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# Synthesis and reactions of some new halogenated polyethers/

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# SYNTHESIS AND REACTIONS OF SOME NEW HALOGENATED POLYETHERS

A Dissertation Presented

by

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Polymer Science and Engineering

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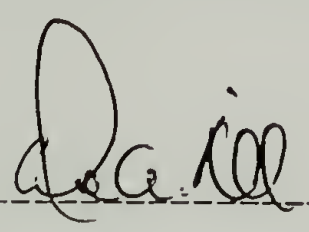

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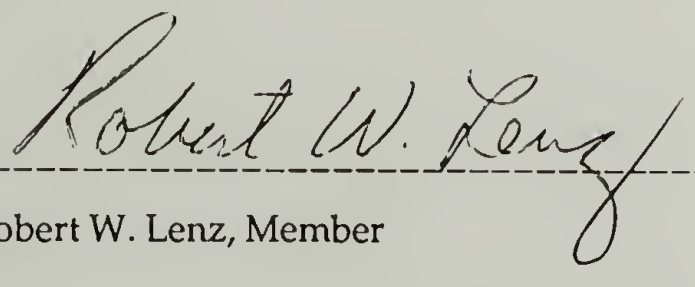

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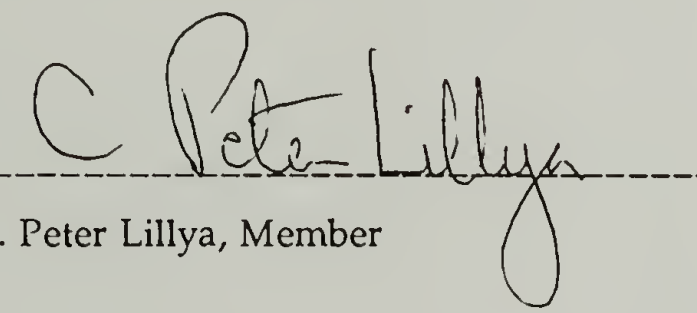

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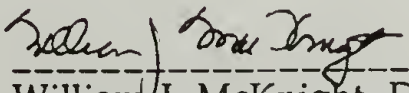

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ABSTRACT

SYNTHESIS AND REACTIONS OF SOME NEW HALOGENATED POLYETHERS

FEBRUARY 1989

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Halogenated polyoxiranes and polyoxetanes with systematic changes in structure were synthesized and used for studying effects of polymer structure on $S_N2$ reactivity.

The synthetic portion of this work has led to the preparation of three new heterocyclic monomers and four new halogenated polyethers. The ω-haloalkyloxirane monomers used were synthesized in greater than 50% yield by epoxidation of the corresponding haloalkenes. 3-Chlorooxetane was synthesized in 5 steps in 32% yield starting from epichlorohydrin. The 2- and 3-chloromethyloxetanes were prepared in 8 and 24% yields, respectively, from chloroalkenes. Polymerization of these monomers was then carried out using triethylaluminum /water/acetylacetone catalysts to yield high molecular weight elastomeric polymers.

The reactivities of these polymers in solution toward $S_N2$ substitution were evaluated using tetrabutylammonium benzoate (TBAB) as the nucleophile. $^1H$ NMR studies of the reaction of TBAB with the poly[(ω-bromoalkyl)oxirane]s in $CDCl_3$ at 45° C indicated an order of reactivity of butyl ≈ propyl ≈ ethyl >> methyl. All of these polymer reactions showed distinct negative deviations from 2nd order kinetics after conversion progressed beyond 50%.

$^{13}C$ NMR was used in a more extensive study of the reaction of TBAB with all of the chlorinated polyethers in DMAc. For the poly[(ω-chloroalkyl)oxirane]s the order of reactivity was butyl ≈ propyl > ethyl >> methyl. Poly[3-(chloromethyl)oxetane] reacted at a rate approximately twice that of poly(epichlorohydrin). Poly[2-(chloromethyl)oxetane] was found to have equal reactivity.

Reaction conversions were analyzed in terms of three rate constant systems determined by the (unreacted/reacted) state of the nearest neighbors of a reactive group. These analyses indicate that the pendant reactive groups experience a large decrease in reactivity when both neighbors have reacted but that there is only a slight change in reactivity when only one neighbor has reacted. These analyses also indicate that increases in the length of the pendant chain decrease the effects of neighboring reacted.

TABLE OF CONTENTS

LIST OF TABLES

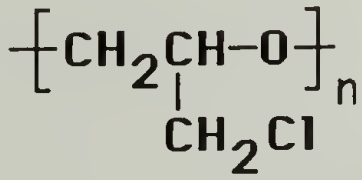
LIST OF FIGURES

LIST OF SCHEMES

# CHAPTER I

# INTRODUCTION

The desired applications for polymers often require that an available polymer be modified through the reaction of attached functional groups in order to adjust its physical and chemical properties . Some examples of common procedures include crosslinking, synthesis of polymers that are not directly accessible (e.g. polyvinyl alcohol), covalent attachment of groups to enhance polymer properties and synthesis of polymeric reagents. In all cases a basic knowledge of the reactivities of attached functional groups is important; one would like to control the rate and extent of reaction so that the system can be adjusted to give the desired properties in a minimum amount of time, with no deleterious side reactions. There are many references in the literature dealing with the optimization of reaction conditions for given systems or the effects of changes in the nonpolymeric reagents.[1,2,3] Currently, however, there is not a comprehensive body of literature to correlate variations in reactivity of an attached functional group with systematic changes in the chemical and structural composition of a polymer. With relation to the project covered by this dissertation, we would like to be able to predict what chemical and structural changes can be made to poly(epichlorohydrin) to get a higher pendant group reactivity without sacrificing the physical properties required for its applications. When we look at the structure of poly(epichlorohydrin) (1) it is apparent that it is hardly optimal from the point of view of its reactivity as a substrate for nucleophilic substitution: chloride is modest in its leaving group ability, and the β-branch point (on the polymer backbone) and the close proximity of the backbone ether linkage would be expected to significantly depress reaction rates.



(1)

The work presented here is part of what I believe to be the first attempt to provide a general set of structure-reactivity relationships for nucleophilic substitutions on halogenated

polymers. Additionally, to accomplish this work the synthesis of several new heterocyclic monomers and halogenated polyethers was required and these will be discussed as well.

In the introductory sections that follow, I will give a background survey of relevant work on polyether synthesis and on reaction kinetics of small molecules and macromolecules.

## A. Polyethers Derived from the Polymerization of Oxiranes and Oxetanes.

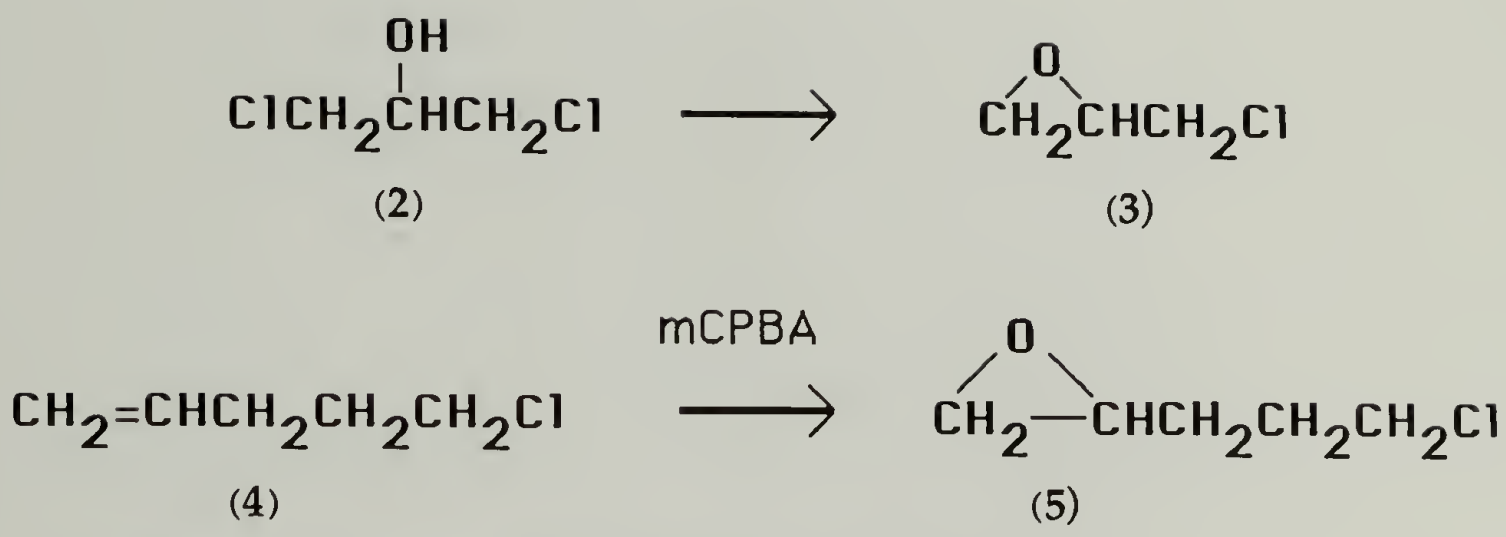
With the exception of poly(epichlorohydrin) all of the polymers used in this project are not commercially available; in fact the first synthesis of most of them took place in this laboratory. The monomers from which the polymers are derived, except the epihalohydrins, had to be synthesized as well. Some of these monomers are new compounds and were synthesized for the first time.

### 1. Preparation of Monomers.

Cyclic ethers can be made by any of a multitude of methods but only a few are relevant to the project. These are described below.

#### a. Functionalized oxiranes.

The most important functionalized oxirane, epichlorohydrin (3), is synthesized by base mediated intramolecular condensation between the hydroxyl group and one of the chlorides in 1,3-dichloro-2-propanol (2) (Scheme I.1). This method has been applied to the synthesis of a large number of oxiranes and is useful provided there are no base sensitive moieties in the starting material. A more convenient method, which allows oxirane formation in the presence of base sensitive moieties is the reaction of peracids with olefins.[4] This method, with m-chloroperoxybenzoic acid as the peracid, was used by J. S. Shih of our group to synthesize a large number of monomers that contained halides and esters[5], such as (3-chloropropyl)oxirane (5) which was made from 5-chloro-1-pentene (4) as shown in Scheme I.1. Groups such as these would have reacted in a deleterious fashion if base mediated cyclization had been attempted.




Scheme I.1. Examples of the Preparation of Oxiranes

**b. Oxetane monomers.**

(1) Williamson ether synthesis

The majority of reported methods used to prepare oxetane monomers are variations of the Williamson ether synthesis involving the intramolecular displacement of a good leaving group by a γ-alkoxide to form the oxetane ring. The most important commercial syntheses involve the reaction of 1,3-halohydrins or their derivatives with base as shown in Scheme I.2 for the ring closure of pentaerythritol trichloride (**6**) to form 3,3-bis(chloromethyl)oxetane (**7**). A list of oxetanes synthesized by this method can be found in a review article by Okamura.[6] Yields reported there vary from very poor to almost quantitative and there appears to be no correlation between yield and final product. It was found that the structure of the starting material has a large effect on the yield. The use of the halohydrin acetate increased yields significantly in all cases and the reaction of secondary halides led mainly to elimination products. Variation of the leaving group is also possible; oxetanes have been successfully produced from substrates in which sulfonate, hydrogen sulfate and phosphate esters were substituted for the halide.[7,8,9]

(2) Pyrolysis of carbonate esters

Oxetanes can also be formed by the pyrolysis of cyclic carbonate esters derived from 1,3-diols. The typical reaction sequence consists of the reaction of a 1,3-diol with a dialkyl carbonate to form the intermediate cyclic carbonate which is then heated to approx 200° C in the presence of base catalyst to give the oxetane in high yield.[10] The best results are obtain in the synthesis of 3,3-disubstituted oxetanes, the yields of these compounds typically exceed 80% whereas the yields of oxetanes with one substituent or no substituents in the 3-position rarely exceed 40%.[6] This reaction has been successfully used to form oxetanes from triols such as trimethylolethane (**8**) to form 3-(hydroxymethyl)-3-methyloxetane (**9**) (see Scheme I.2).[11] The synthetic utility of this reaction is limited to compounds that do not contain base sensitive moieties and do not have hydroxyl functionality in a position that allows the formation of ring sizes other than 4 (e.g. a 1,3,4 -triol will form furan rings exclusively).

(3) Photochemical reaction of olefins with carbonyls

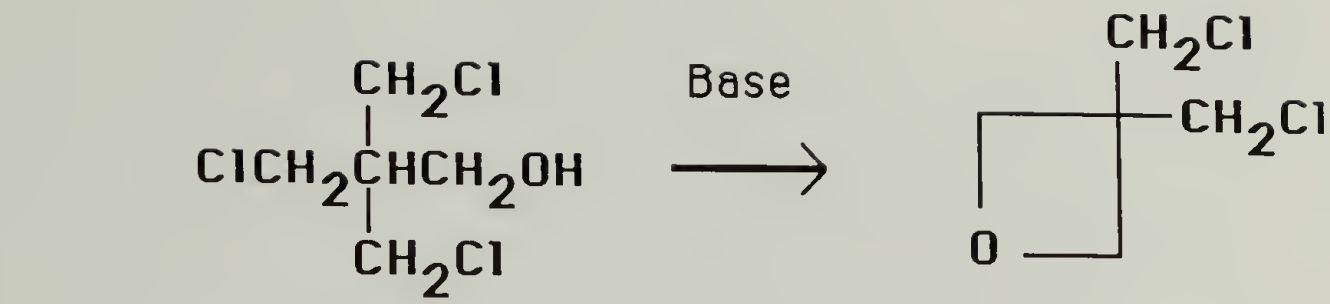
Under uv light aldehydes and ketones can react with olefins to give oxetanes. The reaction, called the Paterno-Buchi reaction, has been used to obtain a large number of highly substituted oxetanes in high yield. An example is shown in Scheme I.2 for the synthesis of 2,2-dimethyl-3,4-dicyanooxetane (**10**) from acetone (**11**) and fumaronitrile (**12**).[12] Unfortunately the reaction does not produce oxetanes from systems that contain formaldehyde, ethylene or monosubstituted olefin as one of the reaction components,[13] and this limits the synthetic utility of the reaction to the production of polysubstituted oxetanes.

**2. Preparation of Polyethers.**

**a. Polyoxiranes.**

Oxiranes are highly reactive compounds. They react rapidly both with nucleophiles and electrophiles to yield products that result from ring opening. Polymerizations of oxiranes have been carried out with a large number of initiating systems ranging from potassium hydroxide to Lewis acids to organoaluminum coordination catalysts.[14] Anionic catalysts, such as potassium hydroxide, are primarily used for the polymerization of nonfunctionalized alkyl oxiranes such as propylene oxide.[15] The resulting polymers are usually of low molecular weight and atactic.

For the polymerization of oxiranes containing base sensitive moieties, such as the halides as used in the present work, cationic or coordination initiators must be used. Cationic polymerization of oxiranes can be accomplished with a large variety of initiators, the most common being Lewis acid-water systems[16] and sulfonic acids or esters.[17] High molecular weight polymers are obtained but there is a lack of control over tacticity and head-to-head addition of monomer.[18]

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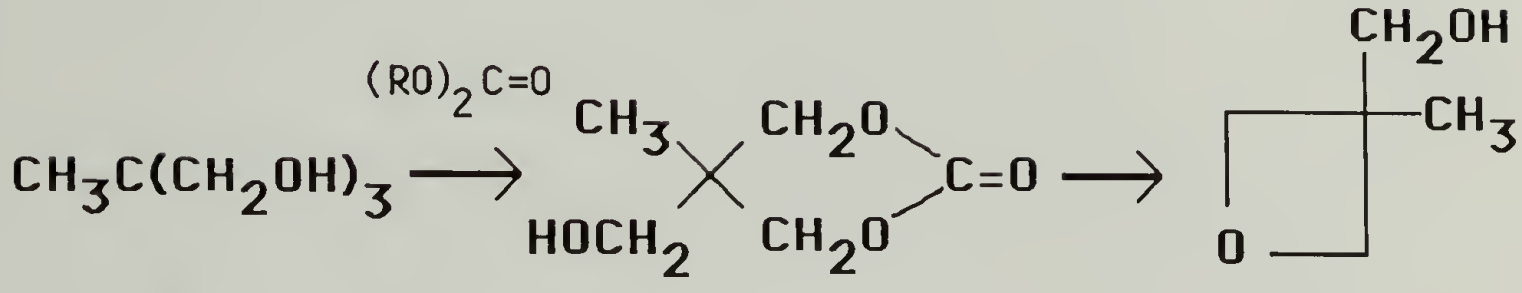


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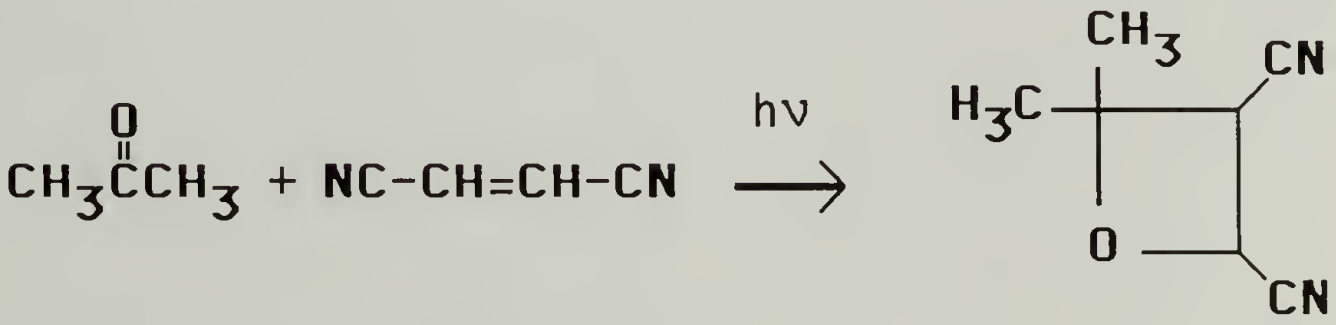


(10) (11) (12)

Scheme I.2. Examples of the Preparation of Oxetanes

Recently there has been active research on the utility of coordination type initiators for oxirane polymerization. Catalysts based on aluminum alkyls[19,20], zinc alkyls[21] and ferric chloride[22] have been found to polymerize oxiranes to very high molecular weight. The most versatile of the catalysts are the chelated aluminum alkyl/water systems developed by Vandenberg.[19,20] For these initiators, the polymerization site is believed to be bidentate in nature with two aluminums linked together by an oxygen derived from water.[23] When acetylacetone is added it chelates the acidic aluminum sites resulting in formation of polymers with very few defects that would result from head-to-head addition of monomer or from reaction of attached functional groups.[19,24] Vandenberg [25,26,27] used such an initiator with 1 equivalent of acetylacetone per aluminum center, to polymerize oxiranes with halomethyl, olefin, trimethylsilyl ether, acetoxy and methacrylate functional groups. In all cases the polymerization resulted in polymers with high molecular weight and no apparent reaction of the pendant functionality.

**b. Polyoxetanes.**

The first studies of the polymerization of oxetanes were reported in the 1950's,[28,29] and dealt with the polymerization of 3,3-bis(chloromethyl)oxetane with $BF_3OEt_2$. Poly[3,3-bis(chloromethyl)oxetane] is the only oxetane homopolymer to be commercialized and the majority of reports of oxetane polymerization are based on this particular homopolymer. 3,3-Bis(chloromethyl)oxetane can be polymerized with any of the cationic initiators that are used for oxirane and tetrahydrofuran polymerizations,[14] and it can also be polymerized effectively using the chelated aluminum catalysts.[30]

There are very few reports of the polymerization of monosubstituted oxetanes, and the majority of these deal only with unfunctionalized alkyl substituents. The polymerization of 2-methyl[31,32] and 3-methyl oxetanes[33,34] has been accomplished using chelated aluminum catalysts and $BF_3OEt_2$ to give high molecular weight, apparently atactic polymers. For 2-methyloxetane Kops and Spanggard[35] noted a change in tacticity with the different initiators. The chelated aluminum catalysts gave polymers of higher molecular weight, and had higher syndiotactic fractions than those obtained using unchelated aluminum catalysts.

