1</sup>In ppm downfield from TMS (benzene and 1,4-dioxane solutions).

<sup>2</sup>Polymer backbone carbon atoms.

TABLE 22  
RELATIVE MOLECULAR WEIGHTS OF MEO COPOLYMERS

No.	Comonomer	$\eta_{inh},^8$ in dL/g	$Mn \times 10^{-5}^9$	$Mw \times 10^{-5}^9$	MWD
1	--	1.02	3.1	7.4	2.4
2	PO <sup>1</sup>	1.23	2.2	5.4	2.5
3	BO <sup>2</sup>	1.77	4.3	11	2.6
4	HO <sup>3</sup>	1.75	1.2	6.0	4.8
5	ECH <sup>4</sup>	0.80	1.4	5.2	3.7
6	PGE <sup>5</sup>	0.80	1.0	3.0	3.0
7	OX <sup>6</sup>	1.26	2.4	6.5	2.7
8	THF <sup>7</sup>	1.02	2.1	5.9	2.9

<sup>1</sup>PO = propylene oxide; <sup>2</sup>BO = 1-butene oxide; <sup>3</sup>HO = 1-hexene oxide;

<sup>4</sup>ECH = epichlorohydrin; <sup>5</sup>PGE = phenyl glycidyl ether; <sup>6</sup>OX = oxetane;

<sup>7</sup>THF = tetrahydrofuran

<sup>8</sup>0.5% (wt/vol) solution in benzene; 30°C

<sup>9</sup>GPC

TABLE 23  
TRANSITION TEMPERATURES OF MEO COPOLYMERS

No.	Comonomer	T <sub>g</sub> in °C	T <sub>m</sub> in °C	Melting Range in °C
1	--	-58	44	27 to 67
2	PO <sup>1</sup>	-62	44	39 to 65
3	BO <sup>2</sup>	-63	amorphous	
4	HO <sup>3</sup>	-63	13	-18 to 32
5	ECH <sup>4</sup>	-43	39, 47	34 to 54
			83	78 to 88
6	PGE <sup>5</sup>	-21	47, 89	36 to 97
	PGE <sup>5, 8</sup>	-10	44	35 to 66
			90	82 to 107
7	OX <sup>6</sup>	-65	66	33 to 79
8	THF <sup>7</sup>	-58	44	34 to 54
			83	75 to 86

<sup>1</sup>PO = propylene oxide;    <sup>2</sup>BO = 1-butene oxide;

<sup>3</sup>HO = 1-hexene oxide;    <sup>4</sup>ECH = epichlorohydrin;

<sup>5</sup>PGE = phenyl glycidyl ether;    <sup>6</sup>OX = oxetane;

<sup>7</sup>THF = tetrahydrofuran

<sup>8</sup>1,4-dioxane insoluble fraction

was separated into 1,4-dioxane soluble and insoluble fractions, and these two fractions were measured separately. The glass transition temperatures were found to lie in a narrower range than the MEP copolymers. This was attributed to a greater similarity in the glass transition temperatures of the MEO homopolymer and the homopolymers of most of the comonomers. Most of the homo- and copolymers were found to be semicrystalline materials which exhibited less complicated melting behavior than the MEA homopolymers. The 1-butene oxide:MEO copolymer was completely amorphous.

A comparison of the glass transition temperatures measured for the copolymers and those calculated for the copolymers using the Fox equation was made. The glass transition temperatures for the homopolymers of the comonomers, the calculated copolymer glass transition temperatures, and the measured copolymer glass transition temperatures are shown in Table 24. Most of the calculated and measured glass transition temperatures were found to deviate from one another by 0 to 4°C. The calculated and measured glass transition temperatures for the phenyl glycidyl ether:MEO copolymer deviated by 13°C. The reason for the large deviation was not clear.

TABLE 24

MEASURED AND PREDICTED GLASS TRANSITION TEMPERATURES (T<sub>g</sub>) FOR THE MEO COPOLYMERS

No.	Comonomer	Tg of Comonomer Homopolymer, in °C	Tg of Copolymer Calculated, <sup>8</sup> in °C	Tg of Copolymer Measured, in °C
1	--	--	-58	-58
2	PO <sup>1</sup>	-67	-62	-62
3	BO <sup>2</sup>	-63	-61	-64
4	HO <sup>3</sup>	-63	-61	-63
5	ECH <sup>4</sup>	-24	-39	-43
6	PGE <sup>5</sup>	29	-7	-20
7	OX <sup>6</sup>	-73	-65	-65
8	THF <sup>7</sup>	-79	-58	-58

<sup>1</sup>PO = propylene oxide; <sup>2</sup>BO = 1-butene oxide; <sup>3</sup>HO = 1-hexene oxide;<sup>4</sup>ECH = epichlorohydrin; <sup>5</sup>PGE = phenyl glycidyl ether; <sup>6</sup>OX = oxetane;<sup>7</sup>THF = tetrahydrofuran<sup>8</sup>Determined using the Fox equation,  $1/T_g = w_1/T_{g1} + w_2/T_{g2}$

## V. Cationic Homopolymerization of Methyl $\omega$ -Epoxyalkanoates

A. Polymerizations using boron trifluoride etherate as the initiator. Boron trifluoride and its complexes with nucleophiles such as diethyl ether and methanol are typical examples of Lewis acid initiators used to prepare low molecular weight polymers from epoxides. The homopolymerizations of MEB, MEP, and MEO using  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  as the initiator were carried out to determine whether the ester groups of the monomers would detrimentally interact with the initiator, and whether a relationship between the methylene spacer length of the monomers and their polymerizability existed. The reaction scheme is shown in Figure 11. As a reference, PO was also polymerized under the same reaction conditions. The polymerizations were carried out at  $-78^\circ\text{C}$  as dichloromethane solutions in order to promote the formation of linear polymers over cyclic oligomers. The results of these polymerizations are shown in Table 25.

During the polymerizations, the reaction mixtures remained clear and colorless, except for the PO reaction mixture, which immediately turned brown and showed signs of a vigorous reaction taking place. The polymerizations were terminated by adding a molar excess of methanol at  $-78^\circ\text{C}$  and pyridine at room temperature. It was hoped that if cyclic oligomers were produced during the polymeriza-

Figure 11. Cationic homopolymerization of MEA.

# CATIONIC HOMOPOLYMERIZATION OF MEA

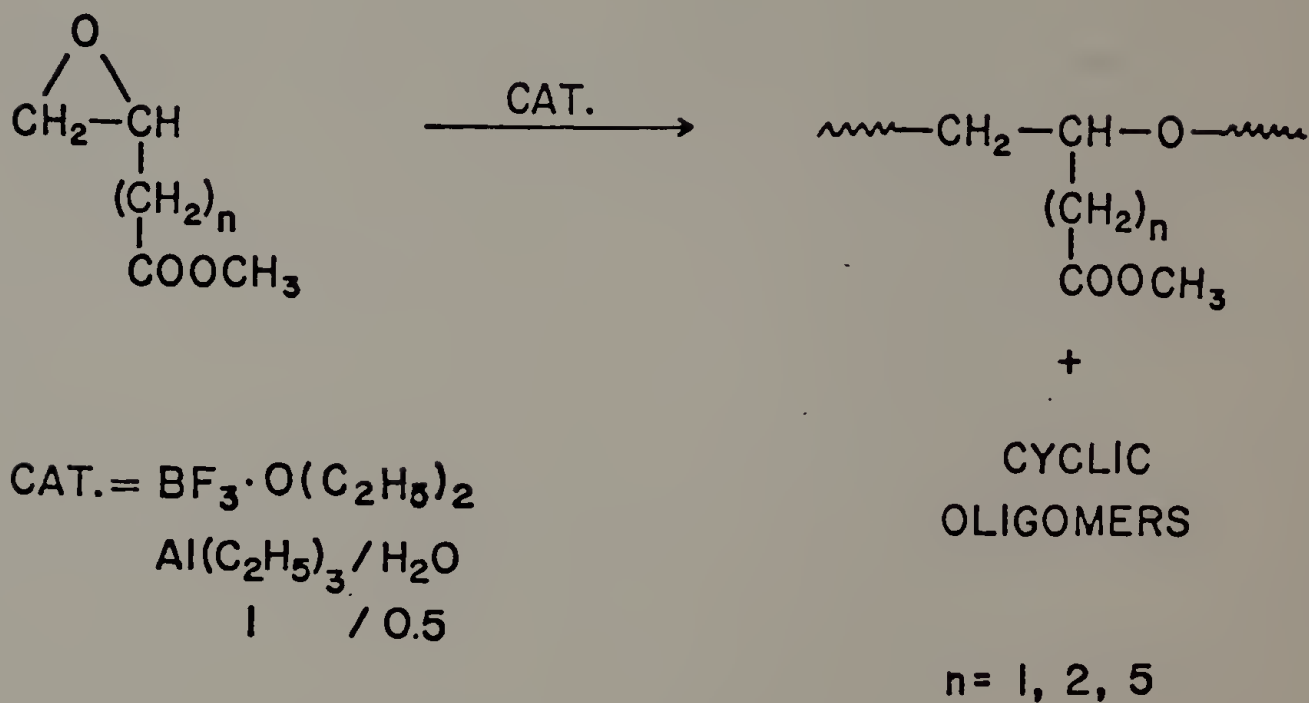


Figure 11.

TABLE 25

POLYMERIZATION OF METHYL  $\omega$ -EPOXYALKANOATES USING  
 $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  AS THE INITIATOR

Monomer	n	Yield, in %	Appearance of Polymer
MEB	1	67	Light tan, viscous oil
MEP	2	25	Light brown, paste-like
MEO	5	100	Light tan, paste-like
PO	-	81	Brown, viscous oil

tions, they would be separable by distillation. This was not the case, however. Polymers were produced in good yields, except for MEP. The reason for this was not clear.

The infrared spectra of the polymers showed absorption bands near  $3460\text{ cm}^{-1}$  (alcohol O-H stretch),  $1740\text{ cm}^{-1}$  (ester C=O stretch),  $1170\text{ cm}^{-1}$  (ester O-C stretch), and  $1100\text{ cm}^{-1}$  (ether C-O-C stretch). The presence of alcohol hydroxyl groups was attributed to the polymer end groups. The  $^{13}\text{C}$  NMR spectra of the polymers showed many more resonances for the backbone carbon atoms than were found in the various polymers described earlier which were prepared using the coordinate initiator. The multiple resonances for the backbone carbon atoms were attributed to the large number of head-to-head, as well as head-to-tail, linkages, and different stereochemical configurations of the polymer repeat unit normally found in cationic epoxide polymerizations. A resonance upfield from the backbone carbon atom resonances, at 66 to 68 ppm, was also observed in these polymers. This resonance was not seen in the polymers prepared using the coordinate initiator. This resonance could be due to cyclic oligomers formed during the polymerizations. 1,4-Dioxane has its  $^{13}\text{C}$  NMR resonance at 67.4 ppm, and 2,5-bis(morpholinomethyl)-1,4-dioxane has its ring methylene carbon resonance at 69.9 ppm.<sup>166</sup>

The polymers were analyzed by determining their inherent viscosities and GPC molecular weights (Table 26).

TABLE 26

RELATIVE MOLECULAR WEIGHTS OF MEA HOMOPOLYMERS PREPARED USING  
 $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  AS THE INITIATOR

Monomer	n	$\eta_{\text{inh}}, \frac{\text{l}}{\text{in dL/g}}$	$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	MWD
MEB	1	0.02	1.2	2.6	1.7
MEP	2	0.03	0.8	1.2	1.5
			0.3	0.4	1.1
			0.2	0.2	1.0
MEO	3	0.01	2.0	3.8	2.0
			0.6	0.6	1.1
PO	-	0.01	0.7	1.0	1.4
			0.3	0.3	1.1

<sup>1</sup> 0.5% (wt/vol) in 1,4-dioxane; 30°C

<sup>2</sup> GPC

The viscosity and GPC molecular weight values were all considerably lower than the same polymers prepared using the coordinate initiator. PMEB exhibited a monomodal GPC elution curve, while PMEP, PMEO, and PPO exhibited bi- and trimodal GPC elution curves. It was not clear what the different elution peaks corresponded to.

B. Polymerizations using the  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}$  (1/1.5) initiator system. While the AcAc-modified  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}$  initiator systems are considered to be coordinate anionic initiators, the  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}$  initiator systems alone are believed to act as cationic initiators.<sup>77</sup> These cationic initiators can be used to form high molecular weight polymers from a variety of epoxide monomers.<sup>72,79</sup> The homopolymerizations of MEB, MEP, and MEO using the  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}$  (1/0.5) initiator system were carried out for several reasons. It was desirable to compare the polymers produced using this "cationic" initiator with the same polymers prepared using  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  as the initiator in order to determine if high molecular weight polymers could be prepared from MEA monomers. It was also desirable to determine whether the ester groups of the MEA monomers would interact with the initiator, in a favorable fashion, resulting in the formation of polymers similar to those prepared using the AcAc-modified initiator. It was also desirable to determine whether the same relationship

existed between the separation of the two functional groups of the MEA monomers and their reactivity towards polymerization as was found using the AcAc-modified initiator. PO was polymerized to serve as a reference. The results of the polymerizations are shown in Table 27. The yields and physical appearances of the MEB, MEO, and PO polymers were found to be very similar to the same polymers prepared using the AcAc-modified initiator. However, the results from the MEP polymerization were found to be more similar to the  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  initiated polymerization.

The infrared spectra of the MEB, MEO, and PO polymers were essentially indistinguishable from the same polymers prepared using the AcAc-modified initiator. On the other hand, PMEP showed a strong alcohol hydroxyl absorption near  $3460 \text{ cm}^{-1}$ , very similar to the spectrum for PMEP prepared using  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  as the initiator. The  $^{13}\text{C}$  NMR spectra of the polymers showed complicated resonance patterns similar to the same polymers prepared using  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  as the initiator.

Characterization of these polymers by determining their inherent viscosities and GPC molecular weights was also carried out (Table 28). The inherent viscosities and GPC molecular weights of the MED and PO polymers showed once again that these materials were high molecular weight polymers. The inherent viscosity and GPC molecular weights of PMEP were similar to those found for PMEP prepared using

TABLE 27

POLYMERIZATION OF METHYL  $\omega$ -EPOXYALKANOATES USING  
THE  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}$  (1/0.5) INITIATOR SYSTEM

Monomer	n	Yield, in %	Appearance of Polymer
MEB	1	4	Off-white, powdery
MEP	2	4	Light brown, paste-like
MEO	5	74	Tough, white elastomer
PO	-	91	Tough, white elastomer

TABLE 28

RELATIVE MOLECULAR WEIGHTS OF MEA HOMOPOLYMERS PREPARED USING  
THE  $\text{Al}(\text{C}_2\text{H}_5)/\text{H}_2\text{O}$  (1/0.5) INITIATOR SYSTEM

Monomer	n	$\eta_{\text{inh}},$ in dL/g	$\bar{M}_n \times 10^{-4}$ <sup>2</sup>	$\bar{M}_w \times 10^{-4}$ <sup>2</sup>	MWD
MEB	1	-- <sup>3</sup>	-- <sup>4</sup>	-- <sup>4</sup>	-- <sup>4</sup>
MEP	2	0.01	0.2	0.2	1.4
MEO	3	1.05	0.03 <sup>5</sup>	0.04 <sup>5</sup>	1.5 <sup>5</sup>
PO	-	0.78	13	66	2.5
					5.0

<sup>1</sup> 0.5% (wt/vol) in 1,4-dioxane; 30°C

<sup>2</sup> GPC

<sup>3</sup> Insoluble in 1,4-dioxane

<sup>4</sup> Insoluble in THF

<sup>5</sup> Includes 2 peaks

$\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  as the initiator.

The glass transition and melting temperatures for these polymers are shown in Table 29. The glass transition temperatures for all of the polymers were less than for the same polymers prepared using the AcAc-modified initiator, especially PMEB and PMEP. PMEB and PMEP also showed no melting behavior. PMEO and PPO did exhibit some crystallinity, although not as much as found for the same polymers prepared using the AcAc-modified initiator.

From these results, it may be concluded that high molecular weight polymers may be prepared from MEA monomers using the "cationic"  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}$  (1/0.5) initiator system. It was not clear from the results whether beneficial interactions between the ester groups of the MEA monomers and the initiator occurred. It was apparent that a relationship between separation of the MEA functional groups and monomer reactivity towards polymerization existed, but not the same one observed when the AcAc-modified initiator was used. The anomalous behavior of MEP in these polymerization systems could be attributed to an unknown monomer impurity. However, this was not felt to be the case because the polymerization results were repeatable, and because the same monomer could give high molecular weight polymer using the AcAc-modified initiator.