Prior to my work there had been only one report of the polymerization of a monofunctional oxetane [poly(3-azidooxetane)].[36] In this case the monomer was polymerized with $BF_3OEt_2$ to give a polymer of low molecular weight ($M_n$=2200). Aside from shock sensitivity tests on this explosive polymer, there was no mention of any attempt to study the reactivity of the attached functionality.

## B. Reactions of Small Molecules

Organic chemists have for a long time studied the effects of structural and chemical composition on functional group reactivity in small molecules. It has been determined that there are 3 major types of structurally related effects that influence reactivity: inductive, steric and resonance effects.[37] The work described in this dissertation deals with reactions on alkyl systems and only the first 2 apply. Inductive effects change reactivity of a functional group through polarization of bonds resulting in a change of electron density at the reaction site. As an example, an inductive group such as an ether can cause a change in the electron density about a nearby reaction site. This could result in a lowering of the electrophilic character of the site, thus making it a less desirable target for a nucleophile. Steric effects restrict reagent access to the reaction site. In $S_N2$ reactions the nucleophile approaches the reaction site from the side opposite the leaving group, and the presence of bulky groups can increase the difficulty of access and depress reaction rate.

### 1. Effects of Structure on $S_N2$ Reactions.

In Table I.1 are shown the effects of increasing substitution at carbons α and β to the reaction site on $S_N2$ halide exchange reaction.[38] Both the displacement of iodide by chloride ion and the bromine exchange reaction show marked decreases in relative rates with increasing substitution at the α position. This decrease is a result of increased steric crowding about the reaction site and of the weak inductive nature of the methyl substituents.[39] Changes in the degree of β-substitution, as shown by comparing ethyl, n-propyl, i-butyl and neo-pentyl entries, do not have as great an effect on relative rate as α-substitution. Addition of each of the first two β-methyl groups (to give n-propyl and i-butyl) results in an order-of-magnitude drop in

relative rate. These drops in rate in addition to the more drastic drop shown for neo-pentyl arise primarily from steric crowding with very little contribution from the inductive effects of the methyl group.[40]

The five entries in Table I.2 show the effects of adding an oxygen to the substrate.[40] It can be seen that by varying the location of the oxygen a substantial decrease in the $S_N2$ reaction rate can be obtained. With the oxygen in the β position one sees an 80% reduction in the rate of reaction when compared to that of the structurally analogous 3-phenyl-1-chloropropane. Moving the oxygen further away from the reaction site, where it has less of an inductive influence, results in a smaller depression of rate.

**2. Effects of Structure on $S_N1$ Reactions.**

In most cases structure plays opposite roles in $S_N1$ rand $S_N2$ reactions. Large steric strains about a reaction site can lead to an increase in reaction rate because these strains can be relieved by the formation of trivalent carbon species as the reaction proceeds through the rate limiting ionization step.[41] Attachment of large alkyl groups which, through induction, place more electron density on the reaction site also increase reactivity by facilitating the ionization to a cationic intermediate.

For $S_N1$ reactions the inclusion and placement of heteroatoms has been shown to cause very dramatic effects on the rates of displacement. If properly placed the heteroatoms can interact through-space with the reaction site to cause an increase in reactivity by anchimeric assistance. Table I.3 shows these effects on the rate of alkyl chloride solvolysis. Inclusion of a β sulfide results in the reaction rate being increased more than 3 orders of magnitude.[42] Moving the sulfide to the δ position precludes the 3-membered sulfonium ring formation necessary for anchimeric assistance to be observed, and there is no enhancement of rate. Inclusion of oxygen atoms at the β or δ positions leads to a decrease in rate due to inductive effects. Table I.4 presents further information concerning the effect of oxygen placement on solvolysis reactions.[43] Once again placement of the ether in the β and δ positions leads to rate inhibition. However, placing the oxygen at the ε position leads to significant rate enhancement. This is a result of oxygen participation in stabilizing the reaction intermediate through the formation of a favorable 5-membered ring.

Table I.1. Effects of Structure on Relative Rate Constants[a] for $S_N2$ Halide Exchanges.[b]

| R | $Cl^- + RI \rightarrow RCl + I^-$ | $Br^{*-} + RBr \rightarrow RBr^* + Br^-$ [c] |
|---|---|---|
| Methyl | 1.00 | 1.00 |
| Ethyl | 0.089 | 0.013 |
| i-Propyl | 0.0028 | $1.4 \times 10^{-4}$ |
| t-Butyl | -- | $3.9 \times 10^{-5}$ |
| n-Propyl | 0.053 | 0.0085 |
| i-Butyl | 0.0034 | $4.4 \times 10^{-4}$ |
| neo-Pentyl | $1.2 \times 10^{-6}$ | $2 \times 10^{-7}$ |

a. Rates relative to the methyl halide for each series.
b. In acetone at 25° C.
c. * indicates radioactive isotope.

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Table I.2 Effect of Ether Linkage on the Relative Rate of Reaction of Alkyl Chlorides with KI in Acetone at 50° C.

| Compound | Relative Rate |
|---|---|
| $CH_3CH_2CH_2Cl$ | 1 |
| $C_6H_5CH_2CH_2CH_2Cl$ | 1.72 |
| $C_6H_5OCH_2CH_2Cl$ | 0.30 |
| $C_6H_5OCH_2CH_2CH_2Cl$ | 1.7 |
| $C_6H_5OCH_2CH_2CH_2CH_2Cl$ | 1.4 |

Table I.3. Relative Rate Constants for Hydrolysis of Alkyl Chlorides.[a]

| RCl | Relative Rate[b] |
|---|---|
| $CH_3CH_2CH_2Cl$ | 1.00 |
| $CH_3CH_2OCH_2CH_2Cl$ | 0.18 |
| $CH_3CH_2SCH_2CH_2Cl$ | 2750 |
| $CH_3CH_2OCH_2CH_2CH_2Cl$ | 0.77 |
| $CH_3CH_2SCH_2CH_2CH_2Cl$ | 1.00 |

a Aqueous dioxane, $[H_2O]$=20M, 100° C
b Rate relative to 1-chlorobutane

Table I.4. Solvolysis of ω-Methoxy-p-bromobenzenesulfonates in Acetic Acid.[a]

| Compound | Relative Rate[b] |
|---|---|
| $Me(CH_2)_3OBs$ | 1.00 |
| $MeO(CH_2)_2OBs$ | 0.28 |
| $MeO(CH_2)_3OBs$ | 0.63 |
| $MeO(CH_2)_4OBs$ | 657 |
| $MeO(CH_2)_5OBs$ | 123 |
| $MeO(CH_2)_6OBs$ | 1.16 |

a. 50° C.
b. Relative to brosylbutane

### C. Reactions of Macromolecules.

The most widely studied area of macromolecular reactions is that which deals with the polymerization of monomers. In the analyzing the kinetics of polymerization it is accepted practice to assume that the reactivities of the growing chain ends are independent of the size of the molecule to which the ends are attached, thus allowing for the use of relatively simple kinetic models . The basis for this assumption was laid down by Flory who demonstrated that, in principle, the reactivity of a functional group should remain unchanged when the group is attached to a polymer.[44,45] Flory compiled data on many reactions which showed that the reactivity of functional groups on linear molecules was independent of molecular size, except in very small chains. An example of the type of data used is listed in Table I.5. The table shows the rate constants for the esterification of mono (a) and dibasic (b) acids with different length alkyl chains attached. For the esterification of the monobasic acid the rate constant is largest for n=1, slightly smaller for n=2 and then stays level at approximately $7.4 \times 10^{-4}$ $(g\ equiv/L)^{-1}$ $s^{-1}$ as the length of the chain is extended from n=3. From results such as these it can be concluded that once a minimum size has been exceeded any further increase in the overall size of the molecule does not effect reactivity. In the esterification of the dibasic acids there is a slightly different behavior for small n values, but it appears that at larger n that the rate constant observed approaches that of the monobasic acid. The results shown for the dibasic acids do not differentiate the reactions of the first or second acid groups allowing one to conclude that the equal rates of mono and dibasic acids for large n indicate no dependence of functional group reactivity on the state,reacted or unreacted, of another group in the chain. In addition to negating the effects of molecular size on the reactivity of functional groups, Flory was also able to show that viscosity and spatial shielding effects of the polymer did not affect the reactivity.

Table I.5. Rate Constants for Esterification of Carboxylic Acids.[45]

(a) $CH_3(CH_2)_{n-1}COOH + C_2H_5OH \rightarrow CH_3(CH_2)_{n-1}COOC_2H_5 + H_2O$

(b) $(CH_2)_n(COOH)_2 + 2\ C_2H_5OH \rightarrow (CH_2)_n(COOC_2H_5)_2 + H_2O$

| Chain Length n | k x$10^{-4}$ 25° C[a] monoacid rxn (a) | k x $10^{-4}$ 25° C[a] diacid rxn (b) |
|---|---|---|
| 1 | 22.1 | - |
| 2 | 15.3 | 6.0 |
| 3 | 7.5 | 8.7 |
| 4 | 7.4 | 8.4 |
| 5 | 7.4 | 7.8 |
| 6 | - | 7.3 |
| 8 | 7.5 | - |
| 9 | 7.4 | - |
| 11, 13, 15 and 17 | 7.6 | - |

a Rate constants expressed in (g equiv/L)$^{-1}$ s$^{-1}$.

The assumption of equal reactivity and the proof thereof by Flory and others, greatly simplifies the kinetic models of polymerization reactions and might lead one to believe that the kinetics of polymer reactions are the same as those of the corresponding small molecules. However, in studies of the reactions of polymer bound functional groups a lot of systems have been found that do show a macromolecular dependence on reactivity with the overall rate constant for the reaction being a function of the degree of conversion. It is assumed in most cases that the cause of the change in reactivity arises from the reaction of the adjacent functional groups on the chain.

**1. Autoinhibitive Reactions.**

In the majority of reactions of polymer functional groups a marked decrease in reactivity has been observed as the reaction proceeds to high conversion.[46,47] . It has been assumed that there is a buildup of steric or electrostatic interference caused by the reaction of nearest neighbor functional groups as the reaction proceeds . The system which has been studied most thoroughly is the hydrolysis of poly(methacrylate)s. During the course of the base hydrolysis of syndiotactic and atactic poly(methyl methacrylate)s (PMMA) there is a large decrease in the rate of reaction with conversion.[48,49] The rate constant of the hydrolysis of a given ester was found to decrease by 50% if one neighboring group had already reacted and by 90% if both had. The decrease was attributed to electrostatic interference to the approach of the base.

In some reactions the reduction of the reaction rate due to nearest neighbors can be extreme, resulting in either a very slow reaction or no reaction of functional groups whose neighbors had reacted. Rempp found that the reaction of methyl sulphinylmethyl lithium with syndiotactic PMMA reached a limiting conversion of 60% of the ester groups even in the presence of large excesses of the lithium reagent.[46] The reaction took place in two stages; first, displacement of the methoxy group by alkyl lithium to form a ketone, which was followed by rapid addition of another alkyl lithium molecule to form an enol moiety. Analysis of the kinetics of reaction showed that the presence of one reacted neighbor (in the enol form) resulted in a 99.5% reduction in rate compared to the reaction of an ester with no reacted neighbors. Ester groups with both neighbors reacted were found to be essentially inert.

**2. Autocatalytic Reactions.**

The rate constants of some reactions on polymers are found to increase dramatically with increasing conversion. It was found during studies of the free radical dehydrochlorination of poly(vinyl chloride) that rate of reaction increased several orders of magnitude after a mere 1% conversion.[50] This increase was a result of the higher reactivity of the allylic chlorides formed after initial dehydrochlorination. As a result almost all dehydrochlorination is believed to have taken place sequentially along the polymer backbone.

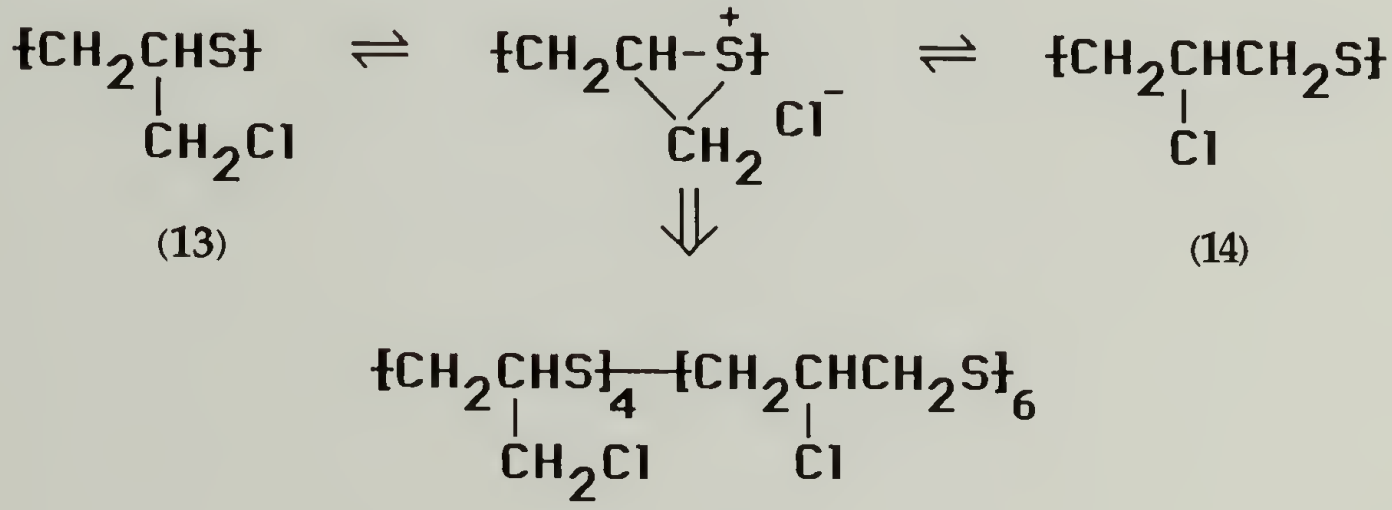
Another example of increased reactivity can be found in the hydrolysis of isotactic poly(methacrylate)s in pyridine-water mixtures. In a previous example, it was shown that the hydrolysis of syndiotactic or atactic poly(methacrylate) was autoinhibitive, but if the tacticity is changed to isotactic a large increase in reaction rate constants with increasing conversion has been reported.[48,46] For syndiotactic PMMA, it was found that the rate of hydrolysis of an ester group increased 8-fold if one of its nearest neighbors had already reacted and increased 100-fold if both were reacted.[51] The increases in reactivity were attributed to the formation of anhydride groups by an ester and a neighboring carboxylate ion; these anhydrides were in turn more reactive towards hydrolysis than the parent ester. The differences in reactivities based on tacticity arise because it is only in the isotactic polymers that the geometry of reactant group spacing allows for facile formation of anhydrides.

**3. Intramolecular Catalysis of Reactions.**

There are some polymer reactions in which one type of functional group will provide anchimeric assistant to catalyze the reaction of another type, or alternatively, some groups can cause a depression of reaction rate. The hydrolysis of isotactic polymethacrylates mentioned above is a good example of this, but with this system partial reaction must first take place before any assistance can take place. A system that has sites present which influence reactivity from the start of the reaction is discussed below.

The behavior of simple chloroalkyl sulfides (Table I.4) would suggest that the replacement of the PECH oxygen with a sulfur should lead to a more reactive polymer through the availability of anchimeric assistance. Furthermore, in the absence of added nucleophiles

poly(chloromethylthiirane) (**13**) (PCMT) and its structural isomer, poly(3-chlorothietane) (**14**) (P3CT) have been shown to undergo repeating unit isomerization to yield a 40:60 copolymer of chloromethylthiirane and 3-chlorothietane repeating units (**15**).[52,53] The isomerization proceeds through formation of an episulfonium ion followed by reopening of the ring by chloride attack on the cyclic structure at either side of the sulfur atom (Scheme I.3). Ring strain apparently precludes significant exocyclic attack of chloride ion, as rearrangement is much faster than chain cleavage. The formation of the episulfonium intermediate has a direct effect on the reactivity of this polymer towards other nucleophiles. This is evidenced by the hydrolysis of poly(chloromethylthiirane) (**13**), as this polymer was found to undergo hydrolysis in a dioxane/water (9:1) system much faster than its structural analog poly(epichlorohydrin) (**1**).[52]



(13) (14)

(15)

Scheme I.3. Isomerization of Poly(chloromethylthiirane) and Poly(3-chlorothietane).

**4. Kinetic Models.**

The dependence of the rate constant for the reaction of a given functional group on the status (reacted or unreacted) of its neighbors requires the use of an appropriate kinetic model if one wishes to analyze the system. If one is analyzing a small molecule second-order reaction of two molecules (A and B), the rate of reaction is described by eq. I.1,[54] with the rate of reaction

$$r = k[A][B] \qquad \text{eq. I.1.}$$

being dependent on the concentration of both species and a single rate constant. On the other hand the neighboring group effects described above for polymers require the assignment of different rates for a functional group depending on whether neither, one or both adjacent groups have reacted (see Figure I.1). Eq I.2 is obtained when the second-order rate law shown in eq I.1 is applied to the polymer reaction , $(Y)_n + B \rightarrow (X)_n$, where [YYY] is the concentration of YYY triads etc.. Solution of this equation is not a straightforward problem given that

$$r = k_0[YYY][B] + 2k_1[XYY][B] + k_2[XYX][B] \qquad \text{eq I.2.}$$

the concentrations of XYY and XYX triads are not readily ascertainable. The determination of $k_0$ is the only straightforward part, since $k_0$ can obtained from analysis of data at low conversion.

Several early investigators of polymer reactions determined the rate constants by use of measurements of the tangents to the slope of rate plots[55] or through determination of actual triad concentrations by isolation of reactants.[48] Both methods were very limited as to what reactions could be evaluated. The first method was only found to be applicable to systems where $k_0=k_1$ or $k_1 = k_2$ and the second route required that the triad concentrations could be directly determined by spectroscopy or other methods.

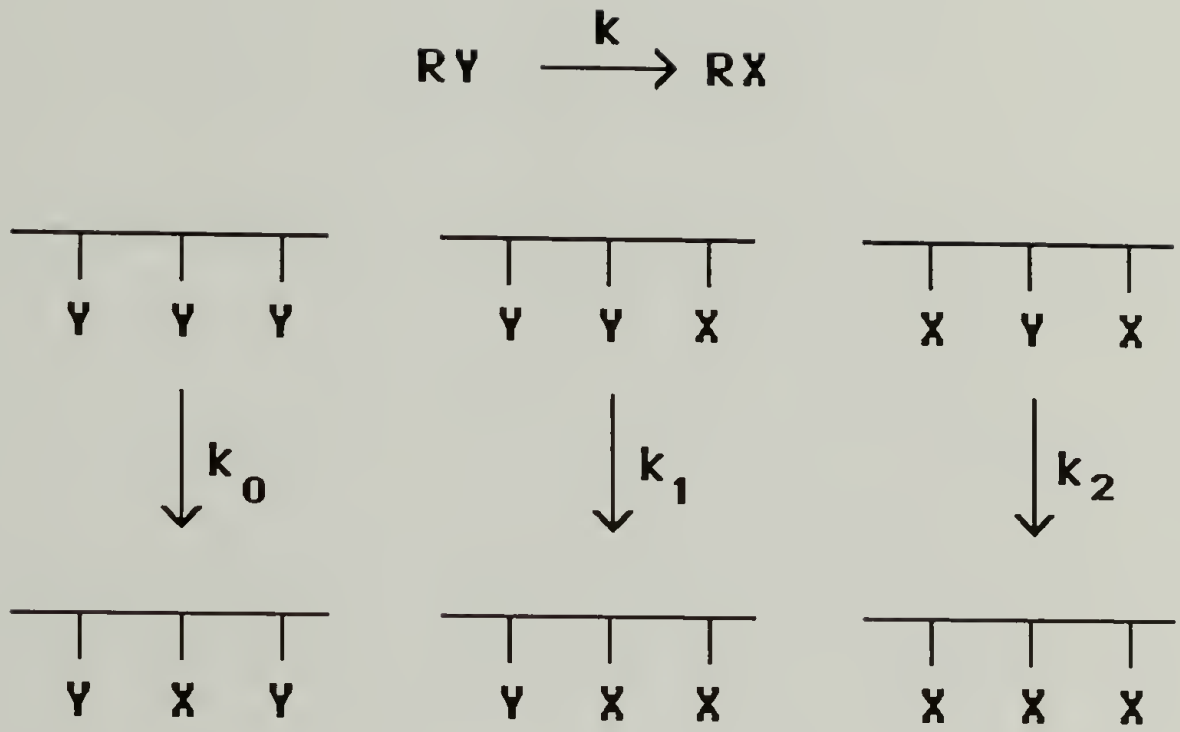



Figure I.1. Assignments of rate constants for reaction of different triads.