TABLE 29

TRANSITION TEMPERATURES OF MEA HOMOPOLYMERS PREPARED  
USING THE  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}$  (1/0.5) INITIATOR SYSTEM

Monomer	n	$T_g$ in °C	$T_m$ in °C	Melting Range in °C
MEB	1	-52	amorphous	--
MEP	2	-67	amorphous	--
MEO	5	-58	63, 72 <sup>1</sup>	32 to 79
PO	-	-67	55 <sup>2</sup>	31 to 62

<sup>1</sup>Inflection at 47°C

<sup>2</sup>Inflection at 41°C

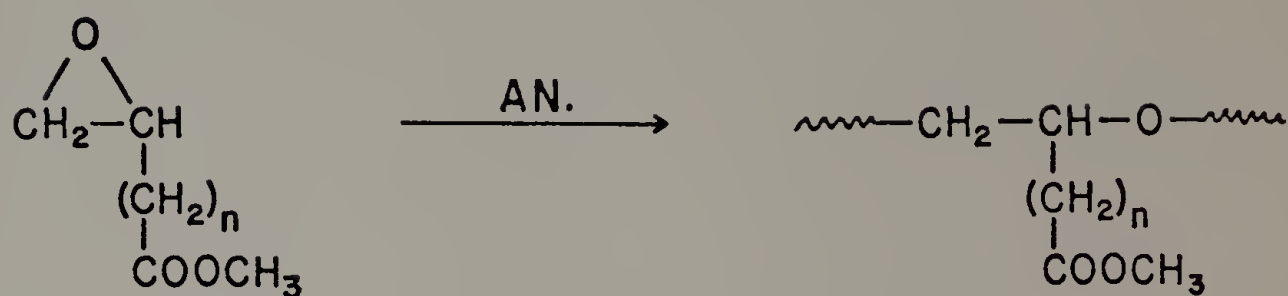
VI. Anionic Homopolymerization of Methyl  
Epoxyalkanoates using Potassium  
Hydroxide as the Initiator

Anionic homopolymerization of MEB, MEP, and MEO were attempted using solid potassium hydroxide as the initiator. It was hoped that the electron withdrawing strength of the ester group on the epoxide could be determined as a function of the methylene group spacer length, and that the polymerizations could be carried out without cleaving the ester groups. A general polymerization scheme is shown in Figure 12. Potassium hydroxide was chosen as the initiator because it is capable of acting as a heterogeneous initiator for epoxide polymerizations.<sup>15</sup> This would present the best chance to prevent ester hydrolysis compared to a homogeneous polymerization. The polymerizations were carried out at room temperature, rather than an elevated temperature, in order to reduce the possibility of ester cleavage. A PO polymerization was also carried out as a reference.

Only PO was successfully polymerized. As expected, the polymer was a low molecular weight material. The polymer yield was low due to the mild reaction conditions used. The infrared and  $^{13}\text{C}$  NMR spectra were consistent with the low molecular weight polymer structure. MEB underwent rearrangement to methyl-3-hydroxy-2-butenate,<sup>167</sup> as shown in Figure 13. The infrared and  $^{13}\text{C}$  NMR spectra

Figure 12. Anionic homopolymerization of MEA.

## ANIONIC HOMOPOLYMERIZATION OF MEA



AN. = KOH

 $n = 1, 2, 5$ 

Figure 12.

Figure 13. Rearrangement of MEB to 3-hydroxy-2-butenate.

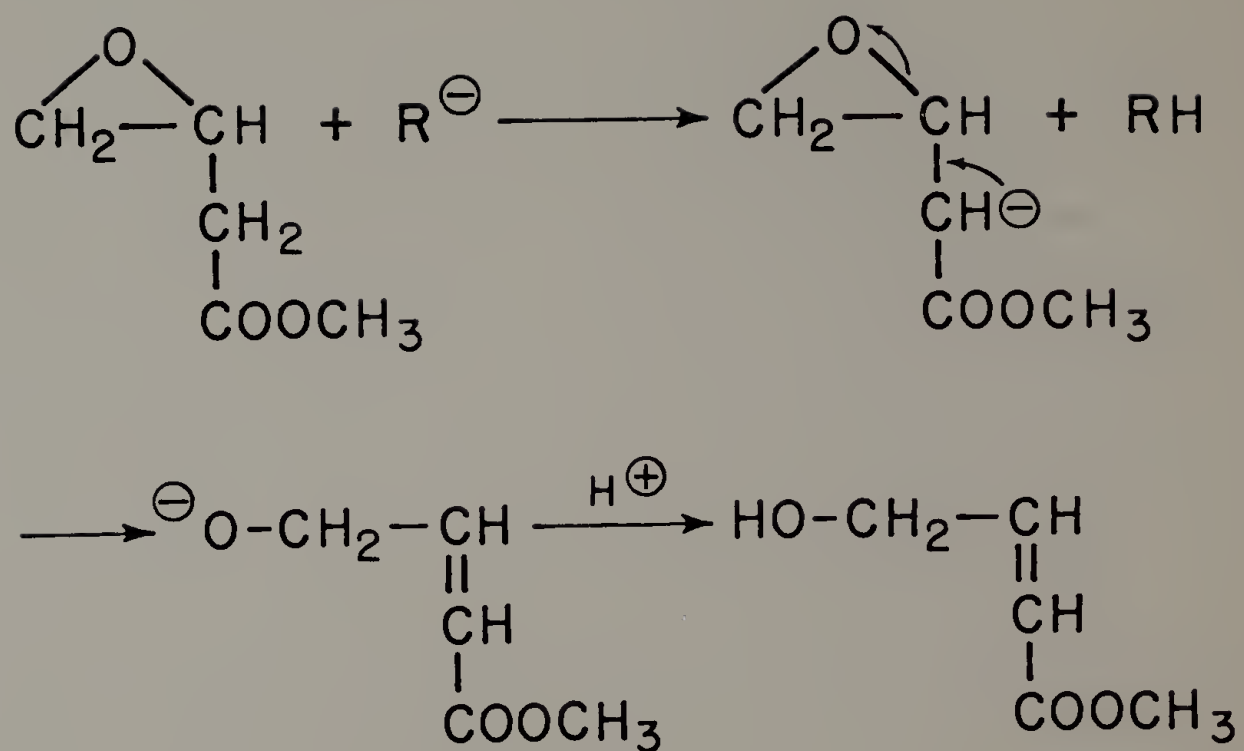


Figure 13.

showed evidence of MEB and the rearrangement product. Both MEP and MEO were completely unreacted. In order for successful anionic polymerizations to occur, more drastic conditions should be used.

## VII. Conclusions and Further Work

The objectives of this research were three-fold. The first was to synthesize several novel ester substituted poly(alkylene oxide) homo- and copolymers, where the ester groups were separated from the polymer backbone by a well defined number of methylene spacer groups. This objective was successfully completed. Methyl  $\omega$ -epoxyalkanoates (MEA) with 0 to 7 methylene spacer groups were homopolymerized using the  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$  (1/0.5/1) initiator system, and it was found that the MEA monomers with 0 through 3 methylene spacer groups only gave low yields of polymer, while the MEA monomers with 4 through 7 methylene spacer groups gave good yields of polymer. Copolymerizations of MEB, MEP, and MEO were carried out with several common cyclic ether comonomers using the  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$  (1/0.5/1) initiator system, and the yields of the copolymers were shown to be strongly dependent on the MEA monomer. When MEB was used, very low yields of the copolymers were obtained, while copolymerizations of MEP, with one more methylene spacer group than MEB, gave much higher yields. Copolymerizations involving MEO gave the highest yields.

Homopolymerizations of MEB, MEP, and MEO were also carried out using the cationic initiators  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  and  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}$  (1/0.5) to give, generally, low and high molecular weight polymers, respectively. Attempts to polymerize MEB, MEP, and MEO using KOH as the initiator were unsuccessful; however, MEB was found to undergo a base catalyzed rearrangement.

The second objective of this research was to determine the proximity effect of the ester group on the epoxide reactivity of the MEA monomers towards polymerization. This second objective was also successfully completed. It was found that the relative reactivity of the MEA monomers towards polymerization could not be predicted in these systems by spectroscopic analysis (infrared and  $^{13}\text{C}$  NMR) of the MEA monomers.

The third objective of this research was to carry out basic characterization of the MEA homo- and copolymers, and this objective was also completed. Elemental analysis of the MEP and MEO copolymers showed that high incorporations of the MEA monomers into the copolymers readily occurred.  $^{13}\text{C}$  NMR analysis of MEA homo- and copolymers prepared using the  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$  (1/0.5/1) coordinate initiator system indicated that regular polymer backbones were obtained, whereas MEA homopolymers prepared using cationic initiators indicated that more irregular polymer backbones were obtained. Inherent viscosity and GPC

measurements of the MEA homo- and copolymers prepared using the  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}/\text{AcAc}$  (1/0.5/1) and  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{H}_2\text{O}$  (1/0.5) initiator systems showed that, in most cases, high molecular weight polymers were formed, whereas low molecular weight MEA polymers were formed using  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  as the initiator. Thermal (DSC) analysis of the high molecular weight polymers demonstrated that most of the polymers were semicrystalline, with glass transition temperatures similar to other poly(alkylene oxides). The low molecular weight polymers were shown to be amorphous.

The results from this research demonstrated that both the polymerization process and polymers themselves were complicated. The polymerization process should be studied to determine the cause of the methylene spacer length dependence of the MEA monomer reactivity towards polymerization, the effect of the coordinate initiator on the rate and yield of the polymerizations, and whether random or block copolymers are formed during copolymerizations of MEA monomers with other cyclic ethers. The polymers should be studied to determine the type, or types, of crystallinity observed by DSC measurements, their suitability as ionomer or polyelectrolyte precursors, and their suitability as thermoplastic elastomers.

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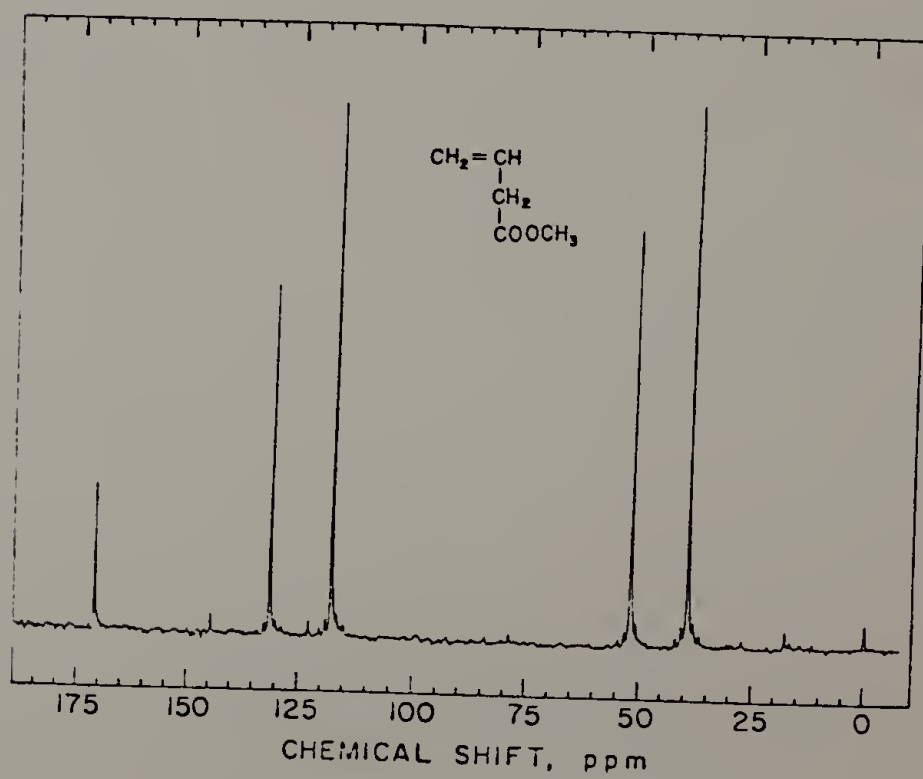
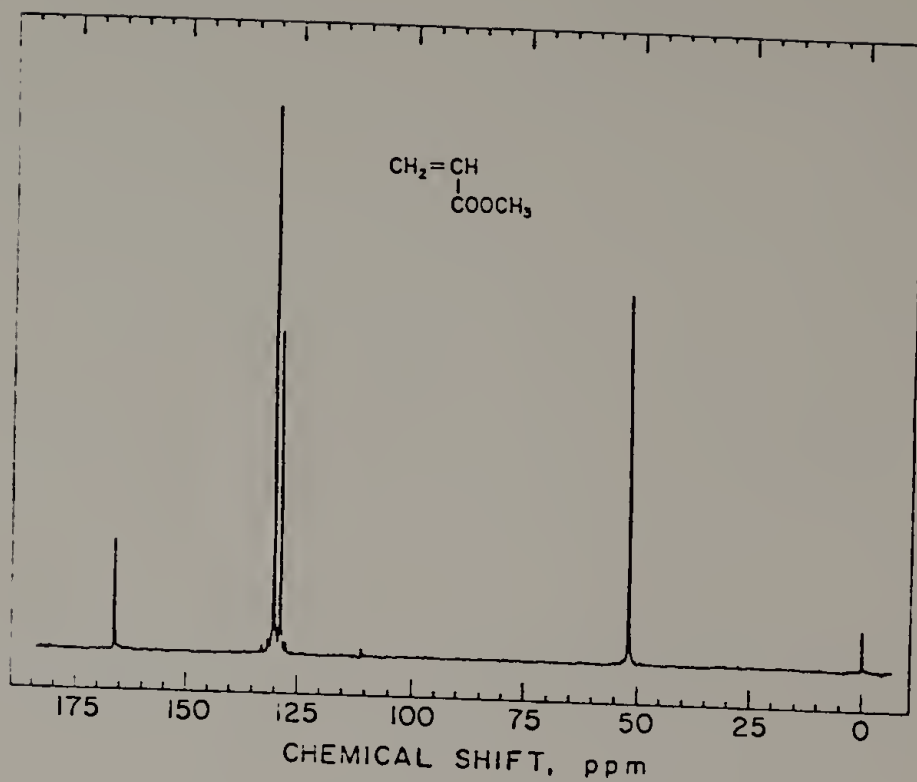
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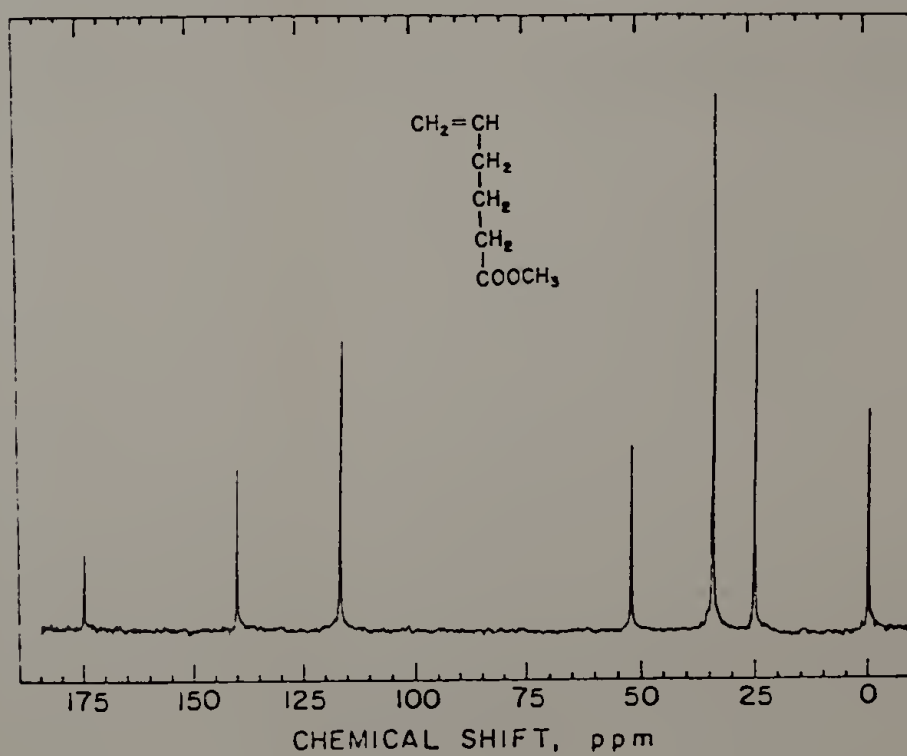
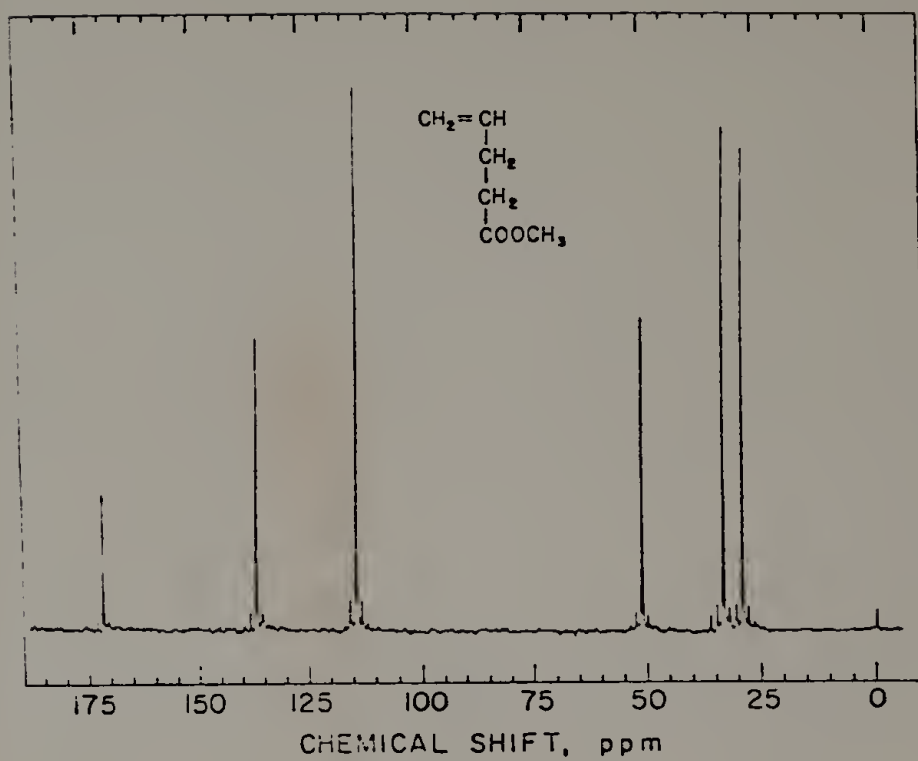
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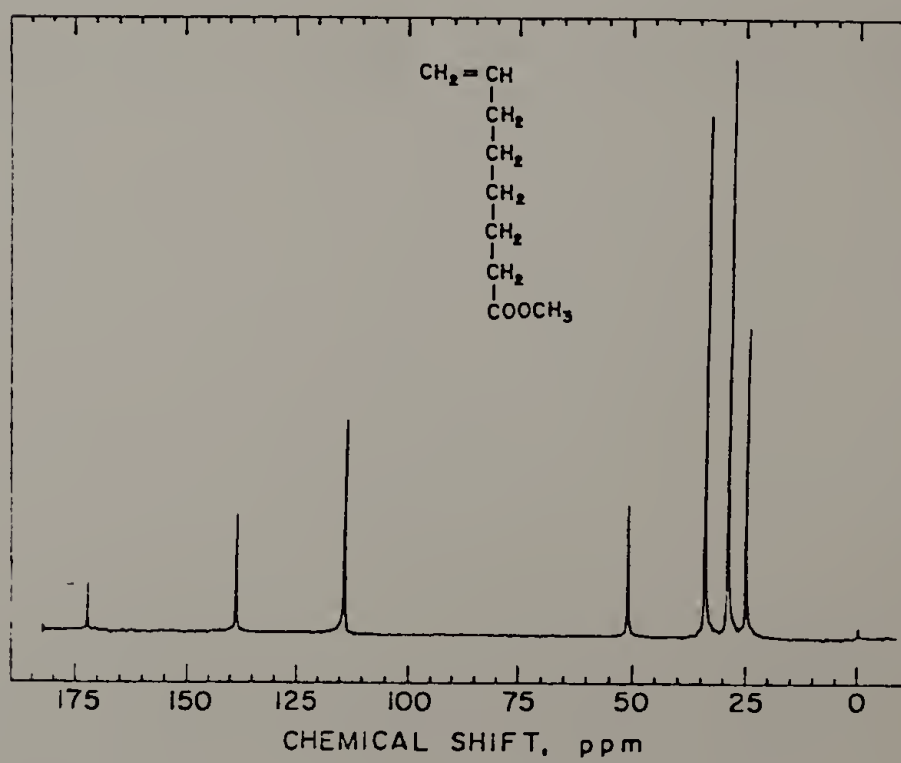
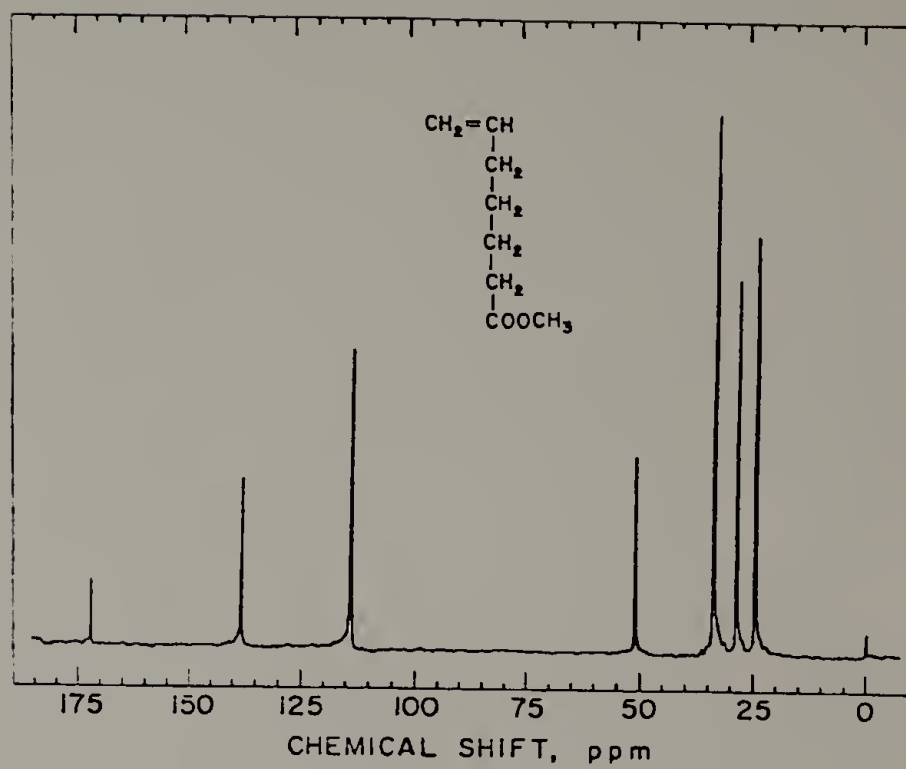
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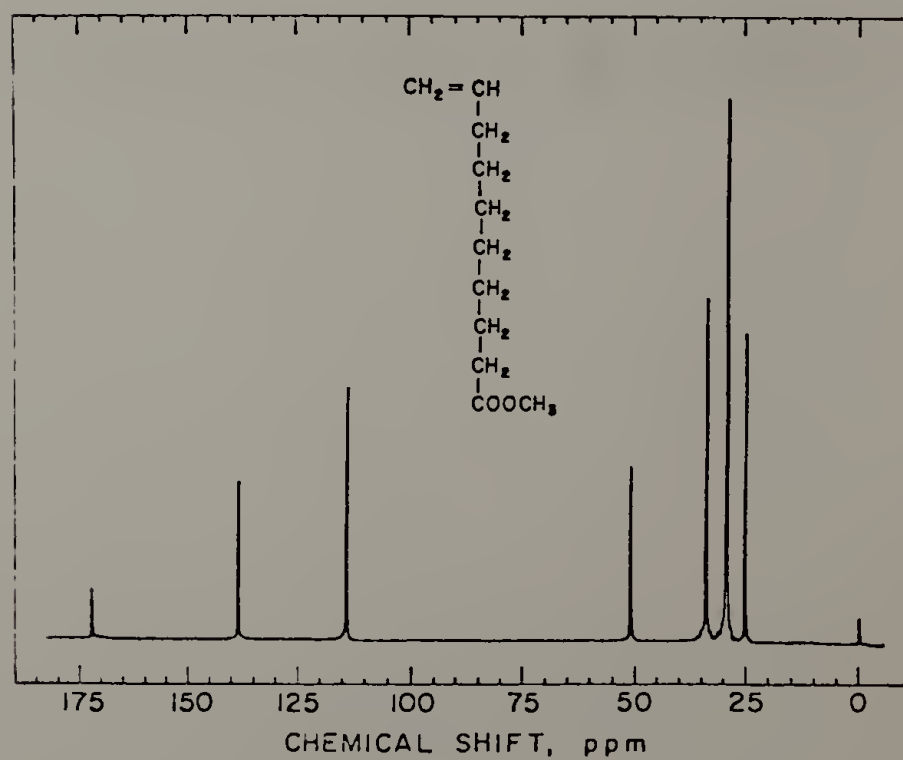
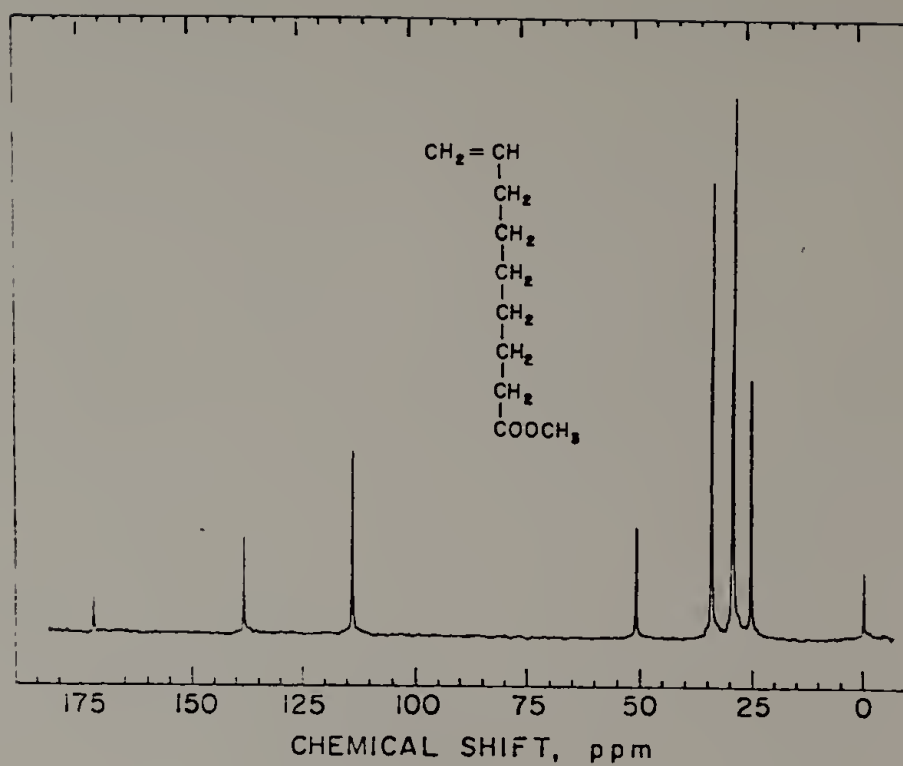
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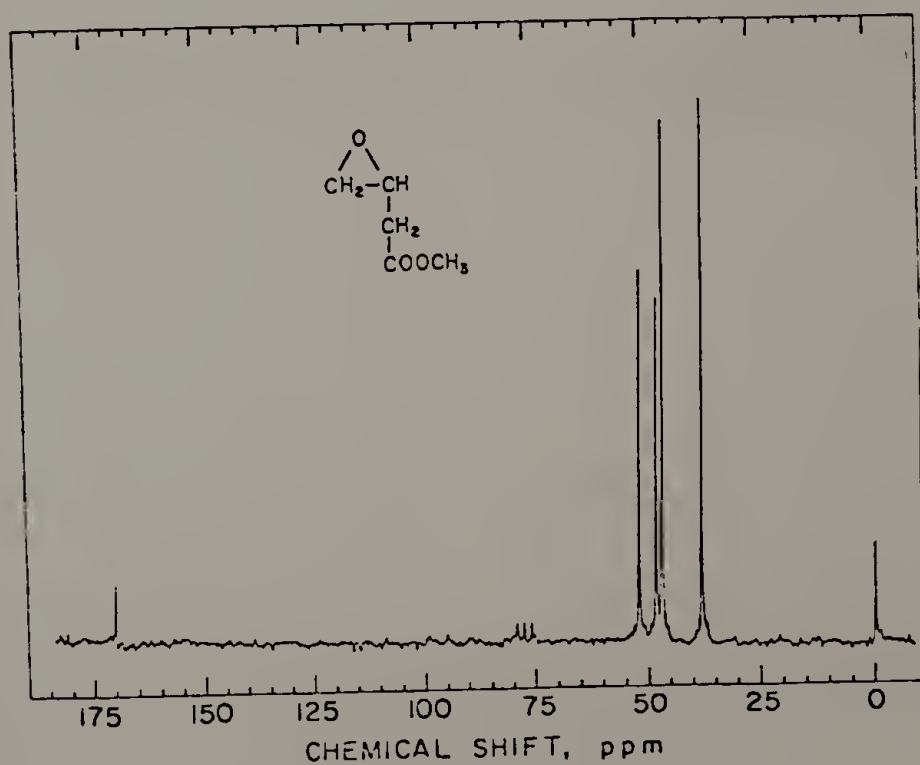
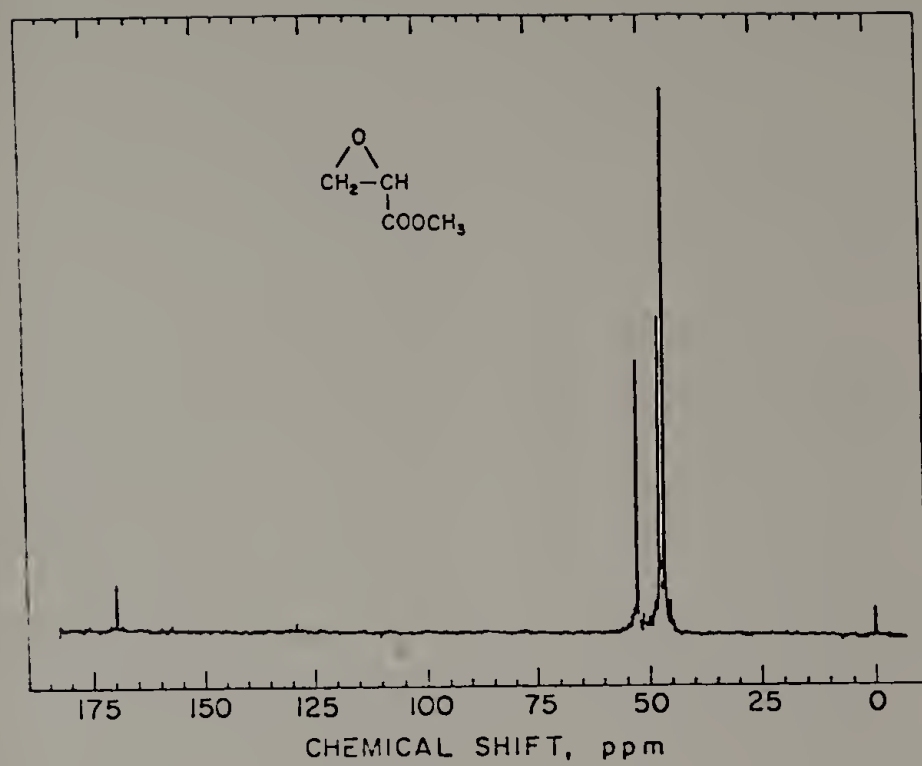
APPENDIX A  
 $^{13}\text{C}$  NUCLEAR MAGNETIC RESONANCE SPECTRA