In the early 1970's Boucher published the first of a series of papers in which he used numerical methods to determine $k_1$ and $k_2$.[56,57] His approach was to develop a mathematical model with which one could derive $k_1$ and $k_2$ from observed conversion vs time data without having to explicitly measure the concentration of each of the triads. In brief, the method defines the observed extent of reaction ($\zeta$) in terms of unreacted sequence lengths (x) as shown in eq I.3.

$$\zeta = 1 - \sum_{x=1,m} xN_x/mM \qquad \text{eq I.3}$$

$\zeta$ = extent of reaction
x = length of sequence containing no reacted members
$N_x$ = total number of sequences containing x unreacted members
m = degree of polymerization
M = number of polymer molecules in system

The total number of sequences containing x unreacted members ($N_x$) can be related to the rate constants $k_0$, $k_1$ and $k_2$ by integrating the differential equations shown below (eq I.4-6), which express the net rate of formation of each of these sequences in terms of the rate constants.

$$dN_m/dt = -[2k_1 + (m-2)k_0]N_m \qquad \text{eq I.4}$$

$$dN_x/dt = 2k_1N_{x+1} + 2\,k_0 \sum_{j=x+2,m} N_j - [2k_1 + (x-2)k_0]N_x \qquad \text{eq I.5}$$

$$dN_1/dt = 2k_1N_2 + 2k_0 \sum_{j=3,m} N_j - k_2N_1 \qquad \text{eq I.6}$$

These equations have been solved by Boucher, and the reader is encouraged to refer to the review paper by Boucher on the subject[58] for a full explanation of the method and derivations of the equations.

For the case of molecules of large degree of polymerization, Boucher obtained eq I.7 after integrating eq I.4-6 and substituting the values for $N_m$, $N_x$ and $N_1$ into eq I.4. In equation I.7 the ratios $K = k_1/k_0$ and $L = k_2/k_0$ were chosen by Boucher as a convenient form in which the rate constants could be handled. This rather messy equation, with the aid of a

$$1-\zeta=(2-\alpha)\alpha^{2K}\exp[-2(1-K)(1-u)] +$$

$$2K\alpha^{L}\int_{\alpha}^{1}(1-u)^{2}u^{(2K-L-1)}\exp[-2(1-K)(1-u)]du +$$

$$2\alpha^{L}\int_{\alpha}^{1}(1-u)u^{(2K-L)}\exp[-2(1-K)(1-u)]du \qquad \text{eq I.7.}$$

$\alpha$ =reduced time variable derived from the reactant concentrations and $k_0$
$K = k_1/k_0$
$L = k_2/k_0$
u = dummy variable for integration purposes

computer, allows the calculation of the extent of reaction vs time for combinations of the 3 rate constants given an independently determined $k_0$. In Figure I.2 are shown 3 curves computed with three different combinations of K and L for hypothetical reaction. All three have the same initial rate constant ($k_0$) and reactant concentrations. The middle curve (K=1, L=1) shows the anticipated conversion with time for a second-order reaction in which there was no dependence of the reactivity of a functional group its nearest neighbors (i.e. $k_0=k_1=k_2$). The other curves graphically demonstrate how much the conversion at a given time is affected in systems that show a marked dependence of the reactivity on neighboring groups. These curves were calculated based on the K and L values found for the base hydrolysis of PMMA samples that were discussed earlier. The top curve with K=8 and L=100 represents the reaction of isotactic PMMA and the lower curve, with K=0.5 and L=0.1 that of atactic PMMA.

The above kinetic treatment is not without flaws. It is a simplified view of the polymer reaction, taking into account only the status of neighboring reactive groups. We have

already seen that tacticity played a major role in the rates of hydrolysis of polymethacrylates, so one would imagine that an accurate model should contain means by which to take triad tacticity into account. The method also assumes that AAB and BAA triads react identically. This is fine for polyolefins, but polymers resulting from ring opening polymerizations have directionality in the polymer backbone and this may result in the reactivities of AAB and BAA not being equal. There are currently no models available that take these two concerns into account but the application of Boucher's model to most systems can be safely accomplished if one is aware of its pitfalls.

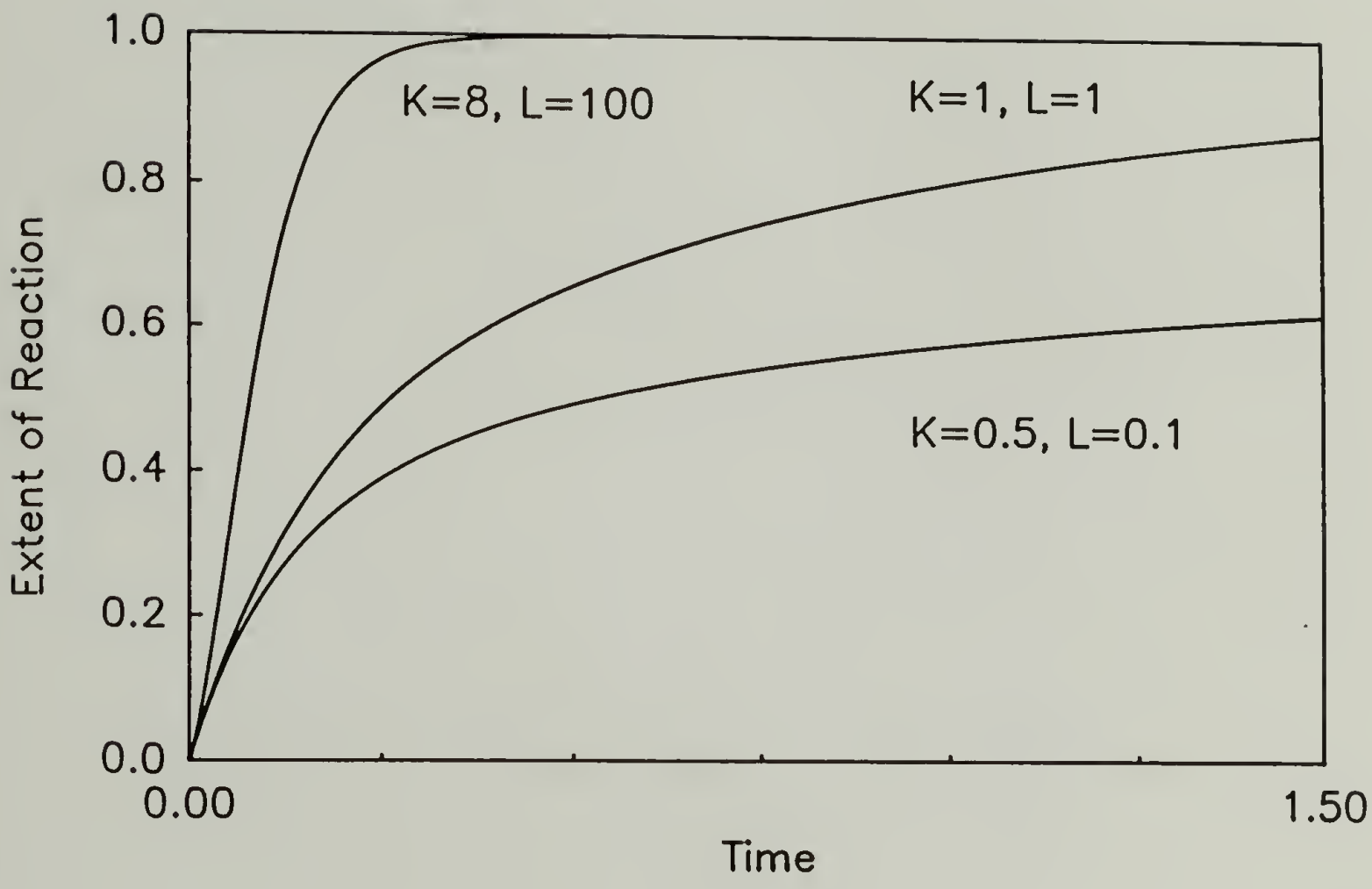



Figure I.2. Calculated conversion vs time plots using eq I.4 for (K , L) values of (1, 1), (8, 100) and (0.5, 0.1).

# CHAPTER II

# EXPERIMENTAL SECTION

## A. Measurements

### 1. Routine Measurements.

$^1H$ NMR spectra were obtained using Varian XL-200, XL-300 and CFT-20 spectrometers with observe frequencies of 200, 300 and 80 MHz respectively. $^{13}C$ NMR were obtained on Varian XL-200 and XL-300 nuclear magnetic resonance spectrometers operating at 50 and 75 MHz respectively. Chemical shifts ($\delta$) are reported in parts per million (ppm) downfield from trimethylsilane (TMS). For samples that contained no TMS, shifts are referenced to the published shifts of resonances from the lock solvent[59]. Variable temperature measurements were made utilizing using the standard Varian XL temperature control system, which was calibrated to ±0.1° C using the known change in relative peak frequencies with temperature of ethylene glycol standards.[60] $^{13}C$ spin-lattice relaxation time ($T_1$) measurements were performed on the Varian XL300 (75 MHz) using the standard inversion-recovery pulse sequence of 180° pulse - delay time array ( $\tau$ ) - 90° pulse - observe. Choice of delay times and actual $T_1$ calculations were performed using standard commands (DOT1 and T1)[61] contained within the Varian VXR version 4.1 software. Error limits given for $T_1$ values are those determined by the $T_1$ program and are based on the goodness of fit of the calculated values of peak height at each $\tau$ value and those observed. Nuclear Overhauser Enhancement factors (NOE) were determined by the comparison of the peak heights from $^{13}C$ NMR spectra obtained using continuous broadband $^1H$ decoupling with those obtained using a gated decoupling pulse sequence in which broadband $^1H$ decoupling was only used during the acquisition time. For all spectra used in NOE determinations, the delay time between the end of the data acquisition time and the next pulse was a minimum of 5 times $T_1$ for the peaks of interest. Resolution enhancement of the 50 MHz $^{13}C$ NMR spectra of poly(3-chlorooxetane) samples was accomplished through the use of the Varian Instruments RESOLV program[62]. This program weights the observed free induction decay with the exponential $e^{t/R}$, where R is a function of spectral acquisition time.

Infrared spectra were obtained on either a Perkin Elmer 283 or a Perkin Elmer 1320 infrared spectrometer. All spectra were referenced to the 1601 $cm^{-1}$ band of a thin polystyrene film. Purity of all monomers was checked to be >99% before attempting polymerization using a Varian Aerograph Model 920 gas chromatograph equipped with a 12 ft aluminum (1/4" ID) SE-30 (15% on Chromosorb) column and thermal conductivity (TC) detector. Glass transition temperatures (Tg) were determined on a Perkin Elmer DSC-2 differential scanning calorimeter at heating rates of either 10° C $min^{-1}$ or 20° C $min^{-1}$. Tg is reported as the temperature at the midpoint of the transition and results from first heating unless otherwise noted.

Gel permeation chromatographic measurements were made using Waters instruments. Those done in tetrahydrofuran used a flow rate of 2.5 mL/min with four μ-styragel columns ($10^5$, $10^4$, $10^3$, $10^2$ Å). Those in chloroform used a flow of 1.0 mL/min with two linear ultra-styragel columns. Peak molecular weight (MW) estimates are based on a calibration curves derived from at least 6 narrow-dispersity polystyrene standards obtained from Polysciences. Number average molecular weights ($M_n$) and weight average molecular weights ($M_w$) were calculated using a Waters 160 Data Module based on calibration curves derived from narrow-dispersity polystyrene standards obtained from Polysciences. Inherent viscosities ($\eta_{inh}$) for polymer solutions with solvents other than DMAc were measured using a Cannon-Fenske #35 viscometer, with a solvent elution time of 102 sec for $CH_2Cl_2$ and 127-128 sec for $CHCl_3$ at 30° C. Viscosities of DMAc solutions were measured using a Cannon #70 viscometer, which gave a solvent elution time of 110 sec for DMAc at 30° C.

Elemental analyses were performed by the University of Massachusetts Microanalytical Laboratory and reported values are % of total. All temperatures listed are uncorrected and reduced pressures for distillations are listed in mm Hg.

**2. NMR Measurements for Kinetic Analyses.**

**a. $^1$H NMR studies.**

Spectra were recorded at 45° C on a Varian XL-300 under the following conditions: 24 transients, pulse width 80°, acquisition time 2 sec and a 3 sec pulse delay. Spectra obtained

were taken to represent the composition of the system half way through the time required to acquire them.

**b. $^{13}C$ NMR studies.**

Spectra were recorded on a Varian XL-300 with an observe frequency of 75 MHz for $^{13}C$. The reactions being observed were run in 10 mm NMR tubes inside of the observe probe with constant temperature control. For each reaction a time based array was initiated allowing for the acquisition of spectra at specified intervals. All spectra were obtained using a 50° pulse width with the following parameters set as indicated in Table II.1; delay time following acquisition before the next pulse (D1); data acquisition time (AT) and number of transients (NT) averaged into the FID (free induction decay). All spectra were obtained without locking on a deuterium reference frequency. Spectra obtained were taken to represent the composition of the system half way through the time required to acquire them.

Calibration for the 90° pulse width (PW90) for these reaction systems was carried out on a DMAc sample containing 0.15 M tetrabutylammonium benzoate and 0.15 M tetrabutylammonium chloride to give PW90 ≈ 25 μsec. All peak assignments reported in DMAc are referenced to the acetamide methyl as 19.63 ppm. This value for the acetamide methyl was determined in a concentrated solution of DMAc in $CDCl_3$ and was referenced to TMS and found to vary by less than ± 0.1 ppm over the temperature range from -15° C to 50° C.

Table II.1. $^{13}C$ Data Acquisition Parameters for Reaction Studies.

| Polymer | D1 (sec) | AT (sec) | NT |
|---|---|---|---|
| PECH | 0.5 | 1.0 | 400 |
| PCEO | 1 | 1.0 | 300 |
| PCPO | 1.5 | 1.0 | 240 |
| PCBO | 2.0 | 1.0 | 200 |
| P2CMO | 0.5 | 1.0 | 1500 |
| P3CMO | 0.5 | 1.0 | 400 |
| P3CO | 2 | 0.9 | 200 |
| PBMO | 0.5 | 1.0 | 200/400 |
| PBEO | 0.5 | 1.0 | 200/400 |
| $C_5H_{11}Cl$ | 1.0 | 1.0 | 300 |

## B. Materials

The following is a list of all reagents and solvents used in the work described here. Unless indicated otherwise all materials were used as received. Letter codes indicate the source of the material.

Acetic acid, glacial (F)(B)

Acetone (F)

Acetone-$d_6$ 99.5% d (A)

Acetyl chloride, distilled bp 50° C (B)

Benzene (B)

Benzene-$d_6$ 99.8% (A)

Benzoic acid, recrystallized from hexanes, mp 123° C (F)

Borane-methylsulfide complex, 2.0 M in THF (A)

Borane-THF complex, 1M in THF (A)

Boron trifluoride etherate (A)

4-Bromo-1-butene (A)

6-Bromo-1-hexene (A)

5-Bromo-1-pentene (A)

3-Buten-1-ol (A)

Carbon tetrachloride (F)

3-Chloro-2-chloromethyl-1-propene, distilled bp 135° C (A)

Chloroform-$d_1$ 99.9% d (A)

Chloroform-$d_1$ 100% d in ampules (A)

5-Chloropentane, fractionally distilled bp 108° C (A)

m-Chloroperoxybenzoic acid, 80-85% (A)

Deuterium oxide (A)

Dichloromethane, reagent grades (A) (B)

Dichloromethane-$d_2$ 99.5% d (A)

2,3-Dihydropyran (A)

N,N-Dimethylacetamide (A)

Epibromohydrin, distilled bp 136° C (A)

Epichlorohydrin (B)

Epichlorohydrin, Gold Label, distilled bp 104° C (A)

Ethyl alcohol, 100%, dried over 3Å molecular sieves (P)

Ethyl ether, anhydrous (B) (F)

Ethyl ether, reagent (F)

Ferric chloride, anhydrous 98% (A) (F)

Hydrogen peroxide, 30% in water (F)

Lithium chloride (B)

Magnesium sulfate (A) (B) (M)

Methanol, reagent grade (F)

2-Methyl-2-propanol (A)

2,4 -Pentanedione, distilled from CaO bp 125-136° C (A)

4-Penten-1-ol (A)

Petroleum ether, Skelly F (F)

Poly(epichlorohydrin) (A)

Potassium bromide (F)

Potassium t-butoxide (A)

2-Propen-1-ol (A)

Pyridine (F)

Pyridinium p-toluenesulfonate, 98% (A)

Silver hexafluorantimonate (A)

Sodium bicarbonate (F)

Sodium hydride (F)

Sodium hydroxide, Certified ACS pellets (F)

Sodium sulfide (F)

Tetrabutylammonium bromide (A)

Tetrabutylammonium chloride (FL)

Tetrabutylammonium hydroxide, 40 wt % in water (A)

Tetrahydrofuran, Gold Label anhydrous in Sure Seal™ bottles(A)

Thionyl chloride (A)

p-Toluenesulfonic acid, practical (K)

p-Toluenesulfonyl chloride, recrystallized from petroleum ethers, mp 69° (A) (B)

Triethylaluminum, 1M in hexanes (A)

Triethylaluminum, 25% in toluene (A)

Triethyleneglycol, dried over $MgSO_4$ and distilled bp 130° C/1mm (A)

Triethyleneglycol dimethylether (A)

Triethyl methanetricarboxylate (A)

Trimethylsulfoxonium iodide (A)

Triphenylphosphine (A) (F)

Sources

A - Aldrich Chemical Company

B - J. T. Baker

F - Fisher Scientific

FL - Fluka

K - Eastman Kodak Company

M - Mallinkrodt

P - Pharmco

## C. Methods

### 1. Preparation of Monomers and Intermediates.

#### a. (2-Bromoethyl)oxirane (BEO).

4-Bromo-1-butene (24 g, 0.18 mol) was added to 250 mL of $CH_2Cl_2$ and cooled under $N_2$ in an ice bath to 0° C. To this was added 37.2 g (0.18 mol) of solid m-chloroperoxybenzoic acid. The reaction was allowed to come to room temperature and stirred for 16 hr under $N_2$. At that time the solution was filtered and washed sequentially with saturated aqueous sodium sulfite, saturated aqueous sodium bicarbonate, distilled water and a saturated aqueous NaCl solution. After drying over $MgSO_4$ and removal of the solvent, fractional distillation yielded 18.8 g (0.12 mol, 69%) BEO (bp 47° C/1 mm). Anal calcd for $C_4H_7OBr$: C, 31.81; H, 4.67. Found: C, 31.69; H, 4.59. $^1H$ NMR (300 MHz, $CDCl_3$) δ: 3.5 (2H, triplet); 3.0 (1H, multiplet); 2.8 (1H, triplet); 2.5 (1H, quartet); 2.1 (2H, multiplet). IR (NaCl, neat) $cm^{-1}$: 3055, 2958, 2862, 1438, 1257, 1218, 910, 855, 830.

#### b. (3-Bromopropyl)oxirane (BPO).

m-Chloroperoxybenzoic acid (mCPBA, 85%; 69.5 g, 0.34 mol) was slowly added as a solid to a stirred cooled solution (0° C) of 49.3 g (0.34 mol) 5-bromo-1-pentene in 500 mL $CH_2Cl_2$ under $N_2$ atmosphere. The reaction mixture was then allowed to warm to room temperature, stirred for 12 hr, and extracted with 2 x 300 mL aqueous $Na_2SO_3$, 300 mL saturated aqueous $NaHCO_3$, 2 x 300 mL distilled water and 2 x 300 mL saturated aqueous NaCl. Fractional distillation (bp 28°/0.4 mm) afforded 45.1 g (69%) of (3-bromopropyl)oxirane. Anal calcd for $C_5H_9BrO$: C, 36.4; H, 5.5. Found: C, 36.02; H, 5.51. $^1H$ NMR (300 MHz, $CDCl_3$) δ: 3.4 (2H, triplet); 2.9 (1H, multiplet); 2.7 (1H, triplet); 2.5 (1H, quartet); 2.0 (2H, multiplet); 1.8 (1H, multiplet); 1.6 (1H, multiplet). IR (NaCl, neat) $cm^{-1}$: 3055, 2998, 2922, 1486, 1438, 1265, 1218, 910, 855, 834, 812.