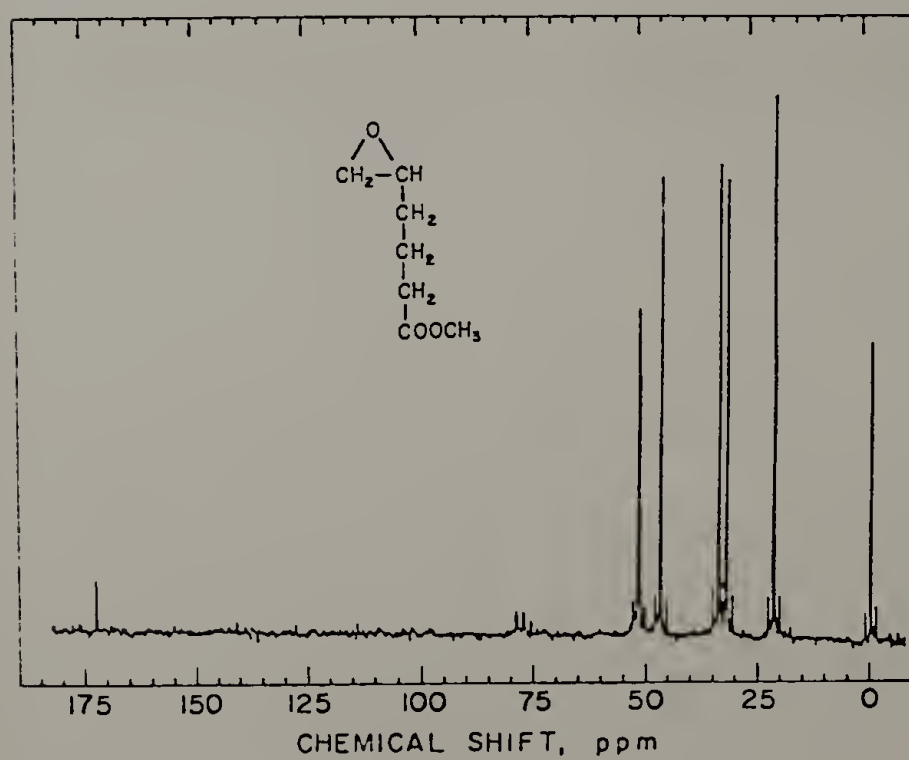
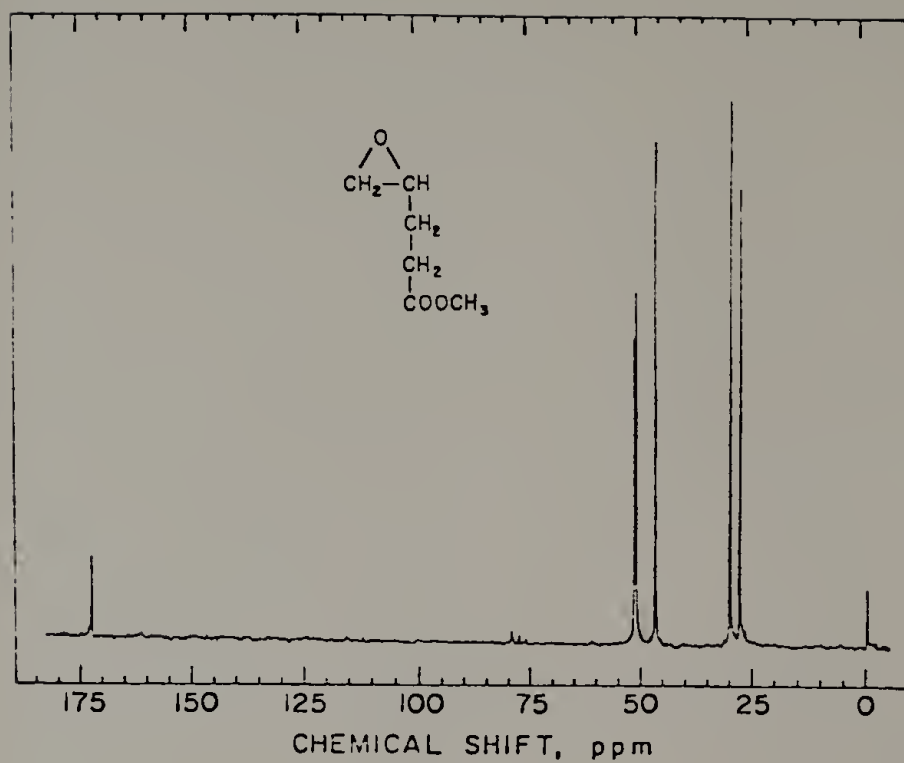


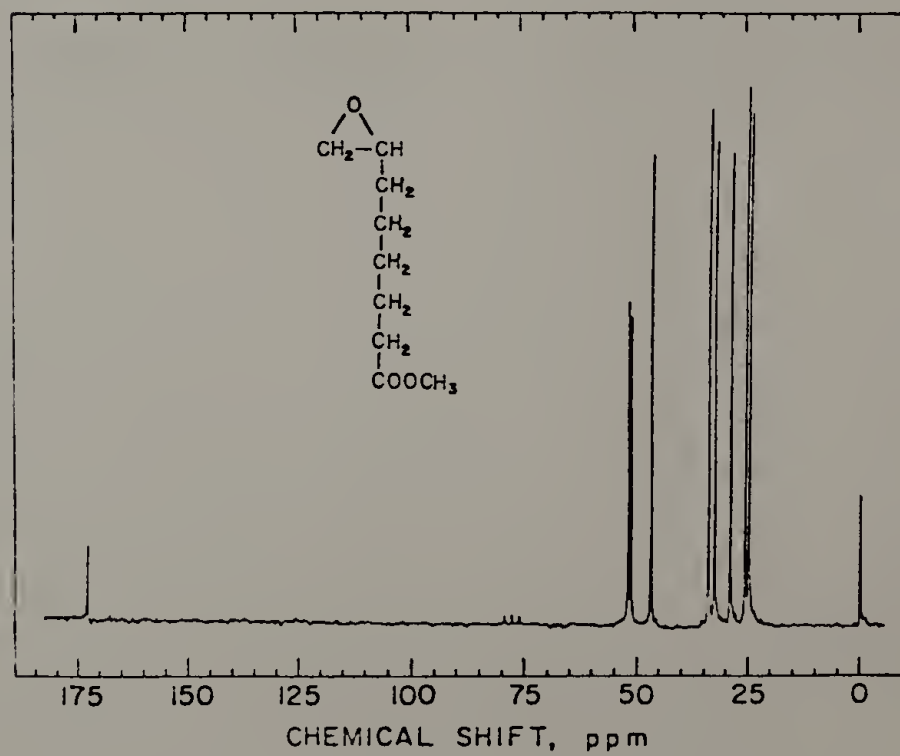
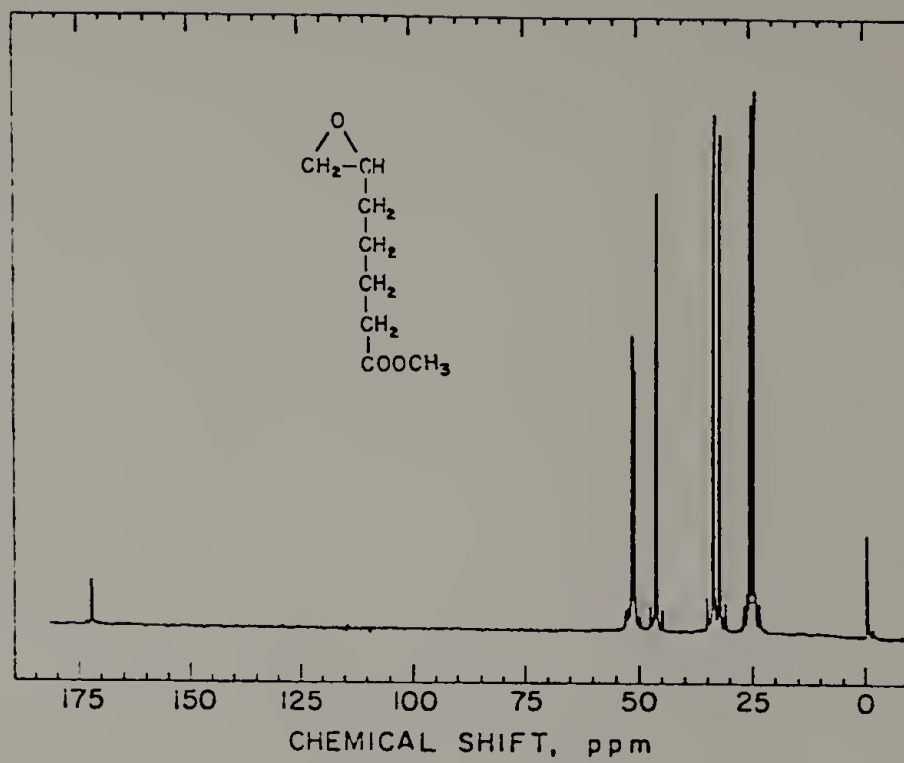


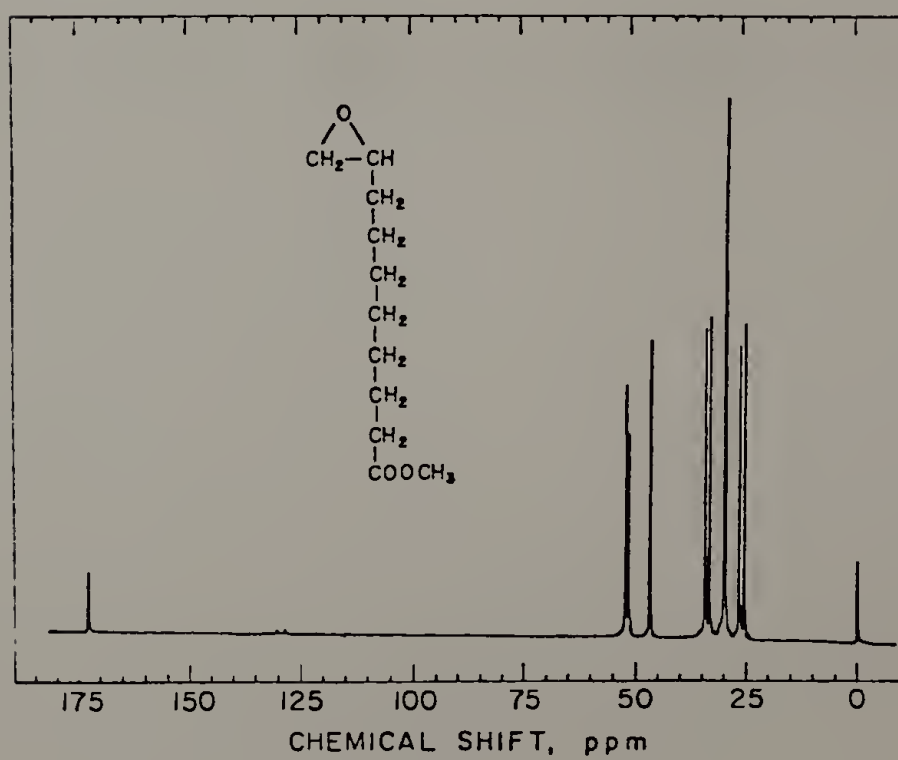
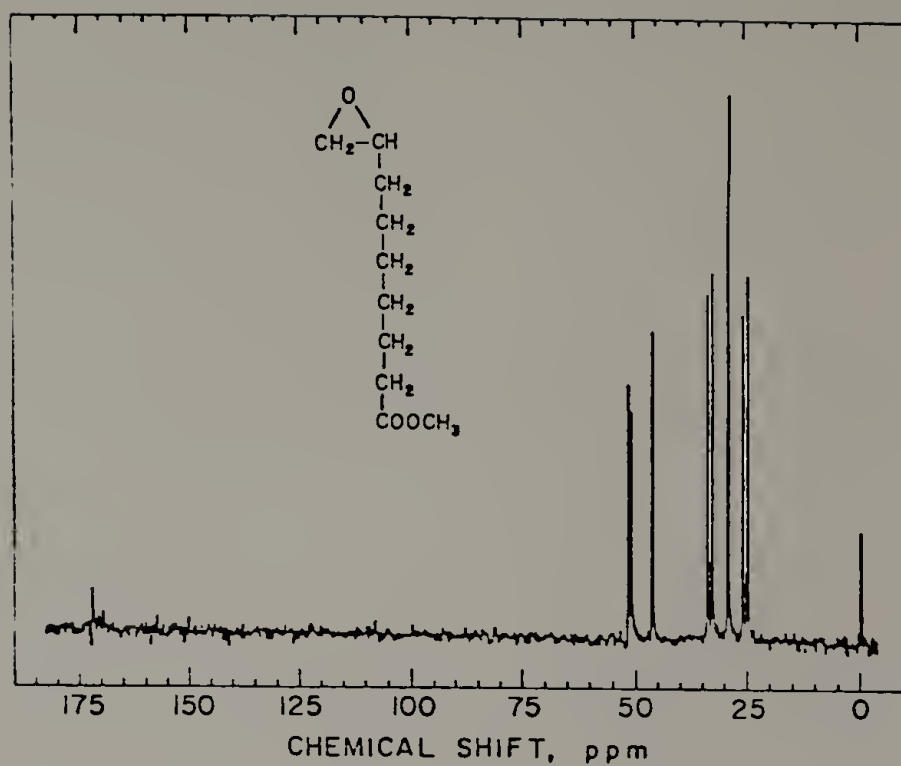


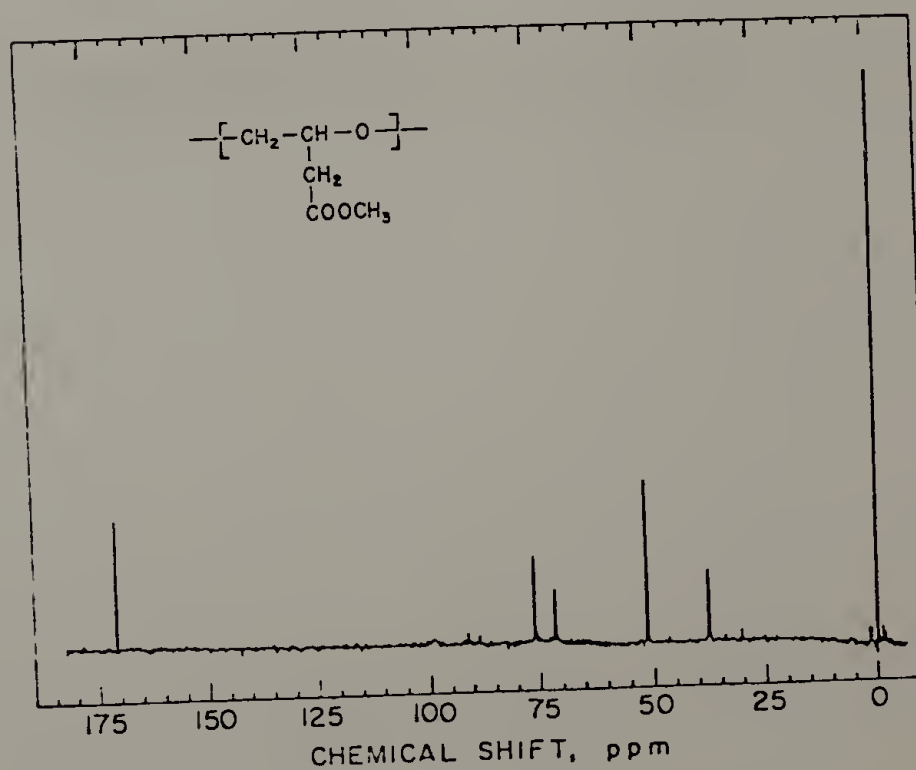
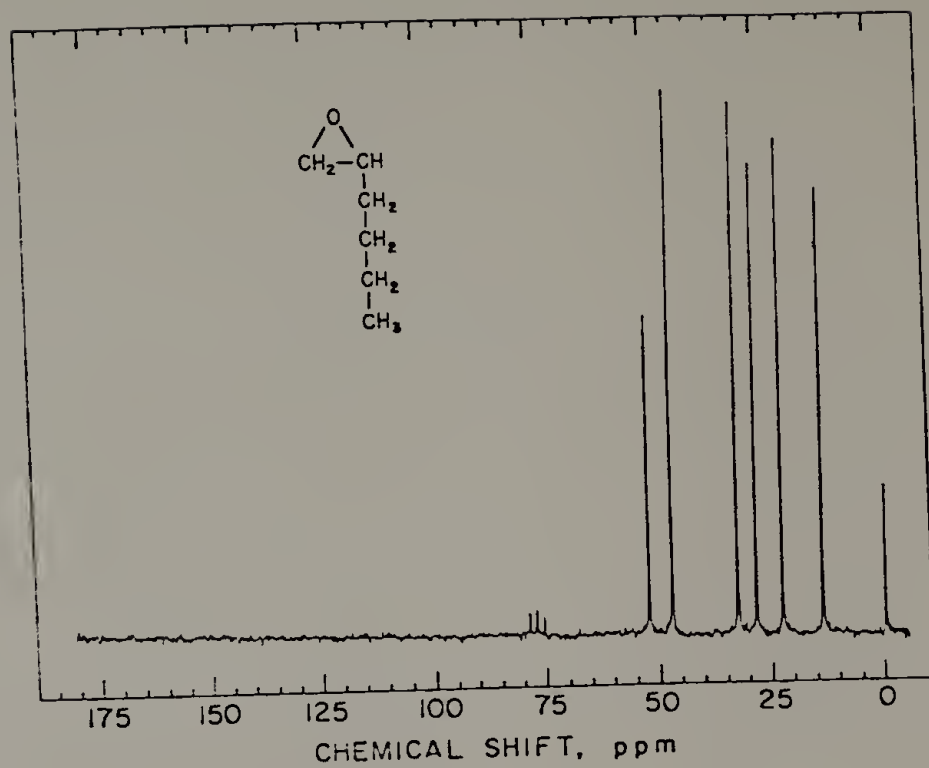


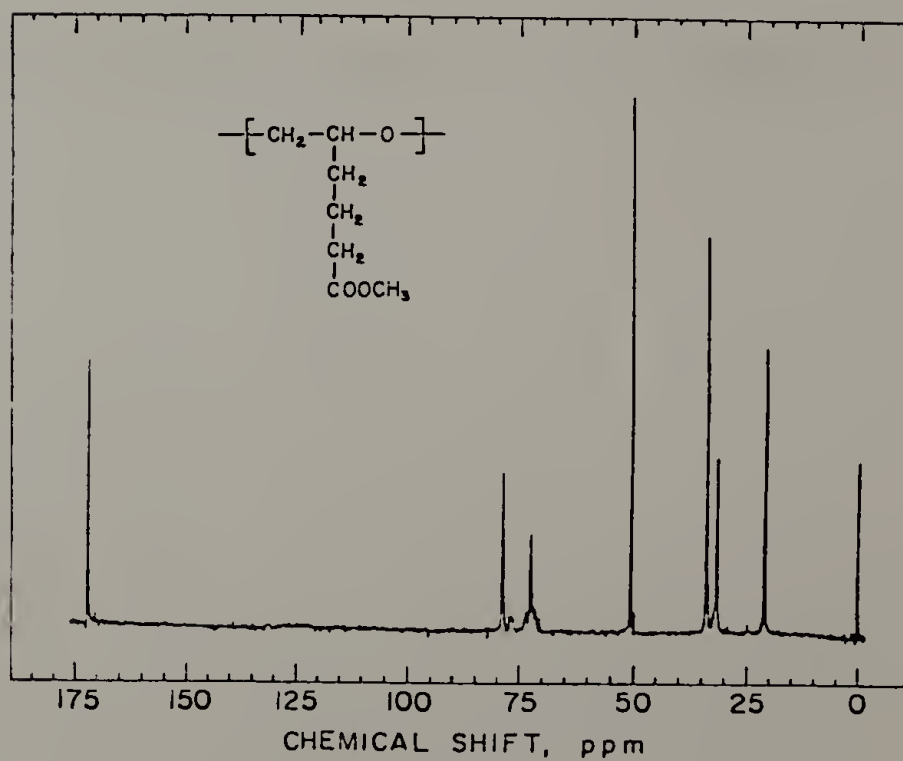
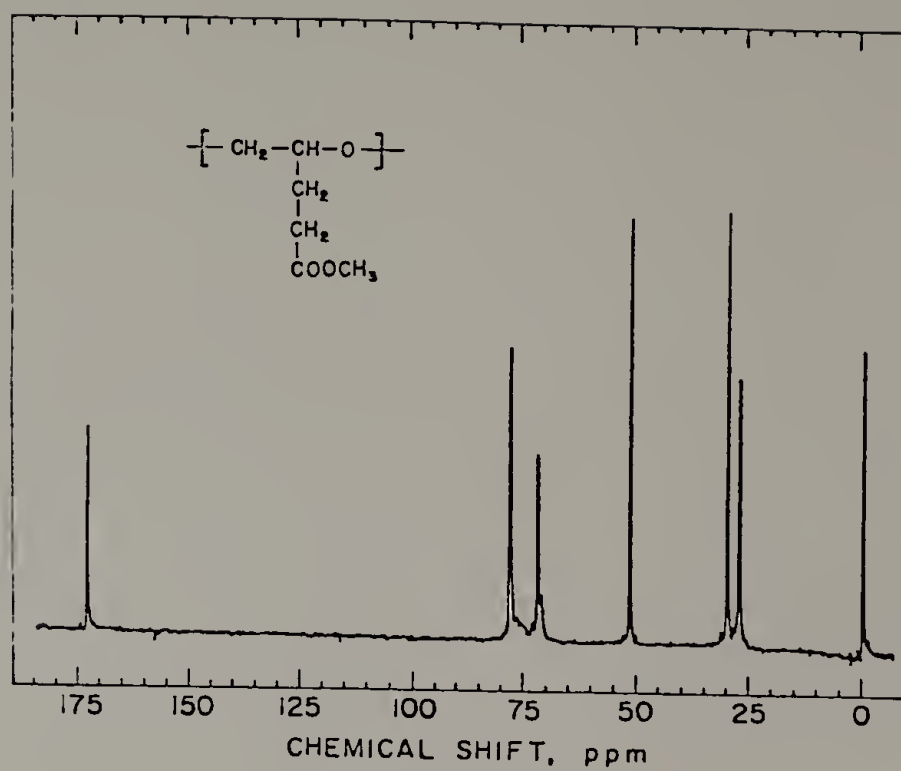


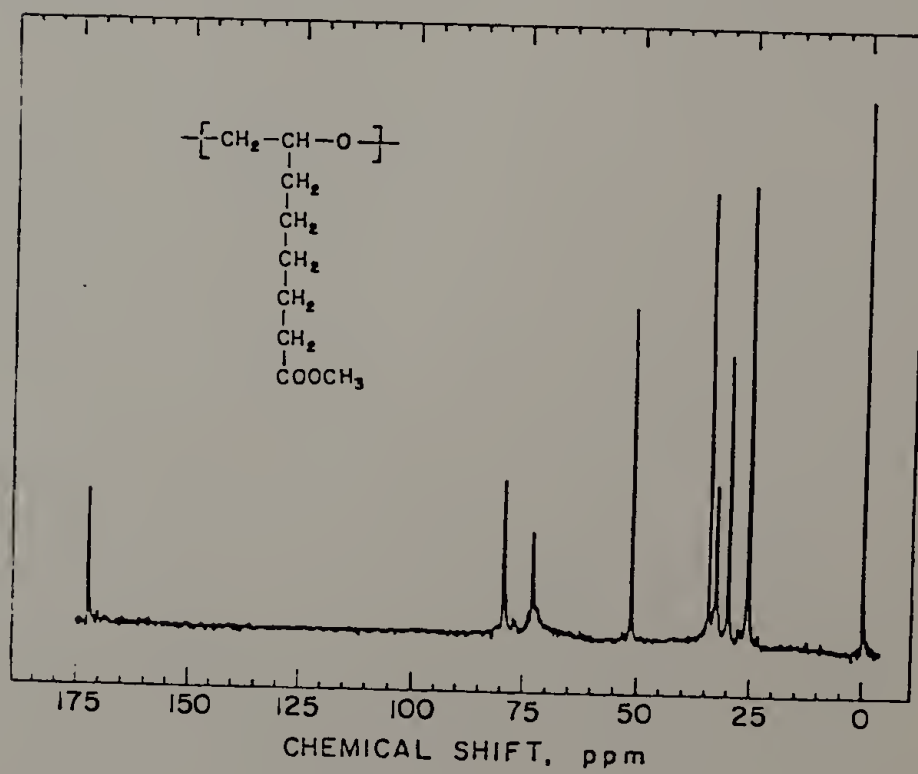
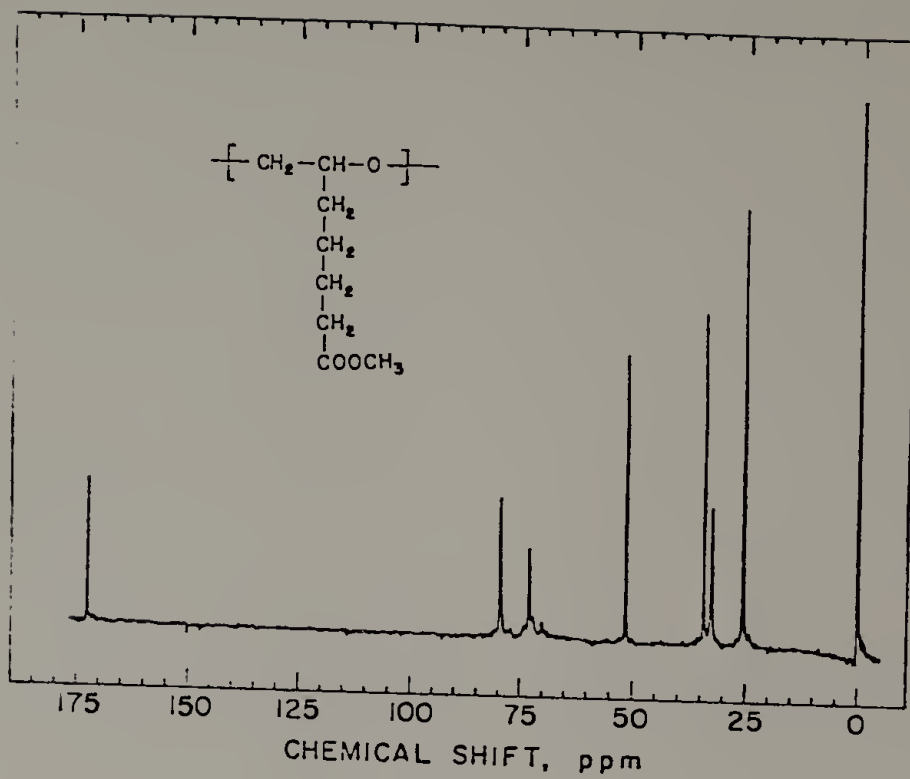


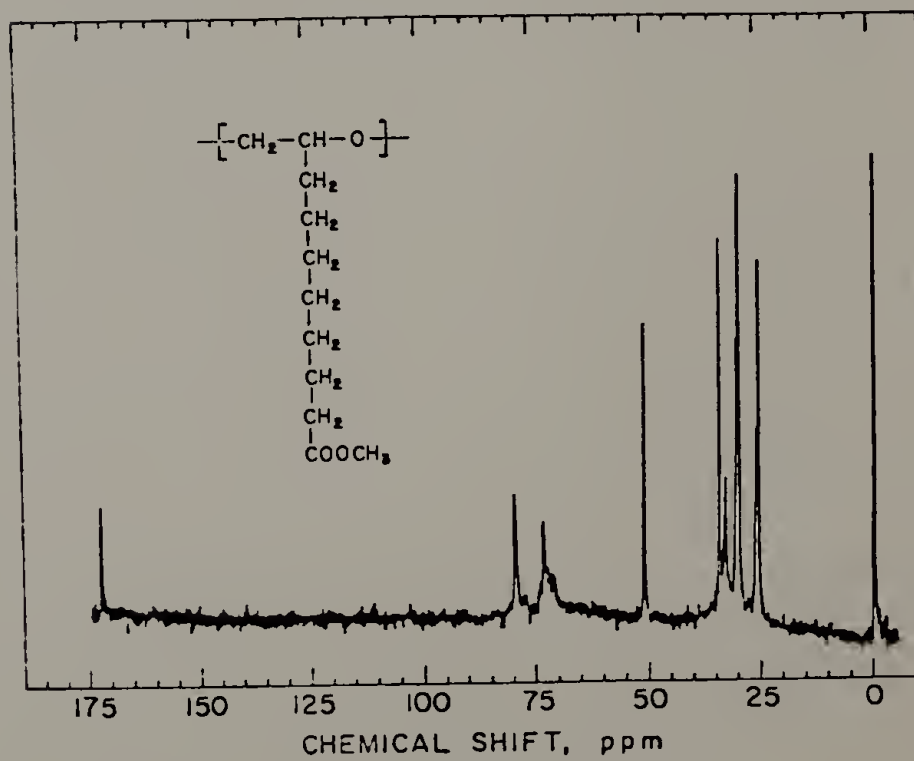
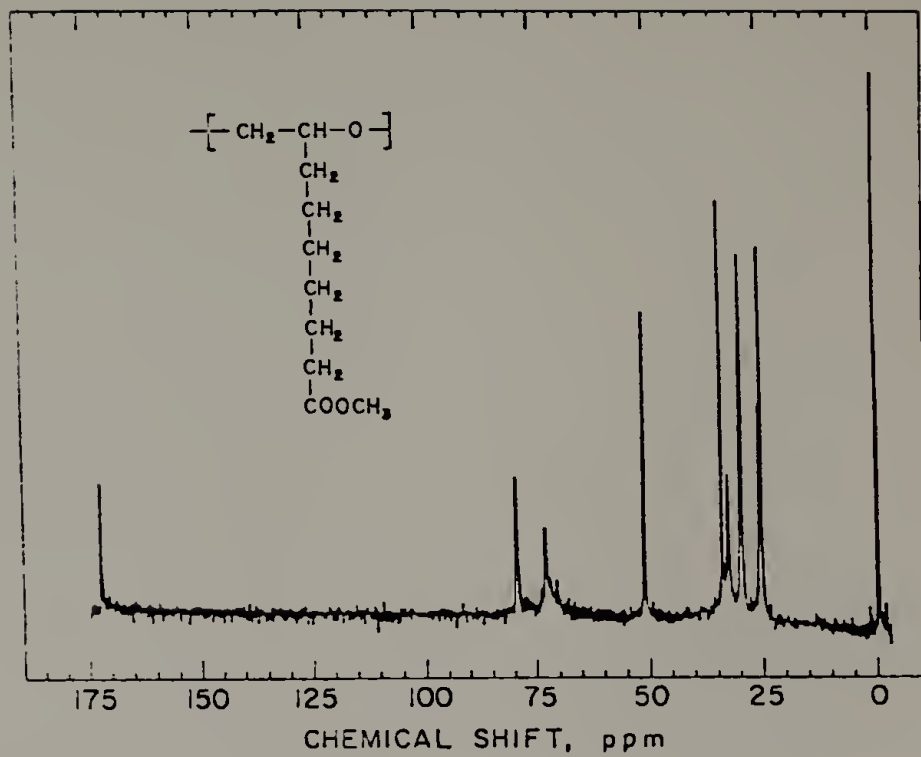


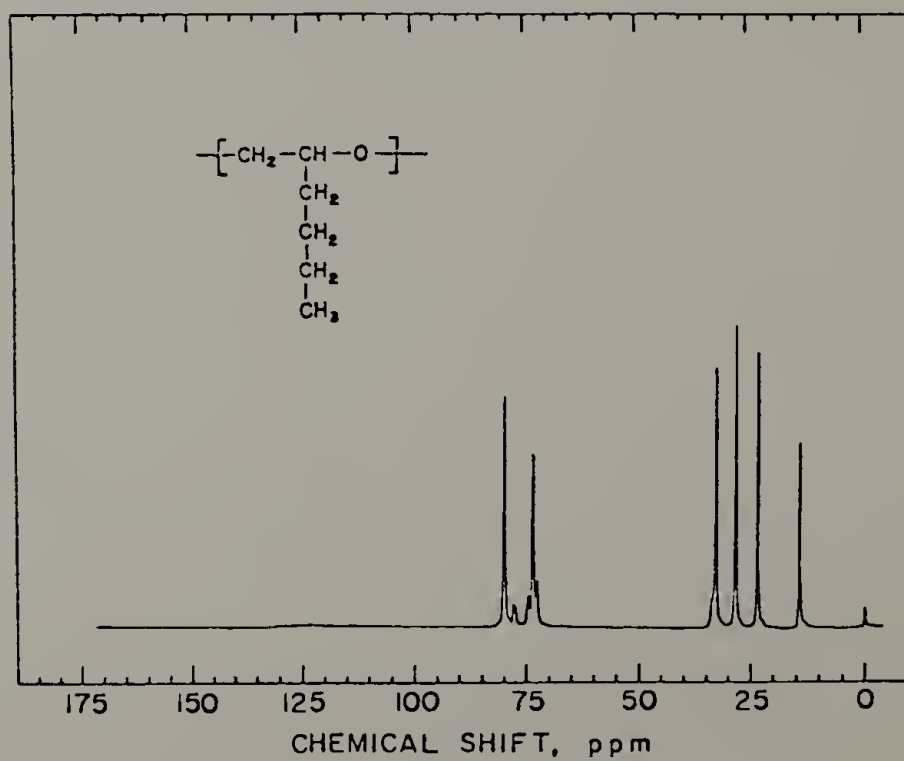
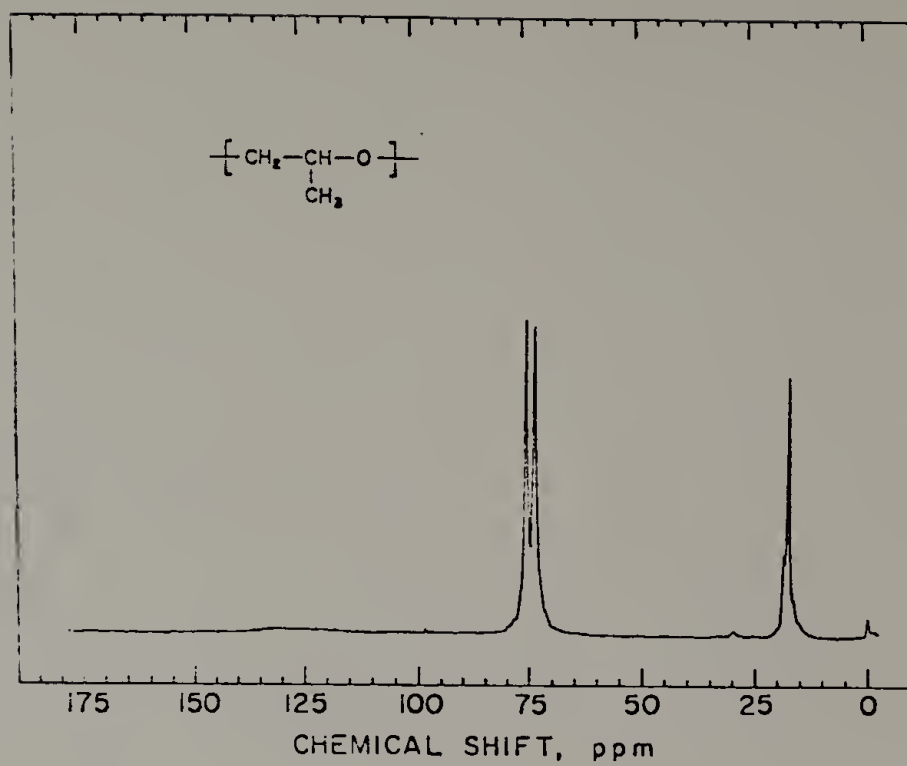