**c. (4-Bromobutyl)oxirane (BBO).**

m-Chloroperoxybenzoic acid (12.75 g, 62 mmol) was slowly added as a solid to a stirred cooled solution (0° C) of 10.0 g (61 mmol) 6-bromo-1-hexene in 100 mL $CH_2Cl_2$ under $N_2$ atmosphere. The reaction mixture was then allowed to warm to room temperature, stirred for 12 hr and extracted with 2 x 100 mL aqueous $Na_2SO_3$, 100 mL saturated aqueous $NaHCO_3$, 2 x 100 mL distilled water and 2 x 100 mL saturated aqueous NaCl. Fractional distillation (bp 36° C/0.5 mm) afforded 8.2 g (75%) of (4-bromobutyl)oxirane. . Anal calcd for $C_6H_{11}OBr$: C, 40.23; H, 6.19. Found: C, 40.48; H, 6.16. $^1H$ NMR (300 MHz, $CDCl_3$) δ: 3.4 (2H, triplet); 2.9 (1H, multiplet); 2.8 (1H, triplet); 2.5 (1H, quartet); 1.9 (2H, multiplet); 1.6 (2H, multiplet).

**d. (2-Chloroethyl)oxirane (CEO).**

(1) 4-Chloro-1-butene.

A solution of 50 g (0.69 mol) 3-buten-1-ol and 10 mL pyridine was cooled to 0° C (ice bath) under an $N_2$ atmosphere. To this cooled solution 83 g (0.70 mol) thionyl chloride was slowly added. After stirring for 12 hr the reaction mixture was rapidly added with vigorous stirring to 500 mL of ice water. This was then extracted 3 times with $CH_2Cl_2$. After washing the combined organic layers sequentially with saturated aqueous sodium bicarbonate and water and evaporation of the solvent, fractional distillation yielded 47.1 g (0.52 mol, 75%) 4-chloro-1-butene (bp 80° C). $^1H$ NMR (300 MHz, $CDCl_3$) δ: 5.77 (1H, multiplet); 5.13 (2H, quartet); 4.02 (2H, multiplet); 2.44 (2H, quartet).

(2) (2-Chloroethyl)oxirane.

Solid m-chloroperoxybenzoic acid (80 g, 0.39 mol (based on 80% purity)) was slowly added under a $N_2$ blanket to a stirred solution of 35 g (0.39 mol) 4-chloro-1-butene in 500 mL $CH_2Cl_2$ that had been precooled to 0° C (ice water bath). The mixture was allowed to come to room temperature and stirring was continued for an additional 14 hr after which the solid chlorobenzoic acid was removed by vacuum filtration. The $CH_2Cl_2$ solution was then extracted sequentially with saturated aqueous sodium sulfite, saturated aqueous sodium bicarbonate, distilled water and brine. After drying over $MgSO_4$ and evaporation of the $CH_2Cl_2$, fractional

distillation yielded 26.8 g (0.25 mol, 64%) (2-chloroethyl)oxirane (bp 42° C/15 mm). $^1$H NMR (300 MHz, $CDCl_3$) δ: 3.64 (2H, triplet); 3.05 (1H, multiplet); 2.79 (1H, triplet); 2.53 (1H, multiplet); 1.90 (2H, multiplet).

**e. (3-Chloropropyl)oxirane (CPO).**

(1) 5-Chloro-1-pentene.

Thionyl chloride (70 g, 0.69 mol) was slowly added under $N_2$ atmosphere to a solution of 4-penten-1-ol (50 g, 0.58 mol) and pyridine (10 mL) which had been cooled to 0° C (ice water bath). After 2 hr the solution was poured rapidly into 500 mL of ice water containing 50 g of sodium bicarbonate. The aqueous mixture was then extracted three times with $CH_2Cl_2$. The combined organic layers were then washed with saturated aqueous sodium bicarbonate, distilled water and brine. After drying over $MgSO_4$ and evaporation of the solvent, fractional distillation yielded 32.1 g (0.58 mol, 53%) 5-chloro-1-pentene (bp 106° C). $^1$H NMR (300 MHz, $CDCl_3$) δ: 5.78 (1H, multiplet); 5.03 (2H, quartet); 3.95 (2H, multiplet); 2.15 (2H, quartet); 1.80 (2H, multiplet).

(2) (3-Chloropropyl)oxirane.

Solid m-chloroperoxybenzoic acid (50 g, 0.25 mol (based on 80% purity)) was slowly added under a $N_2$ blanket to a stirred solution of 26.8 g (0.25 mol) 5-chloro-1-pentene in 500 mL $CH_2Cl_2$ that had been precooled to 0° C (ice water bath). The mixture was allowed to come to room temperature and stirring was continued for an additional 14 hr after which the solid m-chlorobenzoic acid was removed by vacuum filtration. The $CH_2Cl_2$ solution was then extracted sequentially with saturated aqueous sodium sulfite, saturated aqueous sodium bicarbonate, distilled water and brine. After drying over $MgSO_4$ and evaporation of the $CH_2Cl_2$, fractional distillation yielded 21.3 g (0.17 mol, 68%) (3-chloropropyl)oxirane (bp 68° C/15 mm). $^1$H NMR (300 MHz, $CDCl_3$) δ: 3.53 (2H, triplet); 2.91 (1H, multiplet); 2.72 (1H, triplet); 2.48 (1H, quartet); 1.7-2.0 (3H, multiplet); 1.57 (1H, multiplet).

**f. (4-Chlorobutyl)oxirane (CBO).**

Prepared by J. S. Shih[5]

**g. 3-Chlorooxetane (3CO).**

(1) 3-Hydroxyoxetane.

Over a 3 hr period 591 g (6.4 mol) epichlorohydrin was added to 390 g (6.5 mol) glacial acetic acid containing 5 g $FeCl_3$ at 60° C. After 4 hr, 5 g p-toluenesulfonic acid was added. Subsequent slow addition of 540 g (6.4 mol) 2,3-dihydropyran was accompanied by a rapid increase in reaction temperature to a maximum of 77° C. After 2 hr the reaction mixture was added dropwise to a refluxing solution of 560 g (14 mol) of NaOH in 600 mL $H_2O$. After 1 hr at reflux the reaction mixture was cooled and extracted with 4 x 250 mL $CHCl_3$; concentration of these extracts yielded 740 g of material which by NMR contained approximately 40% of 3-(tetrahydropyranyloxy)oxetane. To this mixture was added 300 mL MeOH along with 10 g pyridinium toluenesulfonate. The mixture was then refluxed for 3 hr and the reaction was quenched by the addition of 1 L of saturated aqueous sodium bicarbonate. The mixture was extracted with 500 mL of ether and the ether layer was washed with 2 x 100 mL $H_2O$ and dried over $MgSO_4$. Fractional distillation yielded 110 g (1.5 mol, 23% yield based on epichlorohydrin[63]) of 3-hydroxyoxetane (b.p. 85-87° C/50 mm). $^1H$ NMR (200 MHz, $CDCl_3$) δ: 4.06 (1H, multiplet), 3.68 (4H, doublet), 2.52 (1H, doublet, $D_2O$ exchangeable).

(2) (3-Tosyloxy)oxetane.

p-Toluenesulfonyl chloride (264 g, 1.39 mol) and 100 g (1.36 mol) 3-hydroxyoxetane were combined in 250 mL $H_2O$. Sodium hydroxide (83 g, 2.1 mol) in 90 mL $H_2O$ was slowly added, while the temperature of the reaction mixture was kept below 80° C. After 3 hr the addition of 200 mL petroleum ether caused the precipitation of a white solid. The solid was collected by filtration, washed with $H_2O$ and vacuum dried to yield 190 g (0.89 mol, 66%) of (3-tosyloxy)oxetane (m.p. 83-87° C, ). $^1H$ NMR (200 MHz, acetone $d_6$) δ: 7.7 (2H, doublet); 7.3 (2H, doublet); 5.3 (1H, multiplet); 4.6 (2H, triplet); 4.4 (2H, quartet); 2.4 (3H, singlet).

(3) 3-Chlorooxetane (3CO) from (3-tosyloxy)oxetane and lithium chloride.

(3-Tosyloxy)oxetane (190 g, 0.89) was dissolved in 300 mL triethyleneglycol along with 50 g (1.18 mol) LiCl in a three neck flask equipped with a magnetic stir bar and a horizontal condenser. Heating to 160° C under a vacuum of 120 torr for 6 hr afforded approximately 80 mL of distillate, which was taken up in 100 mL ether, dried over $MgSO_4$ and fractionally distilled to yield 68 g (0.73 mol, 83%) of 3-chlorooxetane (12% overall yield based on epichlorohydrin) (b.p. 60-62° C/100 mm, lit[64] 104° C). $^1H$ NMR (300 MHz, $CDCl_3$) δ: 4.73-5.05 (complex multiplet). $^{13}C$ NMR (75 MHz, $CDCl_3$) δ: 80.53, 48.96.

(4) 3-Chlorooxetane (3CO) from (3-tosyloxy)oxetane and tetrabutylammonium chloride.

A 50 mL round-bottom flask equipped with a condenser and magnetic stir bar was charged with 7.9 g (34 mmol) (3-tosyloxy)oxetane, 9.5 g (34 mmol) tetrabutylammonium chloride and 20 mL triethyleneglycol dimethyl ether. The mixture was heated with stirring to 90° C in an oil bath. Within 1 hr the solution darkened and TLC ( silica gel, ether) indicated complete consumption of the tosylate ($R_f$=0.25). The reaction mixture was diluted with 100 mL of ether, extracted twice with water, and dried ($MgSO_4$). Evaporation of the solvent and fractional distillation yielded 1.4 g (15 mmol, 45%) of 3CO as confirmed by comparison of its $^1H$ NMR spectra with the spectra above.

(5) 3-Chlorooxetane (3CO) from 3-hydroxyoxetane.

Triphenylphosphine (54.7 g, 0.20 mol) was added to 250 mL of $N_2$ purged $CCl_4$ at room temperature. The mixture was heated at 60° C for 2 hr under $N_2$. After this period, 11.1 g (0.15 mol) of 3-hydroxyoxetane in 10 mL $CCl_4$ was slowly added and the reaction stirred for 8 hr at 60° C. After cooling to room temperature 100 mL methanol and 500 mL petroleum ethers were added to the mixture followed by cooling to 0° C. The precipitated triphenylphosphine oxide was removed by filtration. Subsequent removal of the solvent by evaporation and fractional distillation yielded 13 g (0.14 mmol, 94%) 3CO (32% based on ECH).

**h. 2-(Chloromethyl)oxetane (2CMO).**

(1) 3-Tetrahydropyranyloxy-1-propene (AALTHP).

Dihydropyran (1000 g,12 mol) was slowly added to 690 g (11.9 mol) 2-propen-1-ol containing 5.0 g pTSA heated at 40° C. After 12 hr the reaction mixture was taken up into 1 L of $CH_2Cl_2$ and extracted successively with 2 x 300 mL aqueous saturated sodium bicarbonate; 2 x 300 mL distilled water; and 500 mL brine. After drying with $MgSO_4$ fractional distillation yielded 1394 g (10.6 mol, 89%) AALTHP (b.p. 80° C/30 mm). Anal calcd for $C_8H_{14}O_2$: C, 67.6; H, 9.9. Found: C,67.8; H, 9.7. $^1H$ NMR (200 MHz, $CDCl_3$) δ: 5.95 (1H, multiplet); 5.24 (2H, quartet); 4.64 (1H, multiplet); 4.25 (1H, quartet); 4.00 (2H, multiplet); 3.53 (1H, multiplet); 1.4-2.0 (6H, multiplet). $^{13}C$ NMR (75 MHz, $C_6D_6$) δ: 135.5, 115.7, 97.7, 67.9, 61.5, 31.0, 26.0, 19.6. IR (NaCl, neat) $cm^{-1}$: 3095, 2975, 2945, 1470, 1455, 1445, 1355, 1345, 1203, 870, 810.

(2) (Tetrahydropyranyloxymethyl)oxirane (GLYTHP).

m-Chloroperoxybenzoic acid (85%, 289.9 g, 1.4 mol) was added slowly under $N_2$ to 200 g (1.4 mol) of AALTHP in 2 L $CH_2Cl_2$ at 0°C. The reaction was allowed to warm to room temperature and stirred for 14 hr. After removal of the solid m-chlorobenzoic acid by filtration, the mixture was extracted with 2 1L portions of saturated aqueous sodium sulfite, 1L of saturated aqueous sodium bicarbonate, 2 1L portions of distilled water and 2 1L portions of brine. Fractional distillation yielded 160 g (1.0 mol, 71%) GLYTHP (b.p. 48° C/0.2 mm). Anal calcd for $C_8H_{14}O_3$: C, 60.7; H, 8.9. Found: C, 60.5; H, 8.9. $^1H$ NMR (200 MHz, $CDCl_3$) δ: 4.66 (1H, quartet); 3.8-4.0 (2H, multiplet); 3.72 (1H, quartet); 3.3-3.6 (1H, multiplet); 3.20 (1H, multiplet); 2.81 (1H,triplet); 2.65 (1/2H, quartet); 2.60 (1/2H, quartet); 1.4-2.0 (6H, multiplet). $^{13}C$ NMR (50 MHz, $C_6D_6$) δ: 98.7, 98.64, 68.98, 68.07, 61.82, 61.58, 51.05, 50.63, 44.16, 31.05, 26.04, 19.73, 19.55. IR (NaCl, neat) $cm^{-1}$: 2950, 2861, 1470, 1441, 1395, 1270, 1205, 1120, 1035, 900, 815.

(3) 2-(Tetrahydropyranyloxy methyl)oxetane (THPMO).

Dimethylsulfoxonium methylide was formed insitu by reaction of trimethylsulfoxonium iodide (400 g, 1.8 mol) with 205 g (1.8 mol) potassium t-butoxide in 3L of

t-butanol under $N_2$ at 50° C. To this was added 152 g (0.95 mol) THPGLY in a dropwise fashion. After stirring for 96 hr at 50° C the t-butanol was removed by evaporation and the remaining material was taken up into 500 mL of $CH_2Cl_2$, filtered and washed with 3 x 300 mL portions of distilled water. The combined aqueous washings were then extracted with an additional 500 mL of $CH_2Cl_2$. After drying over $MgSO_4$ and evaporation of the solvent, fractional distillation of the combined organic portions yielded 73 g (0.42 mol, 44%) of THPMO (b.p. 58-60/0.2 mm). $^1H$ NMR (200 MHz, $CD_2Cl_2$) δ: 4.90 (1H, multiplet); 4.2-4.7 (3H, multiplet); 3.8 (2H, multiplet); 3.5 (2H, multiplet); 2.3-2.3 (2H, multiplet); 1.4-1.9 (6H, multiplet). $^{13}C$ NMR (50 MHz, $C_6D_6$) δ: 99.0, 98.82, 81.05, 80.95, 71.34, 70.71, 68.52, 61.72, 61.61, 31.22, 31.09, 26.16, 24.60, 24.30, 19.79. IR (NaCl, neat) $cm^{-1}$: 2981, 2865,1452, 1441, 1351, 1202, 902, 865, 810.

(4) 2-(Hydroxymethyl)oxetane (2HMO).

THPMO (57 g , 0.33 mol) was added to 600 mL methanol containing 1.0 g pyridinium tosylate and the mixture was heated to 40° C under $N_2$ for 11 hr. Then 60 mL of saturated aqueous sodium bicarbonate was added and the methanol was removed by evaporation. The remaining aqueous layer was then extracted with 4 x 250 mL petroleum ether and 6 x 250 ethyl ether. After drying over $MgSO_4$ concentration of the ethyl ether extracts yielded 17 g of material estimated by $^1H$ NMR to be 2HMO of approximately 80% purity. Subsequent distillation yielded 9.8 g (0.11 mol, 33%), 2HMO (bp 98-101° C/60 mm) $^1H$ NMR (200 MHz, $CDCl_3$) δ: 4.86 (1H, multiplet); 4.65 (1H, multiplet); 4.52 (1H, multiplet); 3.68 (2H, m) 2.70 (1H, triplet, $D_2O$ exchangeable); 2.64, (2H, multiplet). $^{13}C$ NMR (75 MHz, $CDCl_3$) δ: 82.7, 68.7, 65.1, 22.4. IR (NaCl, neat) $cm^{-1}$: 3400, 2940, 2900, 1450, 1235, 1110, 950, 845.

(5) 2-(Chloromethyl)oxetane (2CMO).

Triphenylphosphine (41 g , 0.15 mol) was added to 300 mL of $N_2$ purged $CCl_4$ at room temperature. The mixture was heated at 60° C for 90 min under $N_2$, and 9.8 g (0.11 mol) of 2HMO in 50 mL $CCl_4$ was slowly added. The reaction was stirred at 60° C for 15 hr, cooled to -10° C and taken up in 1 L of petroleum ether. The solution was filtered to remove the solid triphenylphosphine oxide. Concentration of the sample followed by fractional distillation yielded 10.5 g (0.10 mol, 91%) 2-(chloromethyl)oxetane (bp 65° C/60 mm).

Anal calcd for $C_4H_7ClO$: C,45.1; H, 6.6; Cl, 33.3. Found: C, 45.0; H, 6.5; Cl, 33.0. $^1H$ NMR (200 MHz, $CDCl_3$) δ: 4.92 (1H, multiplet); 4.56 (2H, multiplet); 3.65 (2H, doublet); 2.7 (1H, multiplet); 2.5 (1H, multiplet). IR (NaCl, neat) $cm^{-1}$: 3005, 2950, 2890, 1450, 1360, 1235, 970, 730.

**i. 3-(Chloromethyl)oxetane (3CMO).**

(1) 3-Chloro-2-(chloromethyl)-propan-1-ol (CCMPOL).

To a solution of 66.3 g (0.53 mol) 3-chloro-2-(chloromethyl)-1-propene in 250 mL THF at 0° C, 800 mL (0.80 mol) of a 1 M borane-THF solution (1 M in $BH_3$) was added under $N_2$ over a 20 min period. Upon completion of the $BH_3$ addition the reaction was maintained at 0° C for 1 hr and allowed to warm to room temperature. After 2 hr at room temperature 300 mL 30% aqueous $H_2O_2$ and 300 mL 30% aqueous NaOH were added in turn, at a rate that insured that the temperature of the reaction did not exceed 60° C. After 2 hr of vigorous stirring 300 mL of ethyl ether was added and the aqueous layer extracted with an additional 300 mL of ethyl ether. The combined organic layers were then washed with 2 x 300 mL saturated aqueous sodium sulfite; 300 mL distilled water and 300 mL brine. After drying over $MgSO_4$ fractional distillation yielded 57 g (0.40 mol, 75%) CCMPOL (b.p. 60° C/0.45 mm). Anal calcd for $C_4H_8Cl_2O$: C, 33.6; H, 5.6. Found: C, 33.8; H, 5.8. $^1H$ NMR (300 MHz, $CDCl_3$) δ: 3.76 (2H, doublet); 3.69 (4H, doublet); 2.27 (1H, multiplet); 1.88 (1H, singlet, $D_2O$ exchangeable). $^{13}C$ NMR (75 MHz, $C_6D_6$) δ: 60.7, 45.6, 43.1. IR (NaCl, neat) $cm^{-1}$: 3320, 2960, 2881, 1442, 1284, 1038, 827, 732, 686.

(2) 3-(Chloromethyl)oxetane (3CMO) from CCMPOL.