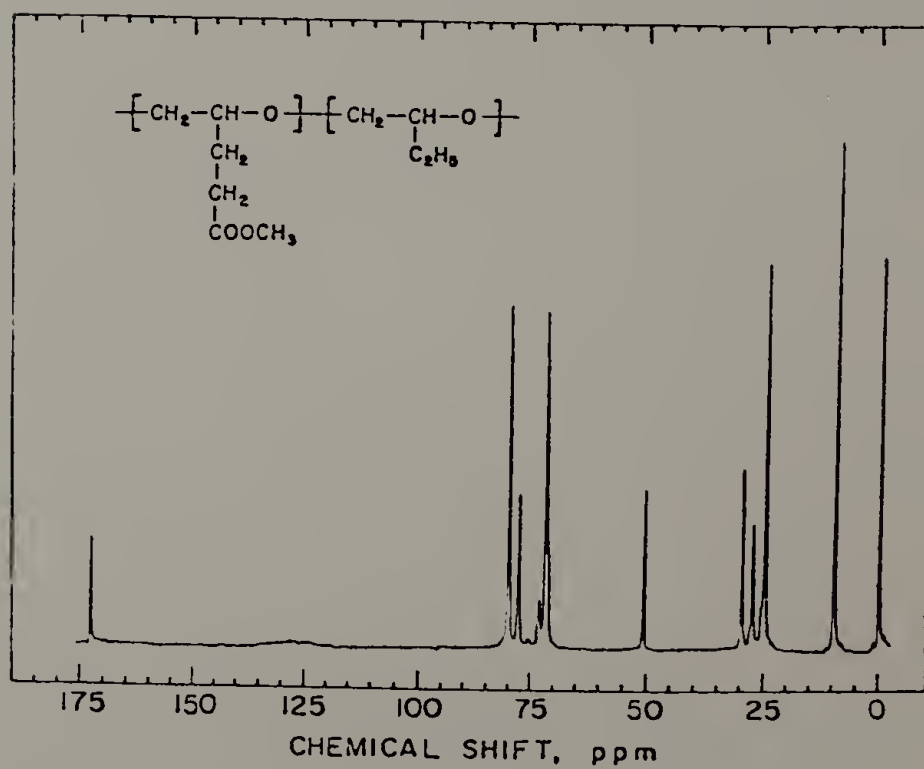
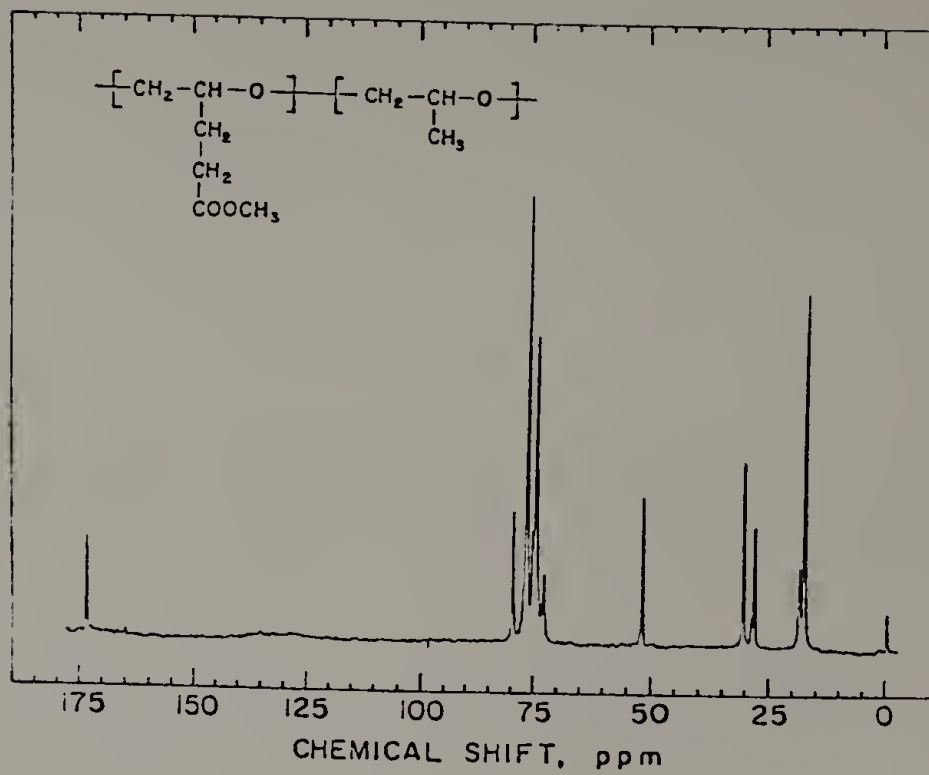


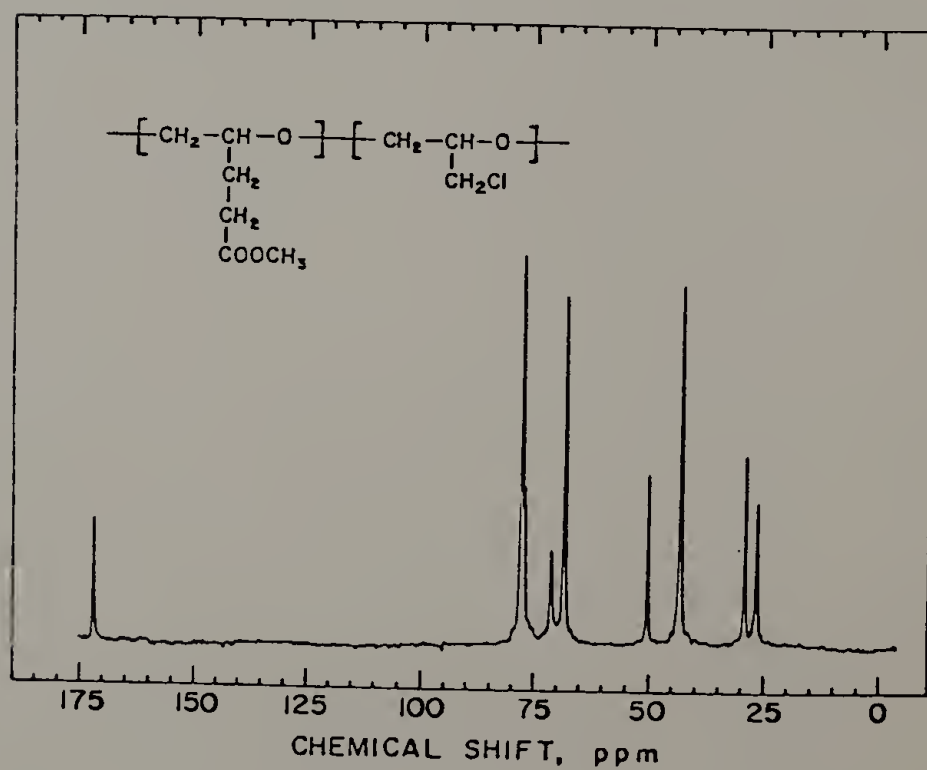
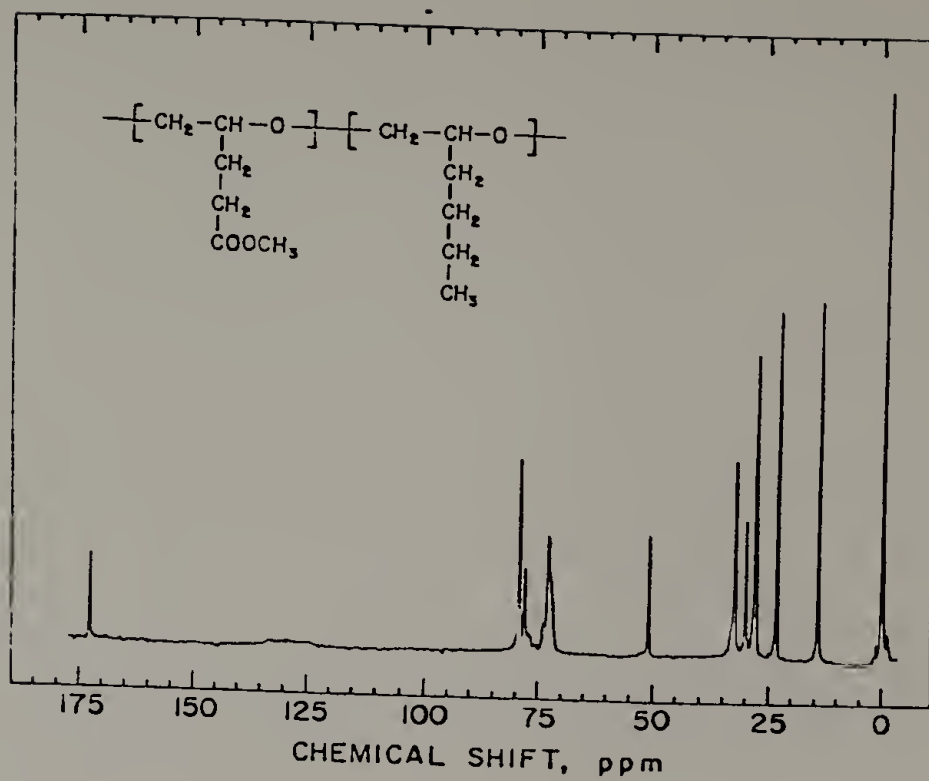


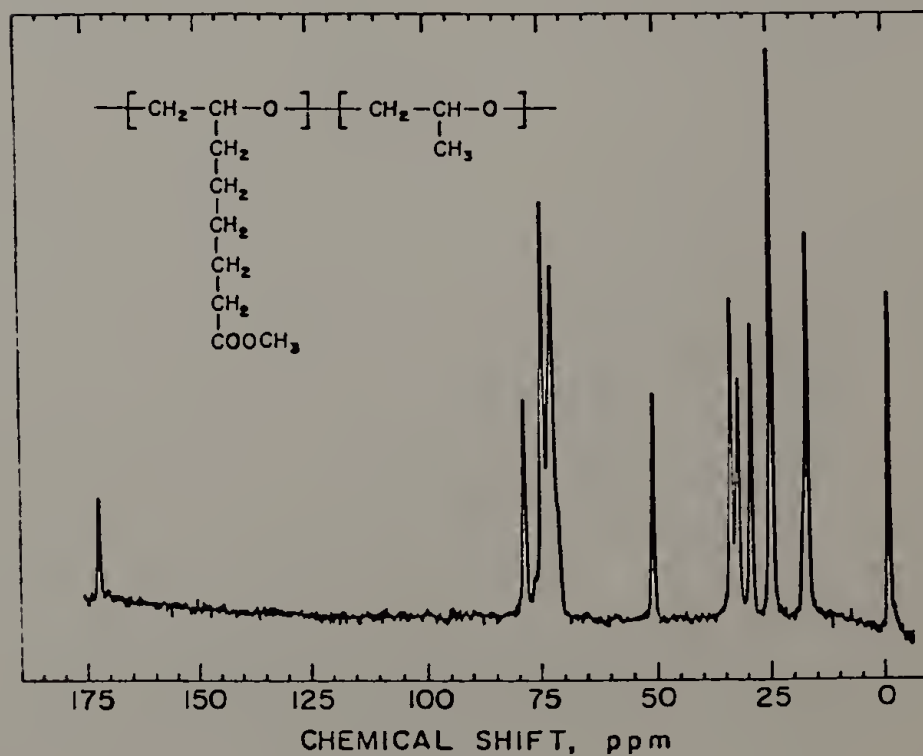
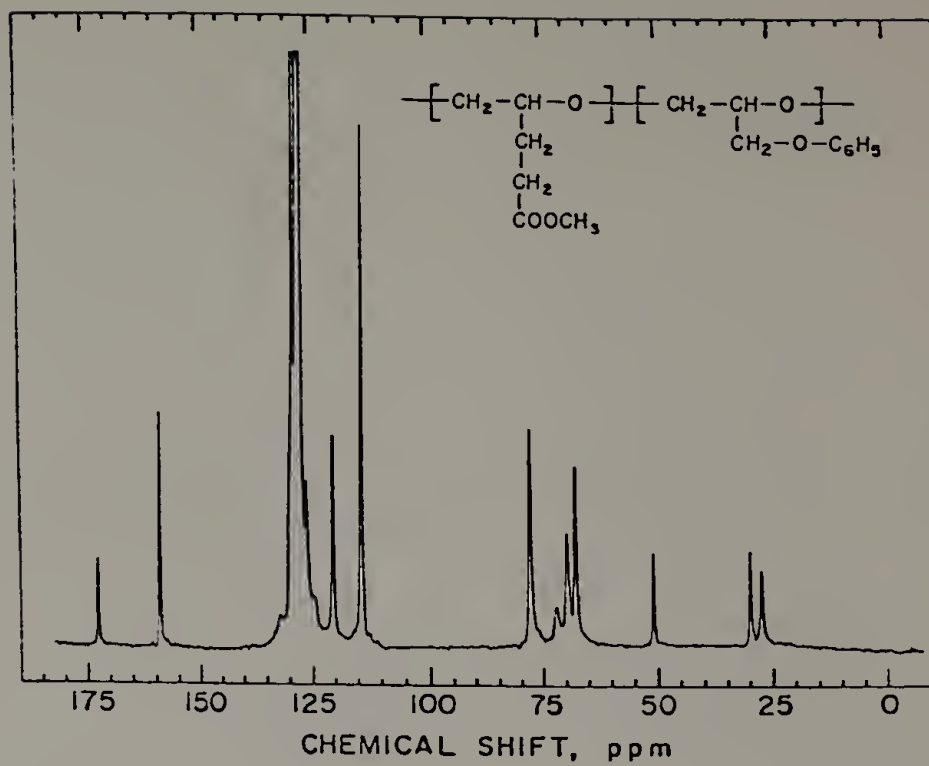