To a solution of 60 g (1.5 mol) sodium hydroxide in water heated to reflux 214.5 g (1.5 mol) CCMPOL was added. The reaction was allowed to reflux for an additional 6 hr at which time it was cooled and extracted with 2 x 500 mL $CH_2Cl_2$. After drying over $MgSO_4$, fractional distillation yielded 47.9 g (0.45 mol, 29%) 3CMO containing some elimination products (b.p. 73° C/60 mm). A final distillation from $BH_3$-THF gave the pure product needed for

polymerizations. Anal calcd for $C_4H_7ClO$: C,45.1; H, 6.6; Cl, 33.3. Found: C, 45.3; H, 6.6; Cl, 33.0 $^1H$ NMR (300 MHz, $CDCl_3$) δ: 4.77 (2H, triplet); 4.41 (2H, triplet); 3.74 (2H, doublet); 3.39 (1H, multiplet). $^{13}C$ NMR (50 MHz, $C_6D_6$) δ: 74.2, 46.1, 37.3. IR (NaCl, neat) $cm^{-1}$: 2955, 2865, 1447, 1274, 1067, 937, 850, 710.

(3) 3-Chloro-2-chloromethyl-1-propylacetate (CCMPAC).

Acetyl chloride (33.2 g, 0.42 mol) was slowly added to 60 g (0.43 mol) CCMPOL at room temperature. The reaction temperature reached a maximum of 35° C and after 3 hr 10 mL of distilled water and 3 grams of sodium bicarbonate were added to terminate the reaction. The reaction was taken up into ethyl ether and washed with 200 mL saturated aqueous sodium bicarbonate, 2 x 200 mL distilled water and 300 mL brine. After drying over $MgSO_4$ fractional distillation yielded 69.2 g (0.37 mol, 89%) CCMPAC (b.p. 140° C/30 mm).of 95% purity (GC). $^1H$ NMR (200 MHz, $CDCl_3$) δ: 4.16 (2H, doublet); 3.66 (4H, quartet); 2.41 (1H, multiplet); 2.06 (3H, singlet). IR (NaCl, neat ) $cm^{-1}$: 2975, 2917, 1735, 1525, 1376, 1250, 1048, 837, 742, 690, 640.

(4) 3-(Chloromethyl)oxetane (3CMO) from CCMPAC.

To a solution of 26 g (0.65 mol) sodium hydroxide in 60 mL water that had been heated to reflux 34 g (0.3 mol) CCMPAC was added via dropping funnel. After 2 hours at reflux the reaction was cooled and extracted with 3 x 100 mL $CH_2Cl_2$ and the combined extracts dried over $MgSO_4$. Fractional distillation yielded 6.7 g (0.06 mol, 21%) 3CMO (b.p. 64° C/30 mm).

**j. Attempted synthesis of 2-(2-bromoethyl)oxetane.**

(1) 4-Tetrahydropyranyloxy-1-butene (BEATHP).

Dihydropyran (30 g, 0.35 mol) was slowly added to 25 g (0.35 mol) 3-buten-1-ol containing 0.20 g pTSA at 45° C. After 16 hr the reaction mixture was taken up into 300 mL $CH_2Cl_2$ and successively extracted with 300 mL saturated aqueous sodium bicarbonate, 300 mL distilled water and 500 mL brine. After drying over $MgSO_4$ fractional distillation yielded 30.5 g (0.195 mol, 56%) BEATHP (bp 52° C/10 mm). Anal calcd for $C_9H_{16}O_2$: C, 69.2; H, 10.3. Found: C, 69.1; H, 10.3. $^1H$ NMR (200 MHz, $CDCl_3$) δ: 5.82 (1H, multiplet); 5.05 (2H, quartet);

4.57 (1H, triplet); 3.78 (2H, multiplet); 3.41 (2H, multiplet); 2.30 (2H, multiplet); 1.4-1.9 (6H, multiplet). $^{13}C$ NMR (50 MHz, $C_6D_6$) δ: 136.0, 116.3, 98.6, 67.0, 61.7, 35.0, 31.2, 26.2, 19.9. IR (NaCl, neat) $cm^{-1}$: 3100, 2960, 2882, 1650, 1450, 1361, 1208, 1145, 1130, 1041, 998, 910, 875, 820.

(2) (2-Tetrahydropyranyloxyethyl)oxirane (THPEO).

m-Chloroperoxybenzoic acid (85%, 39 g, 0.19 mol) was slowly added to 30 g (0.19 mol) BEATHP in 300 mL $CH_2Cl_2$ at 0° C under $N_2$. The reaction was allowed to warm to room temperature and stirred for 14 hr. After removal of the solid m-chlorobenzoic acid by filtration the mixture was extracted with 2 x 200 mL portions of saturated aqueous sodium sulfite, 250 mL of distilled water and 500 mL of brine. The organic layer was dried over $MgSO_4$ and fractionally distilled to yield 24.2 g (0.14 mol, 74%) THPEO (bp 78° C/10 mm). $^{13}C$ NMR (75 MHz, $CDCl_3$) δ: 99.14; 98.72; 64.43; 64.13; 62.52; 62.28; 50.2; 47.3; 33.0; 30.6; 25.8; 19.81; 19.64. IR (NaCl, neat) $cm^{-1}$: 2980, 2890, 1445, 1355, 1200, 1130, 1040, 980, 905, 870.

(3) 2-(2-Tetrahydropyranyloxyethyl)oxetane (THP2EO).

THPEO (20 g, 0.12 mol) was added dropwise to 0.19 mol of dimethyl sulfoxonium methylide in 400 mL of t-butanol at 50° C under $N_2$. After stirring for 96 hr at 50° C the t-butanol was removed by evaporation and the remaining material was taken up into 100 mL $CH_2Cl_2$ and washed with 2 x 100 mL $H_2O$ and 200 mL brine. Fractional distillation yielded 12.5 g (67 mmol, 58%) THP2EO (bp 110° C/10 mm). $^1H$ NMR (300 MHz, $CDCl_3$) δ: 4.99 (1H, multiplet); 4.68 (1H, quartet); 4.57 (2H, multiplet); 3.84 (2H, multiplet); 3.49 (2H, multiplet); 2.71 (1H, multiplet); 2.07 (2H, multiplet); 1.4-1.9 (6H, multiplet). $^{13}C$ NMR (50 MHz, $C_6D_6$) δ: 99.53, 99.26, 80.22, 68.36, 63.61, 63.48, 62.02, 61.85, 38.5, 28.48, 26.06, 20.0. IR (NaCl, neat) $cm^{-1}$: 2950, 2885, 1460, 1450, 1390, 1360, 1205, 1143, 1070, 1040, 982, 904, 875, 820.

(4) 2-(2-Hydroxyethyl)oxetane (HE2O).

THP2EO (12 g, 62 mmol) was added to 200 mL methanol containing 0.2 g pyridinium tosylate and the mixture was heated to 40° C under $N_2$ for 4 hr. Then 200 mL of saturated aqueous sodium bicarbonate was added and the methanol was removed by evaporation. The remaining aqueous layer was then extracted with 3 x 300 mL petroleum ether and 4 x 300 ethyl

ether. Concentration of the ethyl ether extracts yielded 5 g of material shown by $^1$H NMR to be HE2O of approx 75% purity. $^1$H NMR (200 MHz, $CDCl_3$) δ: 5.09 (1H, multiplet); 4.20 (2H, multiplet); 3.78 (2H, multiplet); 2.72 (1H, multiplet); 2.42 (1H, multiplet); 1.98 (2H, multiplet); 3.3 (1H, singlet, $D_2O$ exchangeable).

**k. Attempted synthesis of 3-(bromomethyl)oxetane.**

(1) 3-Bromo-2-bromomethyl-1-propene

Tetrabutylammonium bromide (79.4 g, 0.25 mol) and sodium bromide (105 g, 10 mol) were added to 2 L of t-butanol at 50° C under $N_2$. To this was added 237.6 g (1.9 mol) of 3-chloro-2-chloromethyl-1-propene. After stirring for 48 hr at 50° C the solution was hot filtered and the t -butanol removed by evaporation and the remaining material taken up in 1L of $CH_2Cl_2$. This was washed with 2 x 250 mL $H_2O$ and 1 x 500 mL brine. After drying over $MgSO_4$ fractional distillation (bp 80-90 ° C/80 mm) yielded 220 g (1 mol, 54%) of 3-bromo-2-bromomethyl-1-propene of approximately 90% purity (GC). $^1$H NMR (200 MHZ, $CDCl_3$) δ: 5.34 (2H, singlet); 4.14 (4H, singlet). IR (NaCl, neat) cm$^{-1}$: 3090, 2965, 2821, 1860, 1639, 1422, 1397, 1210, 1105, 925, 730, 665.

(2) 3-Bromo-2-bromomethyl-1-propanol (BBMPOL).

3-Bromo-2-bromomethyl-1-propene 78.3 g (0.37 mol) was slowly added under $N_2$ to 220 mL of $BH_3$-THF (1M in $BH_3$, 0.22 mol $BH_3$) at 0° C. The reaction was allowed to slowly come to room temperature. Stirring was continued for an additional 12 hr under $N_2$ after which 74 g of 30 wt% aqueous $H_2O_2$ (0.66 mol $H_2O_2$) and 70 g of 30% aqueous NaOH (0.64 mol NaOH) were added in turn insuring that the reaction temperature did not exceed 60° C. After 4 hr of stirring at room temperature 500 mL ether was added and the layers separated. The organic layer was washed with 2 x 500 mL saturated sodium sulfite, 2 x 500 mL $H_2O$ and 500 mL brine. Fractional distillation (76° C/ 0.22 mm) yielded 17 g (73 mmol, 20%) BBMPOL. $^1$H NMR (200 MHz, $CDCl_3$) δ: 3.72 (2H, doublet); 3.52 (4H, multiplet); 2.83 (1H, singlet); 2.1 (1H, multiplet). $^{13}$C NMR (50 MHz, $C_6D_6$) δ: 62.1, 44.8, 33.3. IR (NaCl, neat) cm$^{-1}$: 3460, 2965, 2890, 1437, 1260, 1103, 815, 657.

**l. Trimethylolmethane for the attempted synthesis of 3-(hydroxymethyl)oxetane.**

A solution of 50 g (0.22 mol) triethyl methanetricarboxylate in 400 mL THF under inert atmosphere was brought to reflux in a 2 L 3-neck round bottom flask equipped with a fractionating stillhead. To this was added via cannula, 440 mL of $BH_3$-$Me_2S$ complex in THF (2M in $BH_3$, 0.88 mol) at a rate which allowed for the maintenance of the reflux. After 30 min at reflux the stillhead was opened to allow for the collection of $Me_2S$/THF distillate. After obtaining 700 mL of distillate the reaction was cooled and 300 mL of methanol was slowly added. Evaporation of the solvent left a viscous oil which crystallized after vacuum drying to give 21 g (0.20 mol, 90% ) of trimethylolmethane (mp 78° C lit mp 74° C[65]). $^1H$ NMR (200 MHz, $D_2O$) δ: 4.63 (3H, singlet); 3.48 (6H, doublet); 1.73 (1H, multiplet).

**m. Tetrabutylammonium benzoate (TBAB).**

Benzoic acid (245 g, 2 mol) was added to 1300 g of aqueous tetra-n-butylammonium hydroxide (2 mol $Bu_4NOH$) in an open flask at room temperature. After the disappearance of the solid benzoic acid the solution was extracted twice with 1L $CHCl_3$. After drying over $MgSO_4$ removal of the solvent left an off-white solid which was triturated with 1 L of anhydrous ether and then dissolved in 500 mL anhydrous ethanol. The ethanol solution was heated to reflux under $N_2$ at which time an equal volume of hexanes was slowly added. Cooling of the solution to -10° C resulted in crystallization. After filtration and vacuum drying at room temperature with $P_2O_5$ as a desiccant 385 g (1.05 mol, 51%) of TBAB was isolated. $^1H$ NMR (200 MHz, $D_2O$) δ: 8.09 (2H, multiplet); 7.28 (3H, quartet); 3.31 (8H, multiplet); 1.61 (8H, multiplet); 1.43 (8H, multiplet); 0.980 (12H, triplet). $^{13}C$ NMR (75 MHz, $CDCl_3$) δ: 170.6, 140.0, 129.3, 128.6, 126.9, 58.2, 23.7, 19.4, 13.4.

**2. Preparation of Polymerization Initiators.**

**a. Triethylaluminum-based initiators.**

Triethylaluminum-based initiators were prepared in dry $N_2$-purged Schlenk tubes or septum-capped tubes equipped with magnetic stir bars. The needed amount of

triethylaluminum was charged via gas-tight syringe or cannula. After cooling in an ice bath, 2,4-pentanedione [acetylacetone (AcAc)] if needed, was added slowly with vigorous stirring and followed by slow addition of the required amount of distilled water. All of these initiators were aged at room temperature under $N_2$ for a minimum of 10 hr before use. Typical recipes for the triethylaluminum-based catalysts are shown in Table II.2. All catalysts were stored under positive $N_2$ atmosphere, protected from light and used within 48 hr.

Table II.2. Triethylaluminum Initiators.

| Initiator | $Et_3Al : H_2O:AcAc$ | $Et_3Al$ (mL:mmol) | AcAc (mL:mmol) | $H_2O$ (mL:mmol) |
|---|---|---|---|---|
| AL1[a] | 1.0 : 0.5 : 0 | 10:10 | -- | 0.09:5.0 |
| AL2[b] | 1.0 : 0.5 : 0.5 | 10:19 | 0.49:4.9 | 0.17:9.5 |
| AL3[b] | 1.0 : 0.5 : 0.5 | 5:9.5 | 0.49:4.9 | 0.085:4.8 |
| AL4[b] | 1.0 : 0.5 : 0.5 | 10:19 | 1.96:19 | 0.17:9.5 |

a. Prepared from 1M $Et_3Al$ in hexanes.
b. Prepared from 25% $Et_3Al$ in toluene.

During the preparation of initiators AL1-AL3 a white precipitate formed. This precipitate was not transferred during any of the polymerizations. Initiators of type AL4 were consistently found to be homogeneous.

**b. Acetyl hexafluorantimonate initiator.**

$AgSbF_6$ was prepared by the addition under $N_2$ of 5.8 g (75 mmol) acetyl chloride to 50 mL (75 mmol) of an $AgSbF_6$ solution (1.5 M in $CH_2Cl_2$). Removal of the white AgCl by filtration left a dark solution that was kept protected from light until use.

**3. Preparation of Polymers.**

**a. Poly(bromomethyloxirane) (PBMO).**

(1) Polymerization of bromomethyloxirane (BMO) with initiator of type AL3.

To 31 g (230 mmol) bromomethyloxirane in an Ar purged, septum capped beverage bottle was slowly added 6.7 mL (11.3 mmol Al) of an initiator of type AL3. After 4 hr at room temperature the polymer was precipitated by addition of the reaction mixture to 500 mL of MeOH. After vacuum drying the polymer was suspended in 200 mL of hot $CHCl_3$ and stirred for 3 hours. Subsequent filtration of the suspension followed by vacuum drying yielded 16.4 g (53%) of chloroform insoluble material. Concentration of the chloroform solution followed by two precipitations from $CHCl_3$ into MeOH yielded 0.47 g (1.5%) PBMO of $\eta_{inh}$ (30° C, 0.5 g/dl, $CHCl_3$): 1.1 dl/g. $^{13}C$ NMR (75 MHz, $CDCl_3$) δ: 78.7, 70.6, 32.0.

(2) Polymerization of BMO with initiator of type AL4.

To 25 g (183 mmol) bromomethyloxirane in an Ar purged, septum capped beverage bottle was slowly added 7.5 mL (12 mmol Al) of an initiator of type AL4. After 4 hr at room temperature the polymer was precipitated by addition of the reaction mixture to 500 mL of MeOH. After vacuum drying the polymer was suspended in 200 mL of hot $CHCl_3$ and stirred for 3 hours. Subsequent filtration of the suspension and concentration of the chloroform solution to 20 mL followed by two precipitations from $CHCl_3$ into MeOH yielded 3 g (12%) PBMO. $\eta_{inh}$ (30° C, 0.5 g/dl, $CHCl_3$): 0.8 dl/g.

**b. Poly[(2-bromoethyl)oxirane] (PBEO).**

(1) Polymerization of BEO with initiator of type AL3.

To 22 g (150 mmol) (2-bromoethyl)oxirane in an Ar purged, septum capped beverage bottle was slowly added 5 mL (8.5 mmol Al) of an initiator of type AL3. After 24 hr at room temperature the polymerization mixture was dissolved in $CHCl_3$. The solution was filtered, and the polymer was precipitated by addition of the solution to a ten-fold excess of methanol.

After 1 additional dissolution and precipitation 14.7 g (67%) PBPO was obtained as a soft, white elastomer. $\eta_{inh}$ (30° C. 0.5 g/dl $CHCl_3$): 0.6 dl/g. Anal calcd for $[C_4H_7BrO]_n$: C, 31.8; H, 4.7. Found: C, 31.5; H, 4.5. $^1H$ NMR (200 MHz, $CD_2Cl_2$) δ: 3.3-3.7 (5H, broad); 2.0 (2H, broad). $^{13}C$ NMR (75 MHz, $C_6D_6$) δ: 77.58, 72.55, 35.66, 30.50.

(2) Polymerization of BEO with initiator of type AL4.

To 28 g (185 mmol) (2-bromoethyl)oxirane in an Ar purged, septum capped beverage bottle was slowly added 5 mL (8.5 mmol Al) of an initiator of type AL4. The reaction was stirred for 24 hr followed by dissolution into $CHCl_3$. Two precipitations of the polymer from $CHCl_3$ solution into MeOH gave 18.8 g (67%) of PBEO. $\eta_{inh}$ (30° C. 0.5 g/dl $CHCl_3$): 3.5 dl/g. Tg (DSC, heating rate 20° C/min): -18° C.

**c. Poly[(3-bromopropyl)oxirane] (PBPO).**

(1) Polymerization of BPO with initiator of type AL3.

To 15 g (91 mmol) (3-bromopropyl)oxirane in an Ar purged, septum capped beverage bottle was slowly added 10 g (5.5 mmol Al) of an initiator of type AL3. After 3 hr at room temperature the polymerization mixture was dissolved in 200 mL boiling $CHCl_3$. The solution was cooled to room temperature and filtered, and the polymer was precipitated by addition of the solution to a ten-fold excess of methanol. Two further dissolution-precipitation cycles afforded 5.2 g (35%) PBPO as a soft, white elastomer. $\eta_{inh}$ (30° C. 0.5 g/dl $CHCl_3$): 0.5 dl/g. Anal calcd for $[C_5H_9BrO]_n$: C, 36.4; H, 5.5. Found: C, 36.1; H, 5.5. $^1H$ NMR (200 MHz, $CD_2Cl_2$) δ: 3.3-3.7 (5H, broad); 1.9 (2H, broad); 1.7 (2H, broad). $^{13}C$ NMR (75 MHz, $C_6D_6$) δ: 79.15, 73.11, 34.18, 30.92, 29.23.

(2) Polymerization of BPO with initiator of type AL4.

To 10 g (61 mmol) (2-bromoethyl)oxirane in an Ar purged, septum capped beverage bottle was slowly added 2.5 mL (4.1 mmol Al) of a initiator of type AL4. The reaction was stirred for 24 hr followed by dissolution into $CHCl_3$. Two precipitations of the polymer from

$CHCl_3$ solution into MeOH afforded 7.4 g (74%) of PBPO. $\eta_{inh}$ (30° C. 0.5 g/dl $CHCl_3$): 0.6 dl/g. Tg (DSC, heating rate 20° C/min): -39° C.

**d. Poly[(4-bromobutyl)oxirane] (PBBO).**

(1) Polymerization of BBO with initiator of type AL3.

To 4.0 g (22 mmol) (4-bromobutyl)oxirane in an Ar purged, septum capped beverage bottle was slowly added 0.75 mL (1.3 mmol Al) of an initiator of type AL3. After 24 hr at room temperature the polymerization mixture was dissolved in $CHCl_3$. The solution was filtered, and the polymer was precipitated by addition of the solution to a ten-fold excess of methanol. After 1 additional dissolution and precipitation 14.7 g (67%) PBPO was obtained as a soft, white elastomer. $\eta_{inh}$ (30° C. 0.5 g/dl $CHCl_3$): 0.6 dl/g. Anal calcd for $[C_6H_{11}BrO]_n$: C, 40.2; H, 6.2. Found: C, 39.6; H, 6.2. $^1H$ NMR (300 MHz, $CDCl_3$) δ: 3.3-3.7 (5H, broad); 1.8 (2H, broad); 1.5 (4H, broad). $^{13}C$ NMR (75 MHz, $C_6D_6$) δ: 79.73, 73.20, 34.22, 33.51.

(2) Polymerization of BBO with initiator of type AL4.

To 4.2 g (25 mmol) (4-bromobutyl)oxirane in an Ar purged, septum capped beverage bottle was slowly added 0.9 mL (1.6 mmol Al) of an initiator of type AL4. The reaction was stirred for 24 hr followed by dissolution into $CHCl_3$. Two precipitations of the polymer from $CHCl_3$ solution into MeOH, afforded 2.7 g (68%) of PBBO. $\eta_{inh}$ (30° C. 0.5 g/dl $CHCl_3$): 1.7 dl/g. Tg (DSC, heating rate 20° C/min): -52° C.

**e. Poly[(2-chloroethyl)oxirane] (PCEO).**

(2-Chloroethyl)oxirane (17.0 g, 160 mmol) was purged with $N_2$ in a septum capped polymerization ampule and cooled to 0° C. To this was added 5.0 mL (8.0 mmol Al) of an initiator of type AL4 . The ampule was heated in an oil bath at 80° C for 24 hr. Two precipitations from $CH_2Cl_2$ into methanol yielded 6.3 g (59 mmol equivalents, 37%) of PCEO. $\eta_{inh}$ (30° C. 0.5 g/dl $CHCl_3$): 2.3 dl/g. GPC ($CHCl_3$) : Mn-237,000; Mw-688,000. $^1H$ NMR (200 MHz, $CDCl_3$) δ: 3.5-3.8 (5H, broad multiplet); 2.0 (2H, broad multiplet). $^{13}C$ NMR (75 MHz, $CD_2Cl_2$) δ: 76.8, 75.6, 42.1, 35.7.

**f. Poly[(3-chloropropyl)oxirane] (PCPO).**

(3-Chloropropyl)oxirane (8.0 g, 66 mmol) was purged with $N_2$ in a septum capped polymerization ampule and cooled to 0° C. To this was added 2.0 mL (3.2 mmol Al) of an initiator of type AL4 . Then the ampule was heated in an oil bath at 80° C for 24 hr. Two precipitations from $CH_2Cl_2$ into methanol yielded 6.0 g (50 mmol equivalents, 75%) of PCPO. $\eta_{inh}$ (30° C. 0.5 g/dl $CHCl_3$): 1.9 dl/g. GPC ($CHCl_3$) : Mn-198,000; Mw-1,250,000. $^1$H NMR (200 MHz, $CDCl_3$) δ: $^{13}$C NMR (75 MHz, $C_6D_6$) δ: 79.2, 74.1, 45.3, 29.6, 29.2.

**g. Poly[(4-chlorobutyl)oxirane] (PCBO).**

(4-Chlorobutyl)oxirane (20.0 g, 150 mmol) was purged with $N_2$ in a septum capped polymerization ampule and cooled to 0° C. To this was added 4.5 mL (7.2 mmol Al) of an initiator of type AL4 . The ampule was heated in an oil bath at 80° C for 24 hr. Two precipitations from $CH_2Cl_2$ into methanol yielded 11.6 g (87 mmol equivalents, 58%) of PCPO. $\eta_{inh}$ (30° C. 0.5 g/dl $CHCl_3$): 4.6 dl/g. GPC ($CHCl_3$) : Mn-260,000; Mw-1,110,000. $^1$H NMR (200 MHz, $CDCl_3$) δ: 3.2-3.8 (5H, broad multiplet); 2.9 (2H, broad); 2.5 (4H, broad). $^{13}$C NMR (75 MHz, $C_6D_6$) δ: 79.4, 73.1, 45.0, 33.4, 31.6, 23.1.

**h. Poly(3-chlorooxetane) (P3CO).**

(1) Polymerization of 3CO with initiator of type AL4.

3-Chlorooxetane (1.5 g, 16 mmol) was added to an $N_2$ purged polymerization ampule which was then cooled to 0° C (ice water bath). To this was added 0.6 mL of a initiator of type AL4 (0.11 mmol of Al). The ampule was then degassed by three vacuum freeze/thaw cycles and sealed. After heating at 80° C for 24 hr the polymerization was quenched by opening to air followed by dissolution of the mixture in chloroform and precipitation of the polymer into a tenfold excess of cold methanol to give poly(3-chlorooxetane) as a white elastomer. Yield after two precipitations in MeOH: 1.13 g (76%). Anal calcd for $[C_3H_5OCl]_n$: C, 38.9%; H, 5.4%. Found: C, 38.7%; H, 5.6%. $^1$H NMR (300 MHz, $CDCl_3$) δ: 4.1 (1H, multiplet);

3.6 (4H, multiplet). $^{13}C$ NMR (50 MHz, $CD_2Cl_2$) δ: 72.5, 58.0. Tg (DSC, heating rate 10° C/min): -23° C. $\eta_{inh}$ (30° C. 0.5 g/dl $CHCl_3$): 3.10 dl/g.

(2) Polymerization of 3CO with initiator of type AL3.

3-Chlorooxetane (1.5 g, 16 mmol) was added to an $N_2$ purged polymerization ampule which was then cooled to 0° C (ice water bath). To this was added 0.6 mL of a initiator of type AL4 (0.11 mmol of Al). The ampule was then degassed by three vacuum freeze/thaw cycles and sealed. After 1 hr at 0° C the polymerization was quenched by opening to air followed by dissolution of the mixture in chloroform and precipitation of the polymer into a tenfold excess of cold methanol to give poly(3-chlorooxetane). Yield after two precipitations in MeOH: 1.2 g (49%). $\eta_{inh}$ (30° C. 0.5 g/dl $CHCl_3$): 0.29 dl/g.

(3) Polymerization of 3CO with initiator of type AL2.

A dry, $N_2$ purged polymerization vial was charged with 1.6 g (17 mmol) of 3-chlorooxetane. The vial was cooled to 0° C (ice water bath) and 1.4 mL (0.25 mmol Al) of initiator of type AL2 was added via syringe. The reaction mixture was held at 0° C for 1 hr, and the polymer isolated by precipitation into 50 mL methanol. Dissolution in $CHCl_3$ followed by reprecipitation into methanol gave 1.34 g (84%) of poly(3-chlorooxetane). $\eta_{inh}$ ($CHCl_3$, 0.5 g/dl, 30° C): 0.27 dl/g.

(4) Polymerization of 3CO with initiator of type AL1.

A dry, $N_2$ purged polymerization vial was charged with 0.4 g (4.3 mmol) of 3-chlorooxetane. The vial was cooled to 0° C (ice water bath) and 100 μl (0.02 mmol Al) of the $AlEt_3/H_20$ (AL1) initiator was added via syringe. The reaction mixture was held at 0° C for 1 hr, and the polymer isolated by precipitation into 20 mL of acidic methanol. Dissolution in $CHCl_3$ followed by reprecipitation into methanol gave 0.35 g (89%) of poly(3-chlorooxetane) as a soft gum with an inherent viscosity ($CHCl_3$, 0.3 g/dl, 25° C) of 0.11 dl/g.

(5) Polymerization of 3CO with boron trifluoride etherate ($BF_3OEt_2$).

An $N_2$ purged polymerization vial was charged with 1.5 g (16 mmol) 3-chlorooxetane and cooled to 0° C. $BF_3OEt_2$ (0.1 mL, 0.6 mmol) was added via gas-tight syringe. After 1 hr the reaction was quenched by the addition of 5 mL of MeOH. Subsequent dissolution in chloroform and reprecipitation into MeOH gave a tacky white solid. $\eta_{inh}$: 0.09 dl/g (30° C, 0.5 g/dl, $CHCl_3$).

(6) Polymerization of 3CO with acetyl hexafluorantimonate ($AcSbF_6$).

Acetyl hexafluorantimonate (1 mL of 1.5 M solution in $CH_2Cl_2$, 0.15 mmol) was added via syringe to 0.4 g (4.3 mmol) 3-chlorooxetane in an $N_2$ purged polymerization vial at -20° C. After 1 hr the reaction was quenched by addition to 20 mL of MeOH. After removal of the MeOH and unreacted monomer under vacuum, dissolution in acetone and reprecipitation into water yielded a dark viscous oil, confirmed by $^1H$ NMR as poly(3-chlorooxetane). Yield of reaction 0.09 g (24%).

**i. Copoly(3-chlorooxetane/epichlorohydrin).**

Epichlorohydrin (0.5 g, 5.4 mmol) and 3-chlorooxetane (0.5 g, 5.4 mmol) were charged to an $N_2$ purged polymerization ampule fitted with a septum and cooled to 0° C. A initiator of type AL4 (0.7 mL, 0.13 mmol Al) was added via gas-tight syringe. The ampule was then heated to 80° C for 24 hr under positive $N_2$ pressure in an oil bath. Subsequent precipitation from chloroform into MeOH yielded 0.55 g (55%) of a white elastomer. $^1H$ NMR (300 MHz, $CDCl_3$) δ: 4.1 (triplet), 3.65-3.80 (complex multiplet), 3.6 (triplet). Integration of the $^1H$ NMR spectrum shows the copolymer composition to be 65 mol% epichlorohydrin and 35 mol% 3-chlorooxetane. $^{13}C$ NMR (50 MHz, $CD_2Cl_2$) d: 43.5, 58.2, 69.7, 72.2, 79.0.

**j. Poly[2-(chloromethyl)oxetane] (P2CMO).**

2CMO (1.2 g, 12 mmol) was charged to a septum-capped, $N_2$ purged polymerization vial and cooled to 0° C. To this vial was added 1.45 mL (2 mmol Al) of an initiator solution of type AL4. The vial was heated to 75° C for 6 hr and then to 95° C for an additional 16 hr. Precipitation into 100 mL of methanol yielded 0.17 g (14%) of P2CMO of

inherent viscosity 0.23 dl/g (0.5 wt% in $CHCl_3$, 35°C). Anal calcd for $[C_4H_7ClO]_n$: C,45.1; H, 6.6. Found: C, 44.2; H, 6.38. GPC ($CHCl_3$) : $M_n \approx 38{,}000$; $M_w \approx 126{,}000$. $^1H$ NMR (300 MHz, $CDCl_3$) δ: 3.4-3.8 (5H, m); 1.9 (2H, m). $^{13}C$ NMR (75 MHz, $CDCl_3$) δ: 75.9, 65.7, 46.4, 33.1. Tg (DSC, heating rate 20° C/min): -25° C.

**k. Poly[3-(chloromethyl)oxetane] (P3CMO).**

3CMO (3.6 g, 35 mmol) was charged to septum capped, $N_2$ purged polymerization vial and cooled to 0° C. To this vial was added 1.45 mL (2 mmol Al) of an initiator solution of type AL4. The vial was then heated at 75° C for 24 hr. The resulting polymer was then taken up in 30 mL $CH_2Cl_2$ and precipitation into 500 mL MeOH yielded 1.3 g (43%) of P3CMO of inherent viscosity 1.4 dl/g (0.5 wt% in $CHCl_3$, 35° C). Anal calcd for $[C_4H_7ClO]_n$: C,45.1; H, 6.6. Found: C, 44.1; H, 6.3. GPC ($CHCl_3$) : $M_n \approx 65{,}000$; $M_w \approx 173{,}000$. $^1H$ NMR (300 MHz, $CDCl_3$) δ: 3.63 (2H, d); 3.47 (4H, d); 2.25 (1H, m). $^{13}C$ NMR (75 MHz, $C_6H_6$) δ: 69.3, 43.9, 42.1. Tg (DSC, heating rate 20° C/min): -35°C.

**l. Poly[(benzoyloxymethyl)oxirane] (PBeMO).**

Poly(epichlorohydrin) (0.25 g, 2.7 mmol repeating units) was dissolved in 10 mL of DMAc. To this was added 3.25 g (9.0 mmol) of tetrabutylammonium benzoate and the mixture was heated to 45° C for 84 hours. The reaction was stopped by precipitation into 100 mL of $H_2O$ and after two subsequent reprecipitations from $CHCl_3$ into MeOH 0.40 g (81%) PBeMO was isolated. Anal calcd for $[C_{10}H_{10}O_3]_n$: C, 67.4; H, 5.7. Found: C, 65.24%; H, 5.52%. $^1H$ NMR (200 MHz, $CDCl_3$) δ: 8.0 (2H, doublet); 7.2-7.6 (3H, multiplet); 4.2-4.6 (2H, 2 broad peaks); 3.7 (3H, broad). $^{13}C$ NMR (75 MHz, $CDCl_3$) δ: 166.5, 133.4, 130.3, 129.9, 128.8, 78.1, 70.3, 64.4. Tg (DSC, heating rate 20° C/min): 16° C.

**m. Poly[(2-benzoyloxyethyl)oxirane] (PBeEO).**

Poly[(2-chloroethyl)oxirane] (0.25 g, 2.4 mmol repeating units) was dissolved in 10 mL of DMAc. To this was added 2.7 g (7.5 mmol) of tetrabutylammonium benzoate and the mixture was heated to 45° C for 84 hours. The reaction was stopped by precipitation into 100 mL of $H_2O$ and after two subsequent reprecipitations from $CHCl_3$ into MeOH 0.42 g (92%) PBeEO was

isolated. Anal calcd for $[C_{11}H_{12}O_3]_n$: C, 68.7%; H, 6.3%. Found: C, 66.96%; H, 6.33%. $^1H$ NMR (200 MHz, $CDCl_3$) δ: 8.0 (2H, doublet); 7.2-7.6 (3H, multiplet); 4.4 (2H, broad); 3.3-3.8 (3H, multiplet); 1.6-2.1 (2H, broad). $^{13}C$ NMR (75 MHz, $CDCl_3$) δ: 166.3, 132.8, 130.2, 129.5, 128.3, 76.5, 73.0, 61.6, 31.4. Tg (DSC, heating rate 20° C/min): 6° C

**n. Poly[(3-benzoyloxypropyl)oxirane] (PBePO).**

Poly[(3-chloropropyl)oxirane] (0.10 g, 0.8 mmol repeating units) was dissolved in 5 mL of DMAc. To this was added 1.0 g (2.8 mmol) of tetrabutylammonium benzoate and the mixture was heated to 45° C for 84 hours. The reaction was stopped by precipitation into 100 mL of $H_2O$ and after two subsequent reprecipitations from $CHCl_3$ into MeOH 0.083 g (50%) PBePO was isolated. Anal calcd for $[C_{12}H_{14}O_3]_n$: C, 69.9%; H, 6.8%. Found: C, 66.89%; H, 6.89%. $^1H$ NMR (200 MHz, $CDCl_3$) δ: 8.0 (2H, doublet); 7.2-7.6 (3H, multiplet); 4.3 (2H, broad singlet); 3.3-3.7 (3H, broad); 1.7-2.0 (4H, broad). $^{13}C$ NMR (75 MHz, $CDCl_3$) δ: 166.4, 132.8, 130.3, 129.4, 128.3, 79.0, 72.6, 64.9, 28.5, 24.7. Tg (DSC, heating rate 20° C/min): -10° C.

**o. Poly[(4-benzoyloxybutyl)oxirane] (PBeBO).**

Poly[(2-bromobutyl)oxirane] (0.25 g, 1.9 mmol repeating units) was dissolved in 10 mL of DMAc. To this was added 2.5 g (2.4 mmol) of tetrabutylammonium benzoate and the mixture was heat ed to 45° C for 84 hours. The reaction was stopped by precipitation into 100 mL of $H_2O$ and after two subsequent reprecipitations from $CHCl_3$ into MeOH 0.26 g (64%) PBeBO was isolated. Anal calcd for $[C_{13}H_{16}O_3]_n$: C, 70.9%; H, 7.3%. Found: C, 70.28%; H, 7.35%. $^1H$ NMR (200 MHz, $CDCl_3$) δ: 8.1 (2H, doublet); 7.2-7.6 (3H, multiplet); 4.3 (2H, triplet); 3.3-3.7 (3H, multiplet); 1.4-1.8 (6H, broad doublet). $^{13}C$ NMR (75 MHz, $CDCl_3$) δ: 166.5, 133.2 130.8, 129.9, 128.7, 79.8, 73.0, 65.2, 32.2, 29.2, 22.4. Tg (DSC, heating rate 20° C/min): -15° C.

**4. Polymer Modification Studies.**

**a. $^1H$ NMR investigation of the reaction of TBAB with poly[(ω-bromoalkyl)oxirane]s.**

The procedure is illustrated for PBPO. PBPO (0.0113 g, $6.85 \times 10^{-5}$ mol repeating units) was dissolved over a 48 hr period in 1.6210 g $CDCl_3$ at 45° C. TBAB (0.0500 g, $1.38 \times 10^{-4}$ mol) in

0.644 g $CDCl_3$ was added via syringe. After thorough mixing the reaction mixture was transferred via syringe to an $N_2$ purged screw-cap NMR tube, which was immediately placed into the pre-heated NMR probe at 45° C. Spectra were then taken periodically. See Table II.3, for quantities and concentrations for the reactions studied.

**b. $^{13}C$ NMR investigation of the reaction of TBAB with poly[(ω-chloroalkyl)oxirane]s in DMAc.**

Kinetic analyses were done following the format of the following example for poly(epichlorohydrin) (PECH) at 50° C (reaction CR3, see Table II.4):

PECH (137.9 mg, 1.5 mmol repeating unit) was dissolved in 3.47 g $N_2$ purged DMAc over a 36 hr period with continuous stirring at 50° C. To the PECH solution 0.545 g (1.5 mmol) tetrabutylammonium benzoate (TBAB) in 1.37 g DMAc was added via syringe and the reaction mixture was then transferred to a 10 mm NMR tube. $^{13}C$ NMR spectra were acquired at intervals throughout the reaction, with the temperature maintained at 50°C.

All reactant solutions and NMR tubes were equilibrated at the anticipated reaction temperature for a minimum of 30 min prior to start of reaction. Acquisition parameters for each sample were as listed in Table II.1 (see Measurements). The actual reactant concentrations and reaction temperatures are detailed in Table II.4.

**c. $^{13}C$ NMR investigation of the reaction of TBAB with poly[(ω-bromoalkyl)oxirane]s in DMAc.**

Reaction protocol for the poly[(ω-bromoalkyl)oxirane]s reactions in DMAc was the same as detailed above for the chloroalkyloxiranes, with the exception that a pipet was used to mix the solutions for reactions run at 5° C or below. An example of the method is given below.

For reaction BR6 (Table II.5) 77.1 mg (0.510 mmol) PBEO was dissolved in 1.947 g $N_2$ purged DMAc at room temperature. After stirring for 25 hr the solution was cooled to -10° C in a cooling bath and allowed to equilibrate for 1 hr. After this time a cooled (0° C) solution of 0.185 g (0.511 mmol) TBAB in 0.361 g DMAc was added via pipet ,the combined reactants were transferred via pipet to a 10 mm NMR tube, and the tube was placed into the precooled NMR probe.

All reactant solutions and NMR tubes were equilibrated at the anticipated reaction temperature for a minimum of 30 min prior to start of reaction. Acquisition parameters for each sample were as listed in Table II.1 (see Measurements). The actual reactant concentrations and reaction temperatures are detailed in Table II.5.

**d. $^{13}C$ NMR investigation of the reaction of TBAB with poly[3-(chloromethyl)oxetane].**

The conditions for the reaction of P3CMO were as described for the PECH example given above, and utilized 79.3 mg (0.74 mmol) P3CMO in 2.253 g DMAc and 271 mg (0.74 mmol) TBAB in 0.57 g DMAc.

**e. $^{13}C$ NMR investigation of the reaction of TBAB with poly[2-(chloromethyl)oxetane].**

P2CMO (8.5 mg, 0.080 mmol) was dissolved in 0.35 g DMAc at 50° C over a 12 hr period. This solution was charged to a 5 mm NMR tube under $N_2$ and 29.1 mg (0.080 mmol) TBAB in 0.122 g DMAc was added via syringe. The NMR tube was then placed into the preheated NMR sample chamber at 50° C.