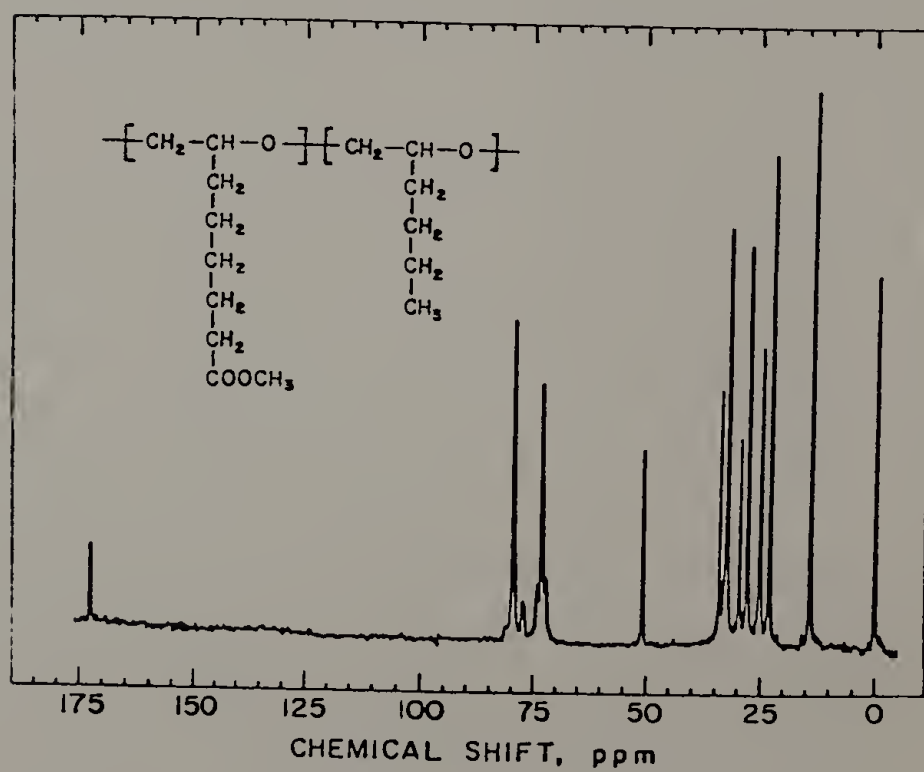
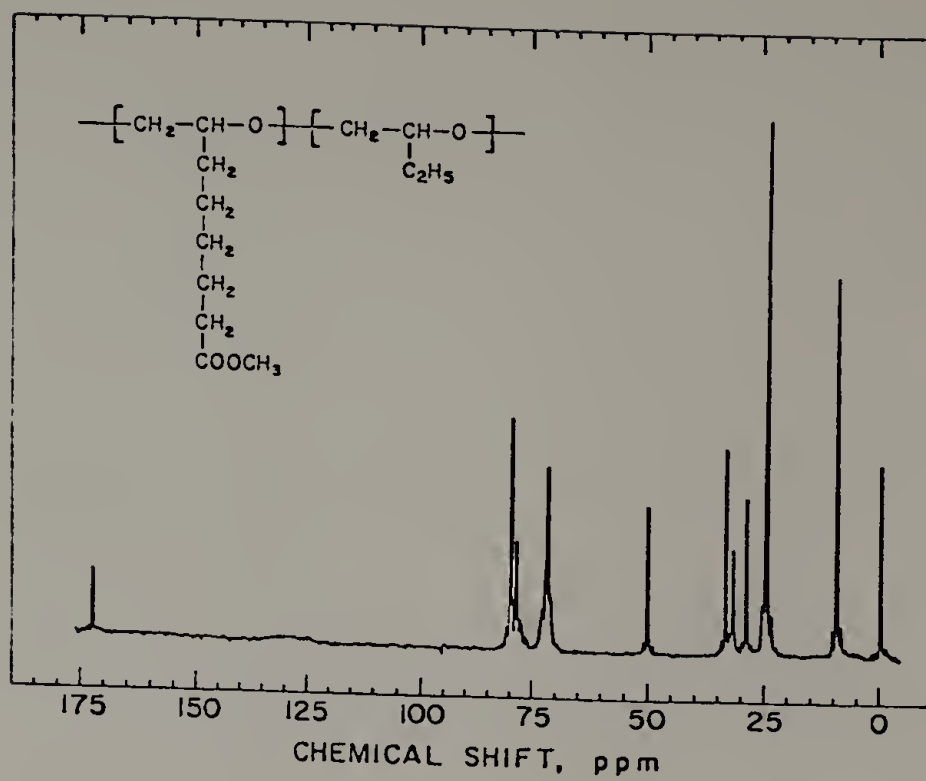


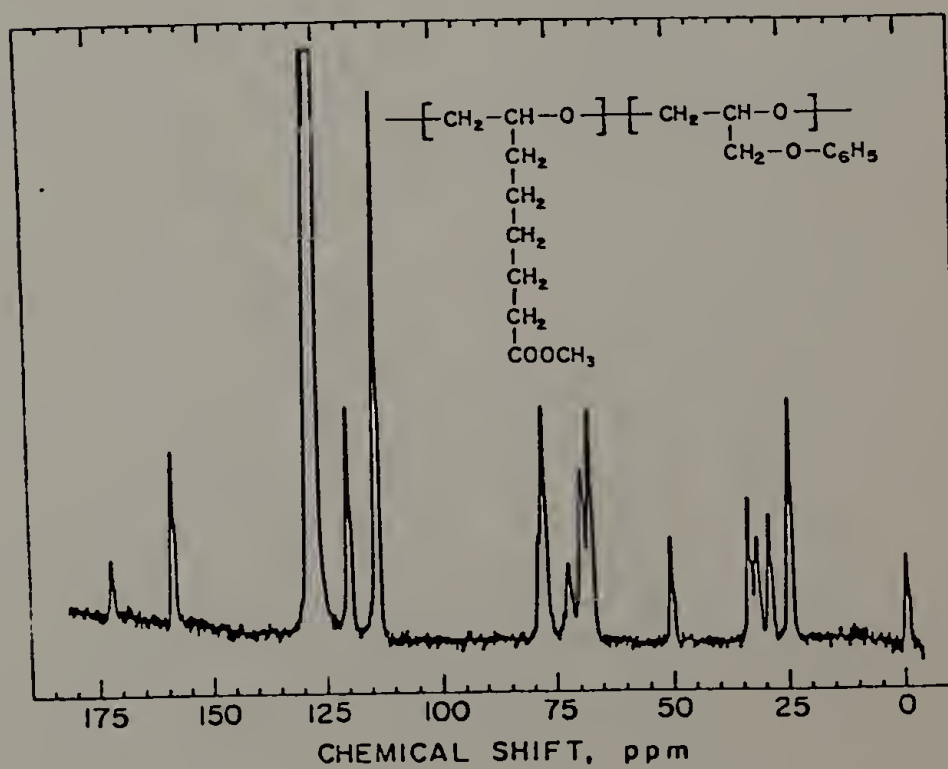
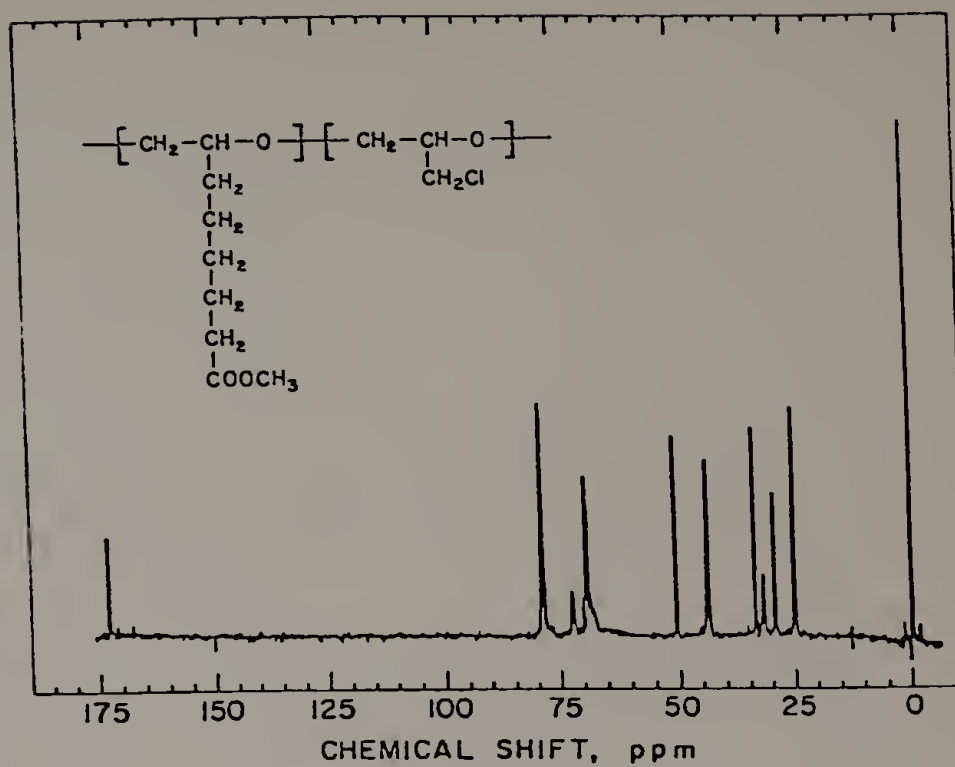


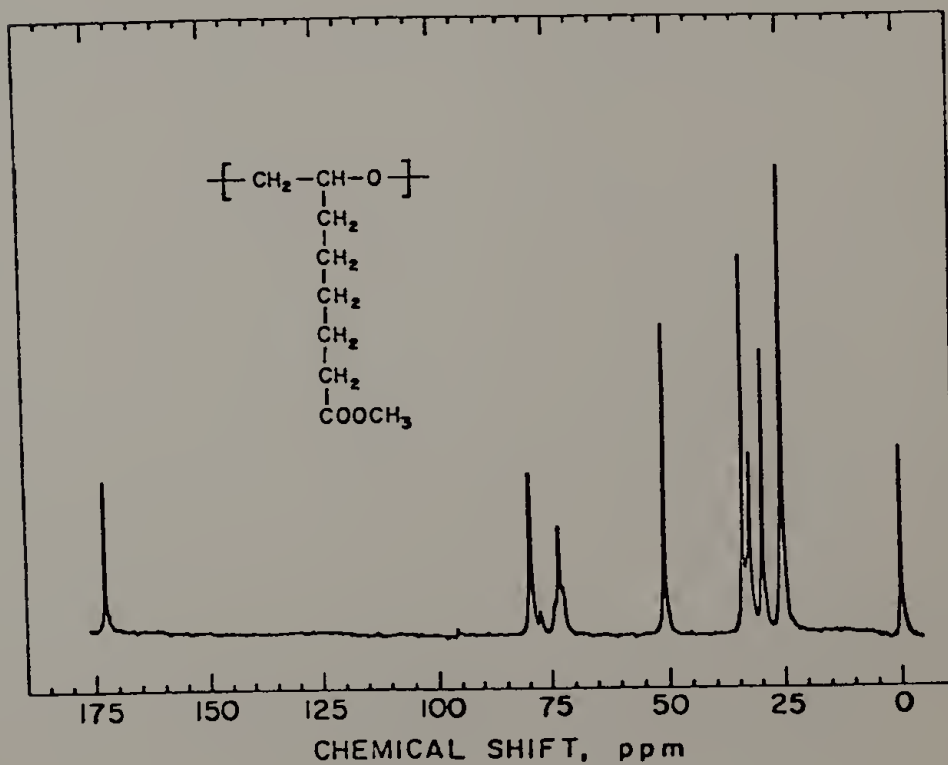
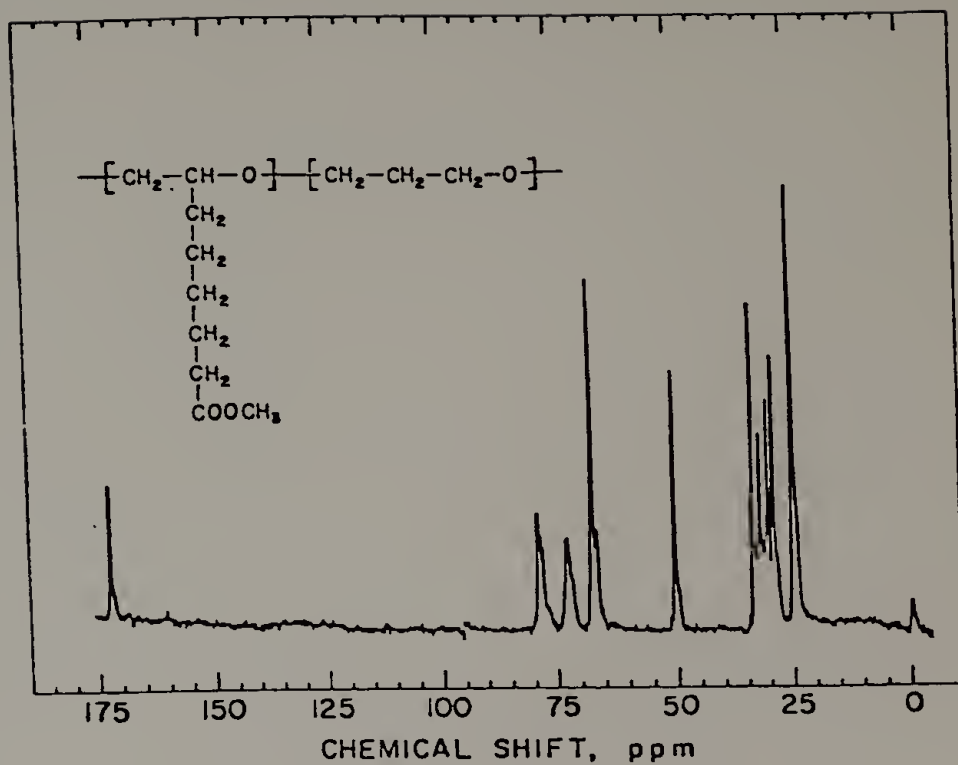


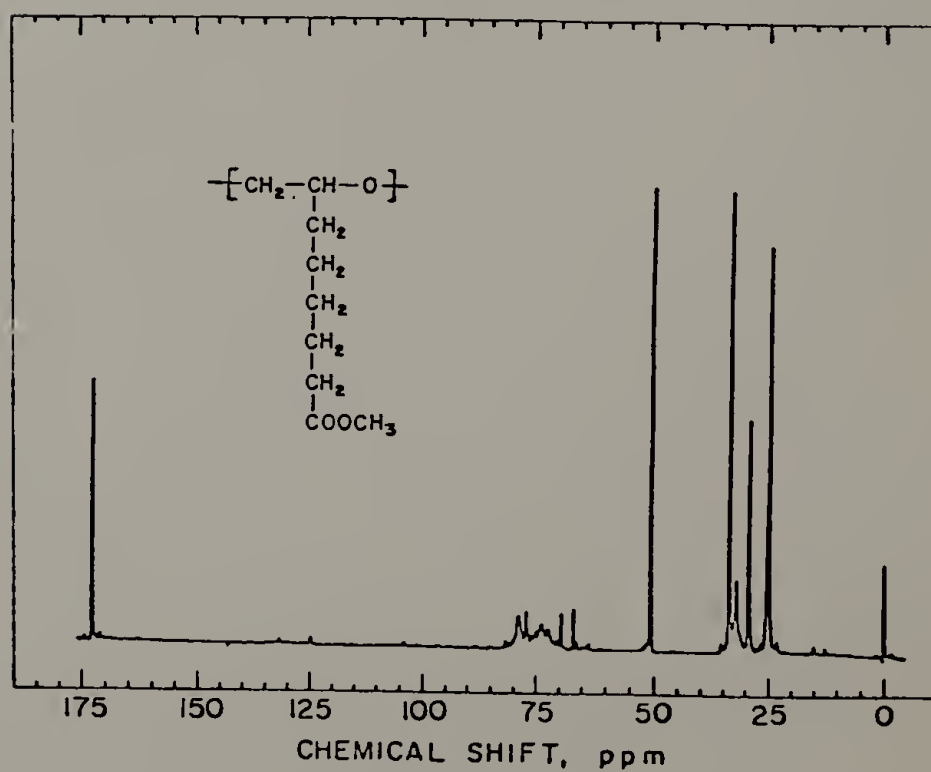
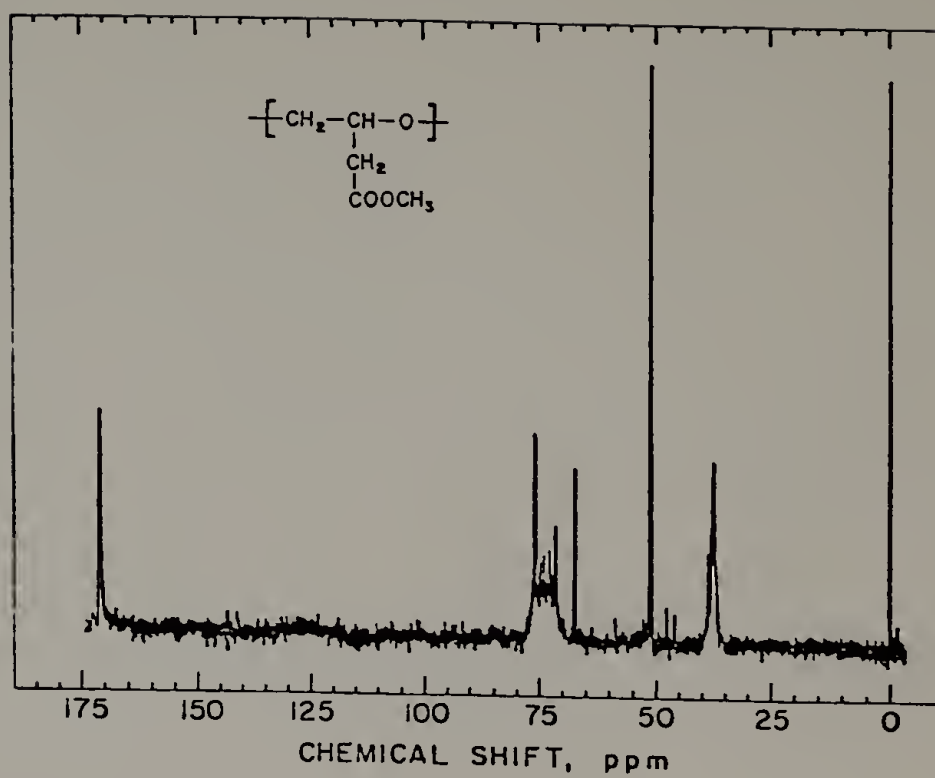