**f. $^{13}C$ NMR investigation of the reaction of TBAB with poly(3-chlorooxetane).**

P3CO (137.9 mg, 1.5 mmol) was dissolved in 3.47 g $N_2$ purged DMAc over a 36 hr period with continuous stirring at 90° C. To the P3CO solution 0.545 g (1.5 mmol) TBAB in 1.37 g DMAc was added via syringe and the reaction mixture was then transferred to a 10 mm NMR tube. $^{13}C$ NMR spectra were acquired at intervals throughout the reaction, with the temperature maintained at 90°C.

**g. $^{13}C$ NMR investigation of the reaction of TBAB with 1-chloropentane.**

The conditions used for the investigation of the kinetics of reaction for 1-chloropentane were the same as those listed above for the poly[(ω-chloroalkyl)oxirane]s. Compositions of reaction mixtures are given in Table II.6.

Table II.3. Reactant Concentrations for $^1H$ NMR Reaction Kinetics Studies in $CDCl_3$.

| Polymer | wt polymer (g) | wt TBAB (g) | $[CH_2Br]_0$ (mol/L) | $[TBAB]_0$ (mol/L) |
|---|---|---|---|---|
| PBMO | 0.0175 | 0.0942 | 0.00857 | 0.0174 |
| PBEO | 0.0108 | 0.0523 | 0.00697 | 0.0140 |
| PBPO | 0.0113 | 0.0500 | 0.00453 | 0.00911 |
| PBBO | 0.0434 | 0.1765 | 0.00388 | 0.00811 |

Table II.4. Compositions of Poly[(ω-chloroalkyl)oxirane] Reactions in DMAc.

| Reaction | Polymer | T (°C) | $[CH_2Cl]_0$ (mol/L) | $[TBAB]_0$ (mol/L) |
|---|---|---|---|---|
| CR1 | PECH | 30 | 0.252 | 0.252 |
| CR2 | PECH | 40 | 0.250 | 0.250 |
| CR3 | PECH | 50 | 0.253 | 0.253 |
| CR4 | PECH | 60 | 0.257 | 0.255 |
| CR5 | PECH | 70 | 0.250 | 0.250 |
| CR6 | PCEO | 5 | 0.220 | 0.220 |
| CR7 | PCEO | 25 | 0.220 | 0.220 |
| CR8 | PCEO | 40 | 0.219 | 0.219 |
| CR9 | PCEO | 50 | 0.220 | 0.220 |
| CR10 | PCEO | 40 | 0.220 | 0.275 |
| CR11 | PCEO | 40 | 0.219 | 0.109 |
| CR12 | PCEO | 40 | 0.146 | 0.220 |
| CR13 | PCEO | 40 | 0.175 | 0.222 |
| CR14[a] | PCEO | 40 | 0.176 | 0.089 |
| CR15 | PCPO | 30 | 0.195 | 0.200 |
| CR16 | PCPO | 40 | 0.194 | 0.198 |
| CR17 | PCPO | 50 | 0.193 | 0.197 |
| CR18 | PCBO | 40 | 0.279 | 0.300 |
| CR19 | PCBO | 40 | 0.174 | 0.174 |

a. Included 0.137 g (0.46 mol) tetrabutylammonium chloride (TBACl) $[TBACl]_0$=0.089 mol/L.

Table II.5. Compositions of Poly[(ω-bromoalkyl)oxirane] Reactions in DMAc.

| Reaction | Polymer | T (°C) | $[CH_2Br]_0$ (mol/L) | $[TBAB]_0$ (mol/L) |
|---|---|---|---|---|
| BR1[a] | PBMO | 20 | 0.137 | 0.143 |
| BR2 | PBMO | 10 | 0.169 | 0.171 |
| BR3 | PBMO | 5 | 0.171 | 0.171 |
| BR4 | PBMO | 0 | 0.137 | 0.139 |
| BR5 | PBEO | 5 | 0.432 | 0.200 |
| BR6 | PBEO | -10 | 0.186 | 0.186 |
| BR7 | PBEO | -10 | 0.232 | 0.172 |
| BR8[a] | PBEO | -10 | 0.309 | 0.162 |
| BR9[a] | PBEO | -10 | 0.385 | 0.158 |

a. Data acquired using 200 transients per spectrum. All others used 400 transients as indicated in Table II.1.

Table II.6. Composition of 1-Chloropentane Reactions in DMAc.

| Reaction | T (°C) | $[CH_2Cl]_0$ (mol/L) | $[TBAB]_0$ (mol/L) |
|---|---|---|---|
| SR1 | 50 | 0.164 | 0.170 |
| SR2 | 40 | 0.163 | 0.163 |
| SR3 | 35 | 0.164 | 0.154 |
| SR4 | 30 | 0.219 | 0.228 |

# CHAPTER III

# RESULTS AND DISCUSSION

## A. Goals and Accomplishments

The goal this work from the outset was to expand upon current knowledge of the effects of polymer structure on the reactivity of attached functional groups. This was to be accomplished by the synthesis of a variety of functionalized polyethers which would encompass a spectrum of structural variations. Subsequent analysis of the reactivity of these polymers toward $S_N2$ substitution would provide a general set of structure-reactivity relations for the polymers.

Polymers were prepared from the polymerizations of a series of ω-bromo- and ω-chloroalkyloxiranes, 3-chlorooxetane, and the two different (chloromethyl)oxetane isomers using $Et_3Al$:$H_2O$:AcAc catalysts to yield high molecular weight elastomeric polymers. The reactivities of these polymers in solution toward $S_N2$ substitution were evaluated using tetrabutylammonium benzoate (TBAB) as the nucleophile in $CDCl_3$ and DMAc.

$^1H$ NMR studies of the reaction of TBAB with the poly[(ω-bromoalkyl)oxirane]s in $CDCl_3$ at 45° C indicated an order of reactivity of butyl ≈ propyl ≈ ethyl > methyl. All of these reactions exhibited distinct negative deviations from second order kinetics after conversion progressed beyond 50%. $^{13}C$ NMR studies in DMAc, of the poly[(ω-bromoalkyl)oxirane]s show that a 60 fold increase in reactivity can be gained by replacement of the chloride functionality with a bromide leaving group.

$^{13}C$ NMR spectroscopy was used in a more extensive study of the reaction of TBAB with all of the chlorinated polyethers in DMAc. For the poly[(ω-chloroalkyl)oxirane]s the order of reactivity was butyl≈propyl>ethyl>>methyl. Poly[3-(chloromethyl)oxetane] was found to react at a rate approximately twice that of poly(epichlorohydrin) while poly[2-(chloromethyl)oxetane] was found to react at a rate equivalent to that of poly(epichlorohydrin). As with the bromide polymers, reactions of the chloride systems in DMAc showed distinct deviations from second order kinetics after moderate conversion.

The reaction conversions were analyzed in terms of 3 rate constants that depend on the state, reacted or unreacted, of the nearest neighbors of a reactive group. These analyses indicate that the pendant reactive groups experience a large decrease in reactivity when both neighbors have reacted but that there is only a slight change in reactivity when only one neighbor has reacted. These analyses also indicate that increases in the length of the pendant chain decrease the effects of having both neighbors reacted.

Rate experiments in DMAc were carried out at a variety of reactant concentrations to demonstrate that the reactions were first order in each of the reactants. Some experiments were carried out at various temperatures to obtain the Arrhenius parameters for the reactions.

The synthetic portion of this work has led to the preparation of three new heterocyclic monomers and four new halogenated polyethers. The kinetic studies reported represent the first attempt to provide a general set of structure-reactivity relationships for nucleophilic substitutions on halogenated polymers.

## B. Monomer and Polymer Preparations

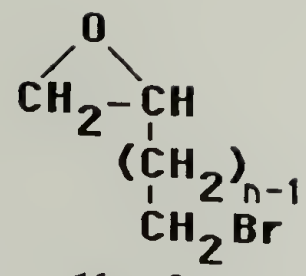
In order to obtain a good understanding of the effects of polymer structure and composition on the reactivity of attached functional groups it is necessary to study a well defined series of systematically different polymers. As mentioned in the introduction, previous work in our laboratory dealt with the modification of polymers of thiiranes and oxiranes containing chloride functional groups. As a continuation of this work a corresponding series of poly[(ω-bromoalkyl)oxirane]s and three novel functionalized oxetane polymers were synthesized. These polymers, aside from being new materials, have allowed us to study the effects of changing the nature and environment of the leaving group. The replacement of the chloride in the oxirane polymers with a bromide should lead to a much more reactive substrate for subsequent modification as is well documented for small molecules.[40] The increased spacing between functional groups found in the polyoxetanes may lead to increased reactivity through reduction of steric interactions.

For the polymerization of all monomers the most satisfactory catalyst system was found to be the 1:0.5:1 $Et_3Al$:$H_2O$:AcAc catalyst developed by Vandenberg for the polymerization of epoxides.[19,20]

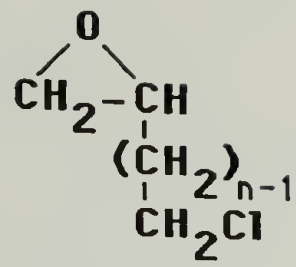
### 1. Poly[(ω-haloalkyl)oxirane] Syntheses.

#### a. Monomer syntheses.

The synthesis of the (ω-haloalkyl)oxiranes used in this work was carried out following the methods established by J. S. Shih.[5] The (ω–bromoalkyl)oxiranes (**16-18**) were obtained by epoxidation of the corresponding commercially available ω-bromoalkenes with m-chloroperoxybenzoic acid. For the (ω-chloroalkyl)oxiranes (**19-21**) an additional step was needed to convert the readily available ω-alkenols into chlorides with thionyl chloride. In all cases, the yields of the epoxidation of the haloalkene exceeded 50% and only a single fractional distillation was needed to obtain monomer of greater than 99% purity (as measured by GC).



16: n=2
17: n=3
18: n=4



19: n=2
20: n=3
21: n=4

**b. Polymerizations.**

(1) (ω-Bromoalkyl)oxirane polymerizations.

Table III.1 summarizes the results of the homopolymerization experiments on (2-bromoethyl)oxirane, (3-bromopropyl)oxirane and (4-bromobutyl)oxirane. In each case, room temperature treatment of the neat monomer with the $Et_3Al$:$H_2O$:AcAc initiators developed by Vandenberg[19,20] afforded the corresponding homopolymer in good yield as a white elastomer. The glass transition temperatures of the polymers were found to decrease with increasing side chain length, and are nearly identical to those reported previously for the corresponding poly[(ω-chloroalkyl)oxirane]s[66] (see Table III.2).

Two aspects of the polymerizations of these monomers are noteworthy. First is the observation that the homopolymers derived from BEO, BPO and BBO are completely soluble in chloroform. This is in contrast to the results of parallel experiments on the homopolymerization of epibromohydrin; treatment of this monomer with the 1:0.5:0.5 triethylaluminum catalyst results in the formation of only 1-2% of chloroform soluble polymer in addition to significant amounts of polymer in a form that was insoluble in hydrocarbons, chlorinated hydrocarbons, cycloheptanone and DMAc. The second point of interest is that higher molecular weights were generally attained by using the initiator prepared from equimolar amounts of $Et_3Al$ and AcAc. This is particularly apparent in the polymerizations of the ethyl and butyl derivatives; the use of different reaction times clouds the issue with respect to BPO. It seems plausible that the improved efficiency of the high-AcAc initiator is a result of chelation of the catalyst sites of highest Lewis acidity and a consequent reduction in chain transfer or termination associated with Al-assisted ionization of the C-Br bond.

Table III.1. Polymerizations of (ω-Bromoalkyl)oxiranes at Room Temperature.

| Monomer | Catalyst[a] | Time (hr) | Yield (%)[b] | $\eta$ inh (dl/g)[c] | $T_g$ (° C)[d] |
|---|---|---|---|---|---|
| BMO | AL3 | 4 | 1.5[e] | 0.8 | |
| | AL4 | 4 | 12 | 1.1 | |
| BEO | AL3 | 24 | 67 | 0.6 | |
| | AL4 | 24 | 63 | 3.5 | -18 |
| BPO | AL3 | 3 | 35 | 0.5 | |
| | AL4 | 24 | 74 | 0.6 | -39 |
| BBO | AL3 | 24 | 65 | 0.6 | |
| | AL4 | 24 | 68 | 1.7 | -52 |

a. $Et_3Al:H_2O:AcAc$ AL3: 1.0:0.5:0.5 AL4: 1.0:0.5:1.0.
b. Isolated after two precipitations.
c. 0.5 g/dl, 30° C, $CHCl_3$.
d. By DSC, with a heating rate of 20°C/min.
e. Yield of chloroform soluble polymer; there was an additional 53% of insoluble material.

(2) (ω-Chloroalkyl)oxirane polymerizations.

Aside from poly(epichlorohydrin), the poly[(ω-chloroalkyl)oxirane]s used in this study were prepared by treatment of the neat monomer with the 1:0.5:1.0 aluminum catalyst. The results of the polymerizations are summarized in Table III.2. J. S. Shih had also prepared this same series of polymers in the course of his research and the yields and molecular weights reported here are in line with his results.[5]

Table III.2. Polymerizations of (ω-Chloroalkyl)oxiranes [a].

| Monomer | Yield (%)[b] | $\eta$ inh (dl/g)[c] | $T_g$ (° C)[d] |
|---|---|---|---|
| CEO | 37 | 2.3 | -27 |
| CPO | 75 | 1.9 | -42 |
| CBO | 58 | 4.6 | -50 |

a. Reaction at 80 ° C for 24 hr with the 1:0.5:1.0 Vandenberg catalyst.
b. Isolated after two precipitations.
c. 0.5 g/dl, 30° C, $CHCl_3$.
d. As recorded by J. S. Shih.[5]

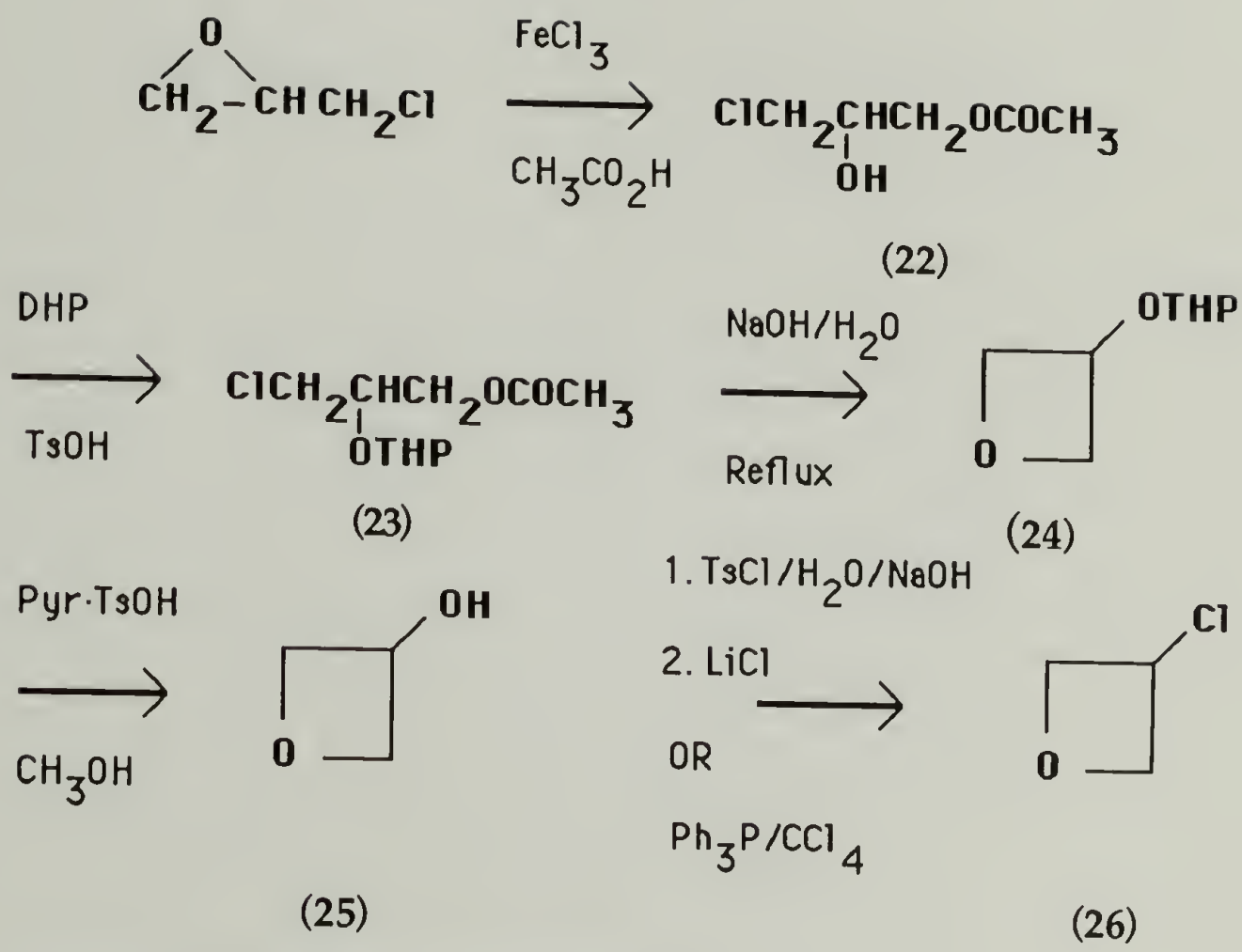
**2. 3-Chlorooxetane, Synthesis and Polymerizations.**

Poly(3-chlorooxetane) (P3CO) was synthesized to give access, with commercial poly(epichlorohydrin), to the ethereal analogs of poly(chloromethylthiirane) and poly(3-chlorothietane). It was of interest to see if these polymers were interconverted in a manner similar to that found for the sulfides. Such a rearrangement was not expected given the low nucleophilicity of ether oxygens and the proven structural stability of PECH.

**a. Monomer preparation.**

3-Chlorooxetane (3CO) was prepared in 12% overall yield from epichlorohydrin using a combination of published methods[36,64] as shown in Scheme III.1. Treatment of epichlorohydrin with acetic acid and ferric chloride afforded the acetoxychlorohydrin (22), which was protected with dihydropyran prior to base catalyzed cyclization to 3-(tetrahydropyranyloxy)oxetane (24). Deprotection, tosylation and displacement of the tosylate with LiCl in triethyleneglycol produced 3CO (26) in a straightforward manner. It was found that displacement of the tosylate could also be accomplished using tetrabutylammonium chloride in triethyleneglycol dimethyl ether. The yields were lower for the latter method (83 vs 45%).

After publication[67] of the initial work on the synthesis 3CO (26) as detailed above, two major improvements were made to the procedure resulting in a 160% increase in overall yield of 3CO based on ECH. The first of these was recognition of the high water solubility of 3-hydroxyoxetane (25), which prompted the use a different workup for the deprotection of 3-tetrahydropyranyloxyoxetane (24) that minimized the loss of the hydroxyoxetane through aqueous washes. The second improvement was to use of triphenylphosphine/$CCl_4$ to produce 3CO (26) directly from 3-hydroxyoxetane (25). Oxetanes are very susceptible to ring opening by acids so all attempts to use acidic chlorinating agents, or those that produce acidic by-products, (e.g., thionyl chloride or phosphorous pentachloride), did not yield 3CO. Triphenylphosphine /$CCl_4$ on the other hand is a very mild chlorinating agent and the by-products of the reaction, triphenylphosphine oxide and chloroform, do not react with either starting or product oxetanes.




(22) (23) (24) (25) (26)

Scheme III.1. Synthesis of 3-Chlorooxetane

**b. Homopolymerization.**

Polymerization of 3-chlorooxetane was accomplished most effectively by treatment of the neat monomer with the $AlEt_3$:$H_2O$:AcAc (1:0.5:1) catalyst developed by Vandenberg.[19,20] Reaction at 80° C for 24 hr afforded a 76% yield of poly(3-chlorooxetane) of inherent viscosity 3.10 dl/g. The uncorrected peak molecular weight of this sample was $5.4 \times 10^5$, based on gel permeation chromatography with polystyrene standards and THF as the elution solvent. The expected ring-opened structure was confirmed by $^1H$ and $^{13}C$ NMR. Poly(3-chlorooxetane) of high molecular weight is a resilient elastomer, and recovers its form rapidly and completely following relief of strains up to 300% at room temperature. Its glass transition temperature as measured by DSC is -23° C , nearly identical to that of its structural isomer poly(epichlorohydrin).[68]

Table III.3 presents the results of the polymerizations initiated with $AlEt_3$ based systems and with the cationic initiators boron trifluoride etherate ($BF_3OEt_2$) and acetyl hexafluoroantimonate ($AcSbF_6$). The latter initiators have been used by Saegusa and coworkers[33] and by Riande *et al* [34] to effect the homopolymerization of 3-methyloxetane. With 3CO, however, the $AlEt_3$ systems are the most effective, and initiator performance improves significantly with increasing chelation by AcAc.