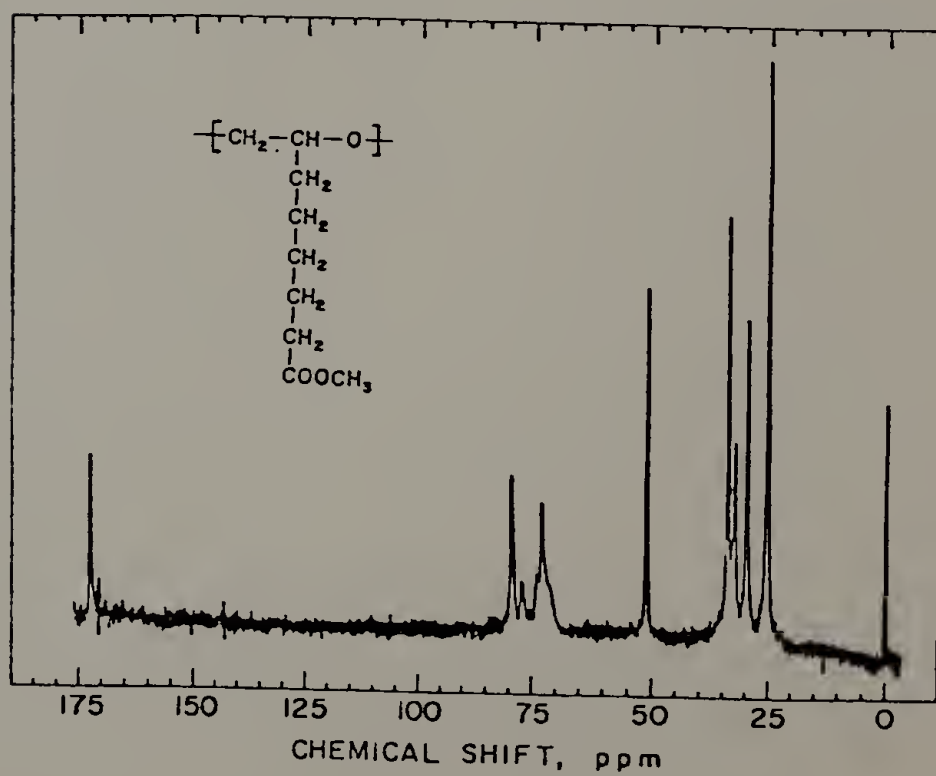
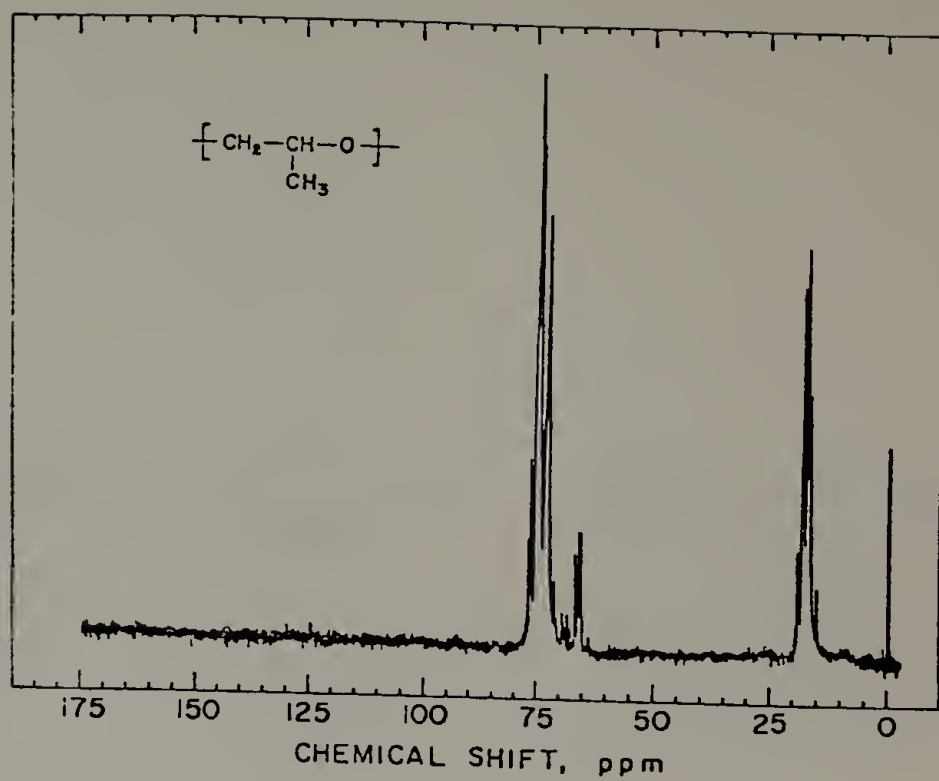


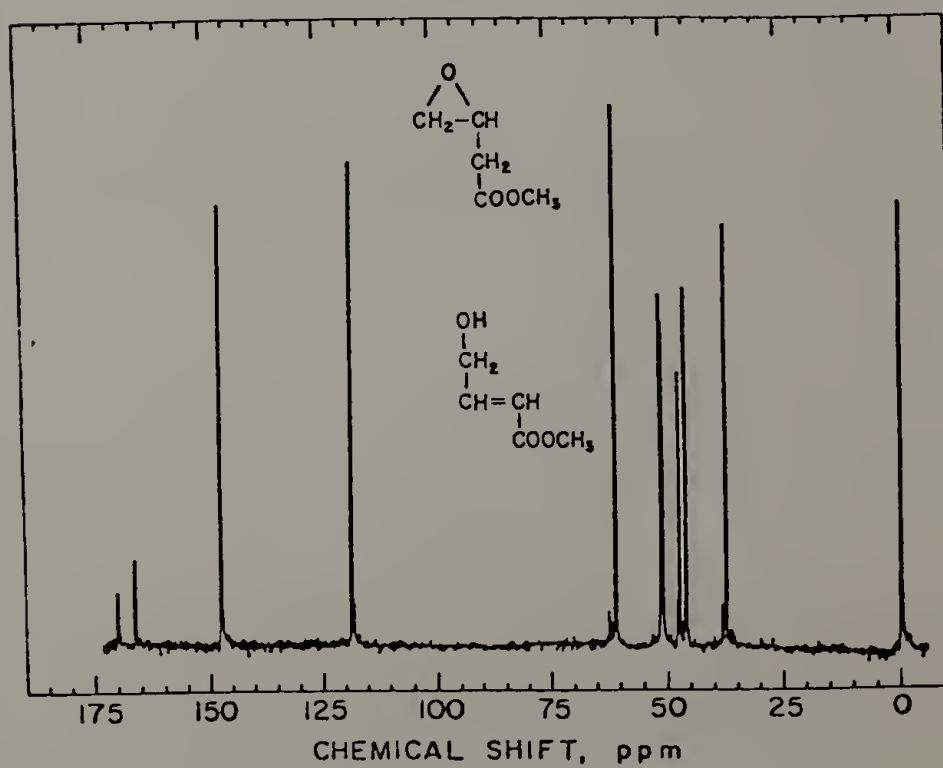
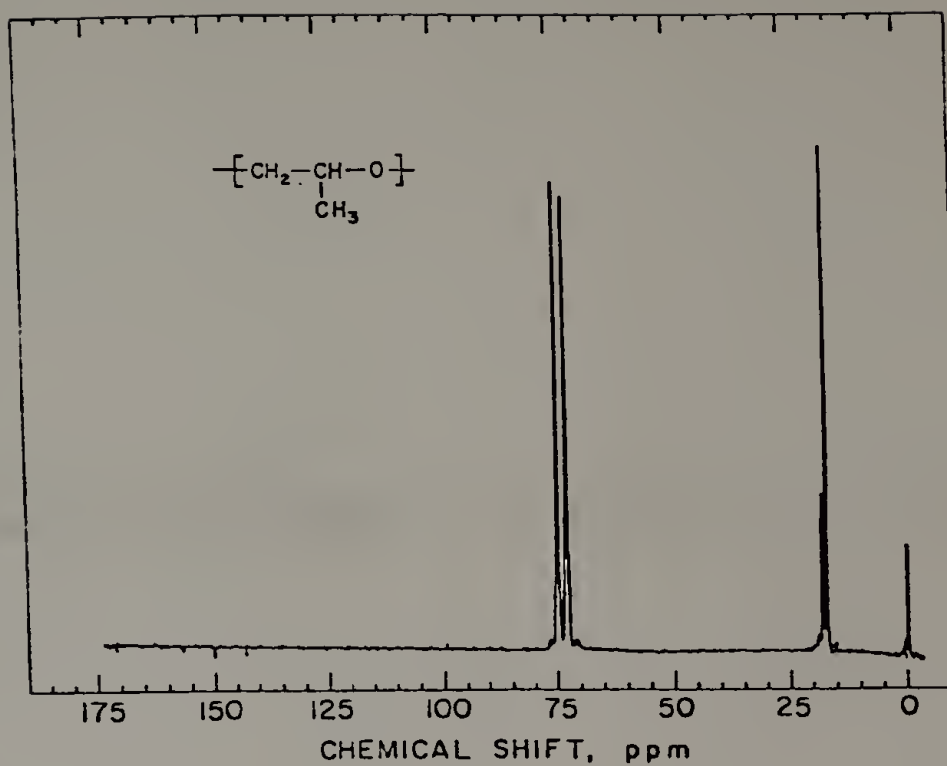


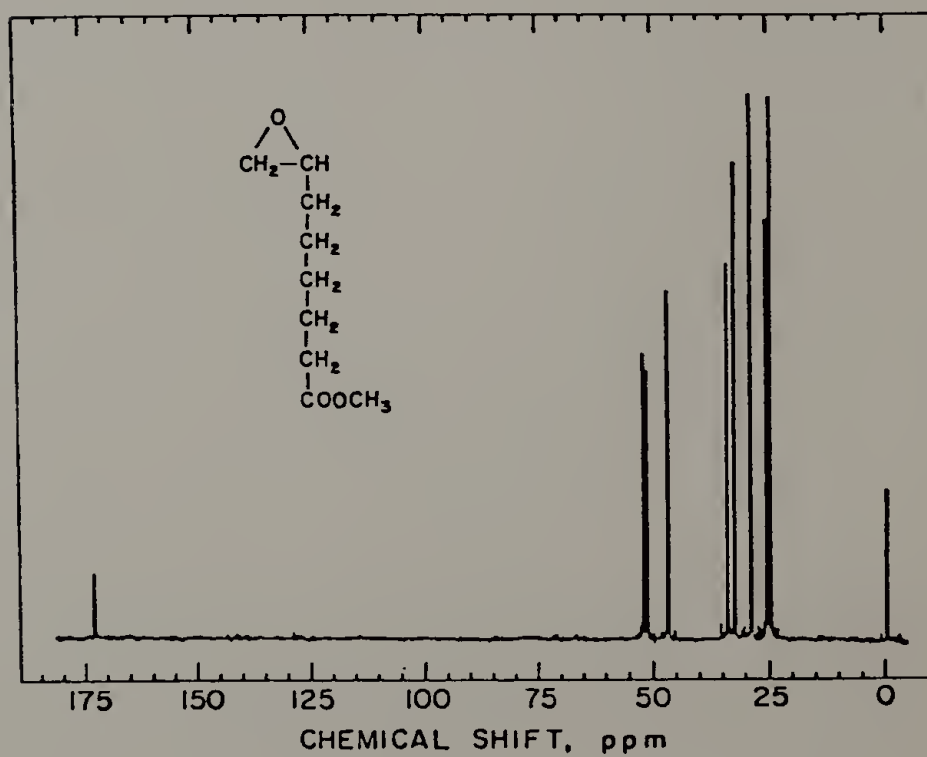
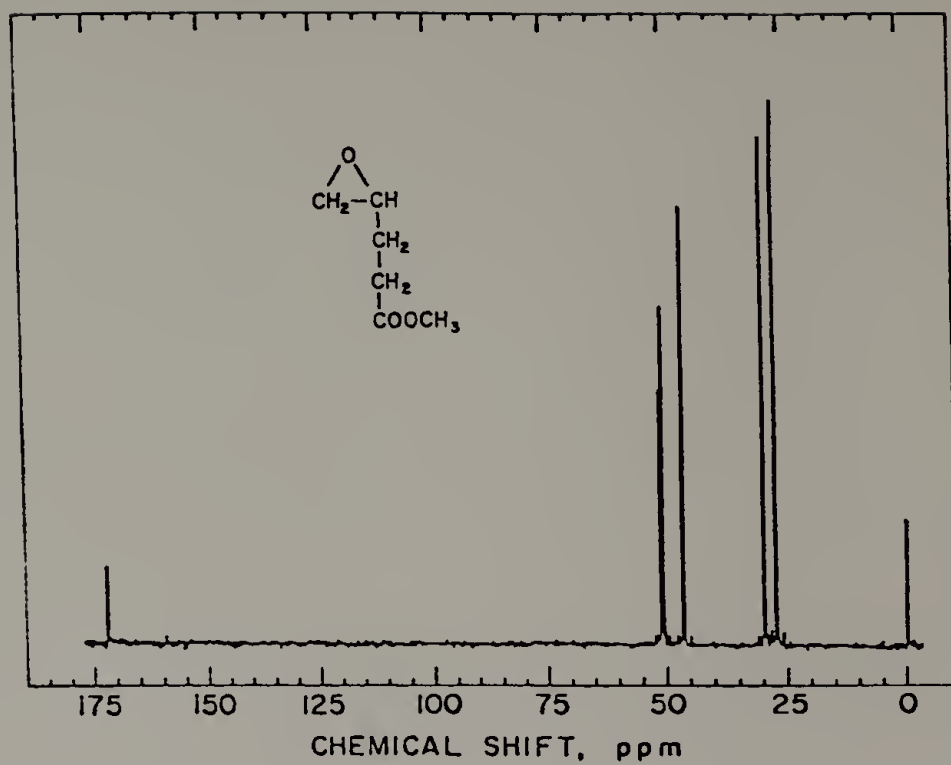


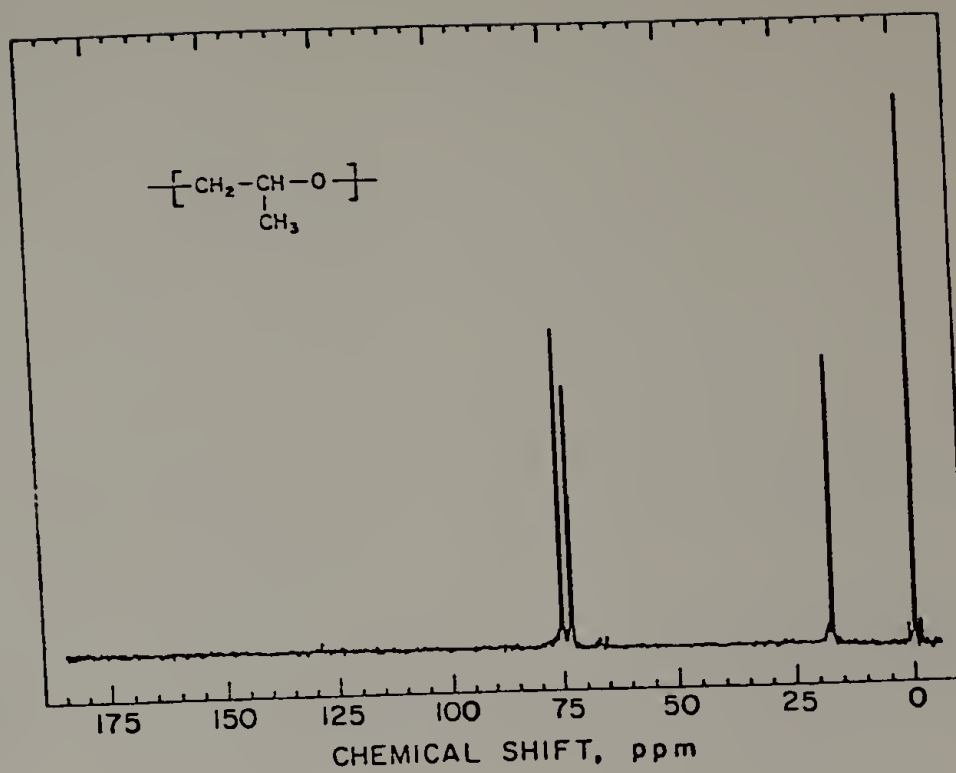












APPENDIX B  
INFRARED SPECTRA