Careful examination of the 50 MHz $^{13}C$ NMR spectra of poly(3-chlorooxetane)s prepared with these initiators reveals differences in microstructure, as well as in molecular weight. Figure III.1 shows the methylene carbon regions of the spectra of samples prepared with two different aluminum catalysts and with $BF_3OEt_2$. Resolution enhancement clearly reveals two distinct methylene signals at 72.06 and 72.11 ppm in each of these spectra; the relative intensities of the signals are dependent on initiator. The lines are approximately equal in intensity in the spectra of polymers prepared with $BF_3OEt_2$ or with the 1:0.5:0.25 $AlEt_3$:$H_2O$:AcAc catalyst system; the polymer prepared with the 1:0.5:1 $AlEt_3$:$H_2O$:AcAc initiator exhibits significantly higher intensity in the upfield resonance. It seems likely that the splitting of the methylene resonance arises from non-equivalence of methylene carbon atoms of meso and racemic dyads. Similar splitting of the O-methylene carbon signal of poly(2-methyloxetane) has been reported by Oguni and Hyoda,[18] who confirmed their assignments in terms of dyad tacticity through the use of optically active monomer. The upfield resonance is

Table III.3. Polymerizations of 3-Chlorooxetane

| Catalyst | Temperature (° C) | Time (hr) | Yield (%) | $\eta_{inh}$ (dL/g) |
|---|---|---|---|---|
| $Et_3Al:H_2O:AcAc$[a] | | | | |
| 1:0.5:0 | 0 | 1 | 89 | 0.11[b] |
| 1:0.5:0.25 | 0 | 1 | 84 | 0.27[c] |
| 1:0.5:0.5 | 0/80 | 1/24 | 49 | 0.29[c] |
| 1:0.5:1.0 | 80 | 24 | 76 | 3.10[c] |
| $BF_3OEt_2$ | 0 | 1 | 39 | 0.09[c] |
| $AcSbF_6$ | 20 | 1 | 24 | oil |

a. $Et_3Al$ 25% by weight in toluene.
b. 0.3 g/dl in $CHCl_3$ at 25° C.
c. 0.5 g/dl in $CH_2Cl_2$ at 30° C.

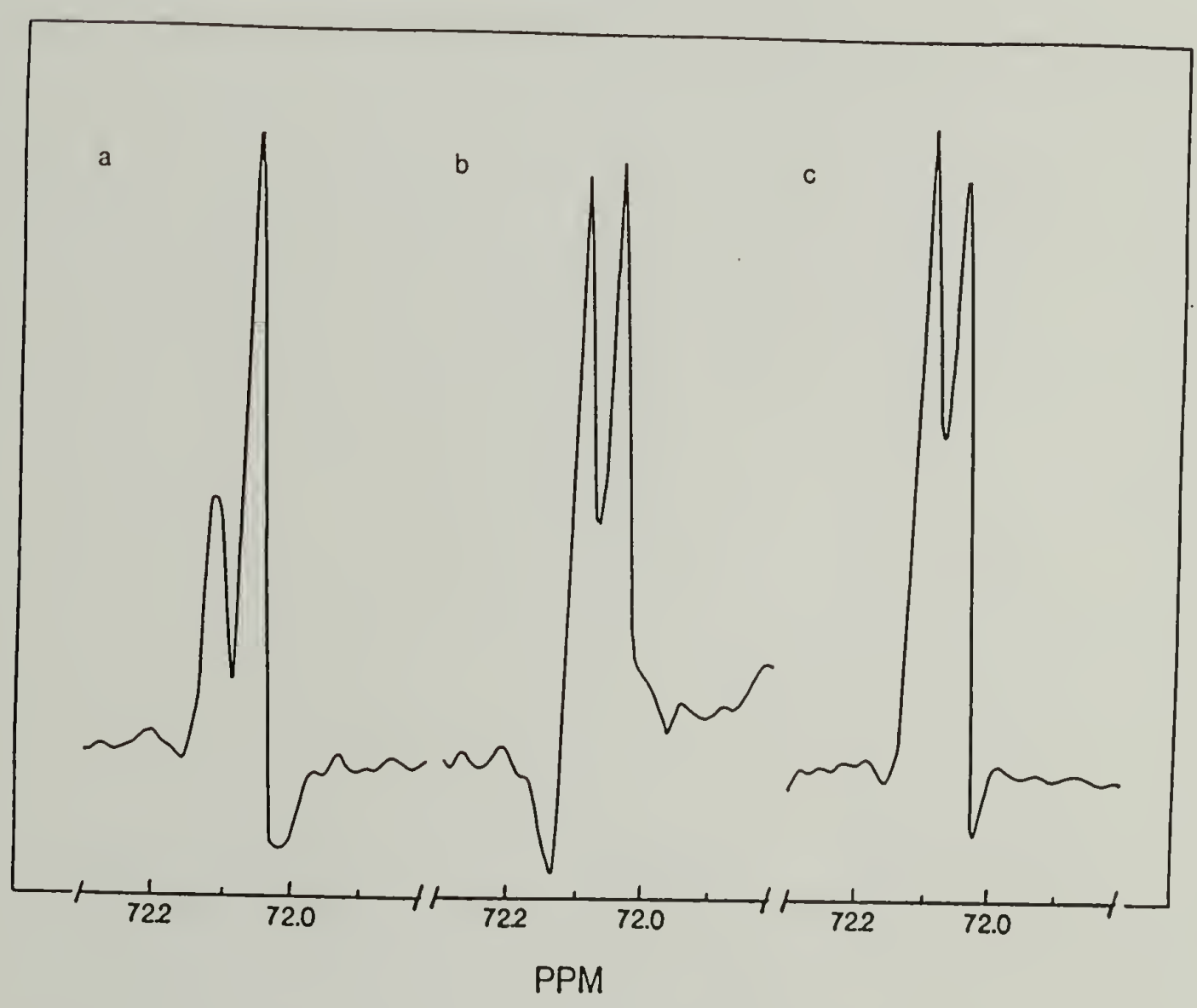



Figure III.1. Resolution-enhanced 50 MHz $^{13}C$ NMR spectra (methylene carbon regions) of samples of poly(3-chlorooxetane) prepared with the following initiators: (a) $AlEt_3:H_2O:AcAc$ (1:0.5:1); (b) $AlEt_3:H_2O:AcAc$ (1:0.5:0.25); (c) $BF_3OEt_2$.

assigned to meso dyads, on the basis of the enhanced intensity of this signal in the spectrum of the polymer prepared with the chelated aluminum catalyst. Chelation by AcAc is known to increase isotacticity in oxirane polymerizations initiated by $AlEt_3$[69], and although the mechanisms of stereoregulation in the two systems differ, it is unlikely that chelation would produce a syndiotactic-specific catalyst for the polymerization of 3CO.

### 3. Synthesis and Polymerizations of (Chloromethyl)oxetanes.

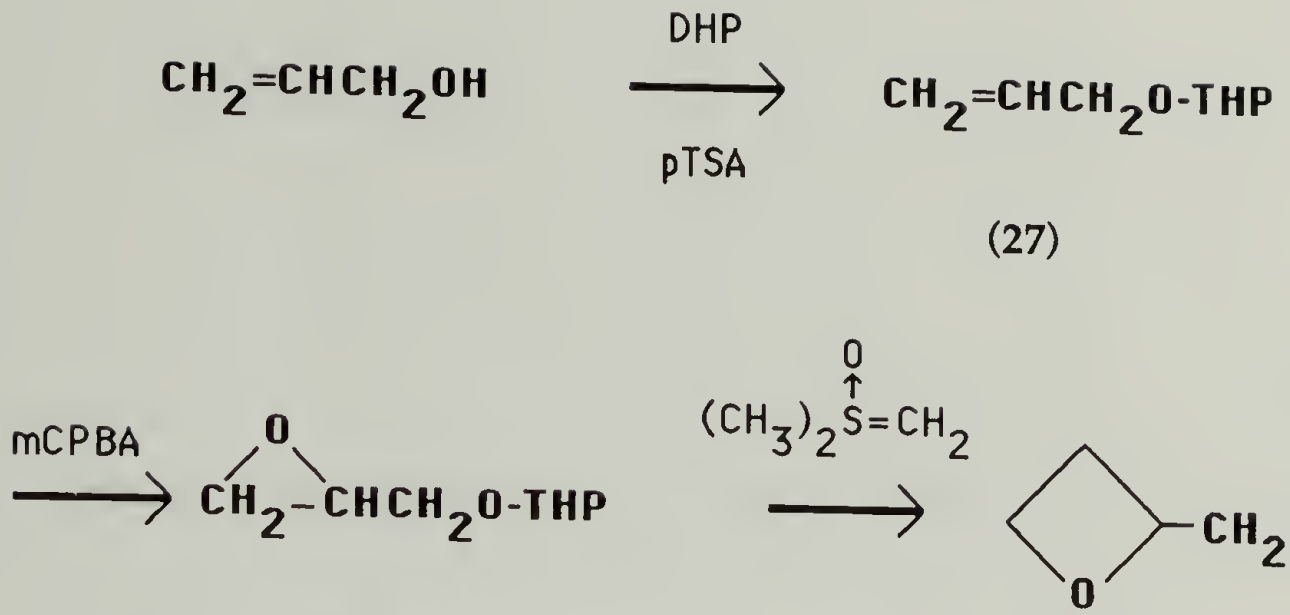
The polymers derived from 2-(chloromethyl)oxetane and 3-(chloromethyl)oxetane present important opportunities to study the effects of variation in polymer structure on bulk properties and functional group reactivity. The two polymers are structural isomers, and each carries a reactive chloromethyl group pendant from the chain backbone. The polymers are, in this regard, analogues of the commercial polyether elastomer poly(epichlorohydrin). There is no prior report of the synthesis of either of these oxetane monomers .

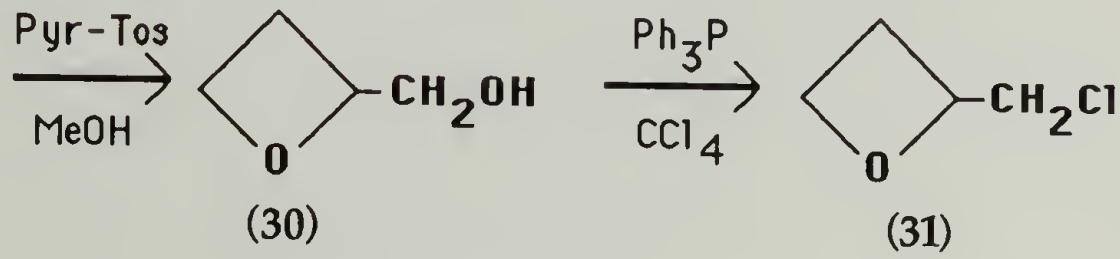
#### a. 2-(Chloromethyl)oxetane.

It was shown by Okuma and coworkers[70] that treatment of epoxides with 2 equivalents of dimethylsulfoxonium methylide gives good yields of oxetanes. Use of this method with a monosubstituted oxirane results in the formation of an oxetane substituted in the 2 position. In Okuma's work only aryl and simple alkyl epoxides were used; however this method should work well for the direct formation of functionalized alkyl oxetanes, provided that the functionality is not base sensitive.

Scheme III.2 shows the route used to obtain 2CMO. Following the protection of allyl alcohol with dihydropyran, the oxirane (**28**) is prepared by reaction with m-chloroperoxybenzoic acid. Ring expansion to the oxetane (**29**) is then readily accomplished with a two-fold excess of dimethylsulfoxonium methylide in t-butanol. After removal of the protecting group with pyridinium tosylate, conversion to the chloride is accomplished with triphenylphosphine in carbon tetrachloride to provide 2CMO (**31**) in 8% overall yield.

The limiting step in the scheme is the removal of the dihydropyran protecting group from the hydroxyl (**29** → **30**). The need for acidic catalysis of the cleavage of the acetal posed a problem as it could lead to a cationic ring opening of either the starting material or more




Scheme III.2. Synthesis of 2-(Chloromethyl)oxetane.

likely the product 2-(hydroxymethyl)oxetane. 2-(Hydroxymethyl)oxetane (30) itself is unstable, and decomposes even when stored at freezer temperatures or on silica gel.

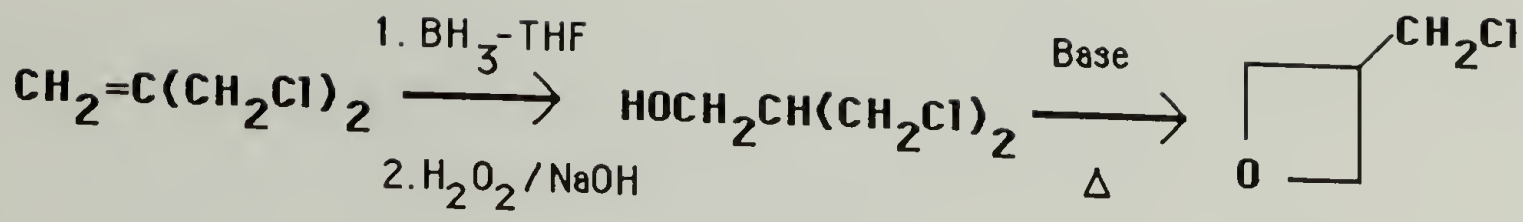
**b. 3-(Chloromethyl)oxetane.**

The syntheses used for 3-(chloromethyl)oxetane were variations on the Williamson ether synthesis which consists of the based mediated intramolecular condensation of an alcohol and a halide. Such a procedure has been successfully used for a variety of 3,3-disubstituted- and 3-alkyloxetanes.[6]

The synthesis of 3-(chloromethyl)oxetane (3CMO) is shown in Scheme III.3. Hydroboration of methallyl dichloride gives 3-chloro-2-(chloromethyl)propan-1-ol (32) in good yield provided that the hydrogen peroxide is added first after the borane addition. The usual procedure of adding NaOH first after borane addition[71] causes the reaction to fail. Cyclization by the reaction with aqueous sodium hydroxide at reflux then follows to give 3CMO (33) in 22% overall yield.

**c. Polymerizations.**

2CMO and 3CMO were polymerized using the $Et_3Al$:$H_2O$:AcAc (1:0.5:1) catalyst, and provided products of high molecular weight as shown in Table III.4. Preliminary investigation of the properties of P2CMO and P3CMO shows that they, like their structural analogue poly(epichlorohydrin), are room temperature elastomers. Their glass transition temperatures of -25° C and -35° C respectively fall below those already mentioned for poly(epichlorohydrin) and their structural isomer poly[(2-chloroethyl)oxirane]; we find no evidence for crystallinity from DSC measurements.




(32) (33)

Scheme III.3. Synthesis of 3-(Chloromethyl)oxetane.

Table III.4. Polymerizations of (Chloromethyl)oxetanes with 1:0.5:1 Vandenberg Catalyst.

| Monomer | Time (hr) | Temperature (° C) | Yield[a] (%) | $\eta_{inh}$[b] (dL/g) |
|---|---|---|---|---|
| 2CMO | c | c | 14 | 0.2 |
| 3CMO | 24 | 75 | 43 | 2.4 |
| 3CMO | 24 | 75 | 37 | 1.6 |

a. Isolated after two precipitations from $CHCl_3$ into MeOH
b. 0.5 g/dl, 30° C, $CHCl_3$.
c. 6 hr at 75° C and 16 hr at 95° C.

**4. Attempted Syntheses of Additional Oxetane Monomers.**

At one time there were plans to study the reactivity of poly[(bromoalkyl)oxetane]s to compare them with the (ω-bromoalkyl)oxirane polymers. This, however, was not to be possible; all attempts to synthesize the monomers came to naught. Following is a brief discussion of the attempted syntheses of some of the monomers.

**a. Attempted synthesis of 2-(bromomethyl)oxetane.**

It was planned to make 2-(bromomethyl)oxetane by a method analogous to that used for 2-(chloromethyl)oxetane described earlier with the only difference between the two syntheses being the use of a brominating agent in the last step for 2-(bromomethyl)oxetane. The addition of 2-(hydroxymethyl)oxetane to the $CBr_4$/triphenylphosphine complex in THF or ether caused complete consumption of the alcohol and formation of the expected by-products, triphenylphosphine oxide and bromoform. However all attempts to isolate pure 2-(bromomethyl)oxetane from the reaction mixture were not successful. The best that was accomplished was the identification of what appeared to be 2-(bromomethyl)oxetane as a minor component in a binary azeotrope with bromoform (bp 50° C /20 mm Hg).

**b. Attempted synthesis of 2-(2-bromoethyl)oxetane.**

The route followed in the attempt to synthesize 2-(2-bromoethyl)oxetane paralleled that used for 2CMO in Scheme III.2, and started with 3-buten-1-ol. The route was successful up through the synthesis of 2-(2-hydroxyethyl)oxetane. Separate attempts to brominate this material with carbon tetrabromide/triphenylphosphine and phosphorus tribromide failed.

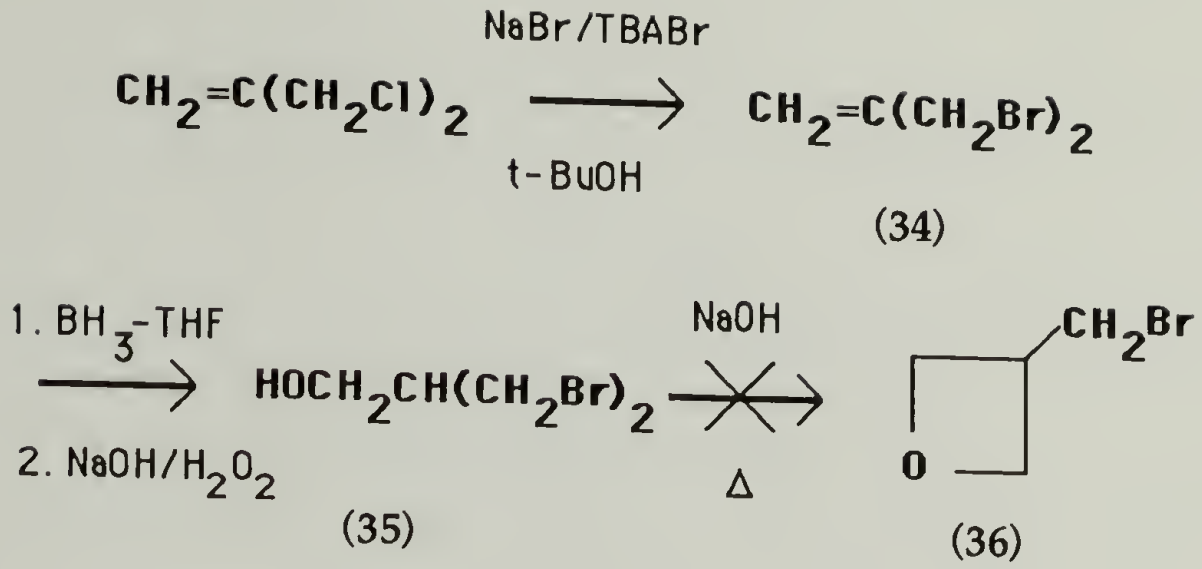
**c. Attempted cyclization of 3-bromo-2-bromomethyl-1-propanol.**

It was believed that 3-(bromomethyl)oxetane (**36**) could be obtained following a route similar to that used for 3-(chloromethyl)oxetane (**33**) as described earlier. The route detailed in Scheme III.4 . 3-Bromo-2-bromomethyl-1-propene (**34**) was made by halide exchange of 3-chloro-2-chloromethyl-1-propene with NaBr and tetrabutylammonium bromide in t-butanol. Hydroboration of this alkene with $BH_3$-THF yielded 3-bromo-2-bromomethyl-1-propanol (**35**) in 20% yield. This yield is significantly below the 73% yield obtained from the corresponding

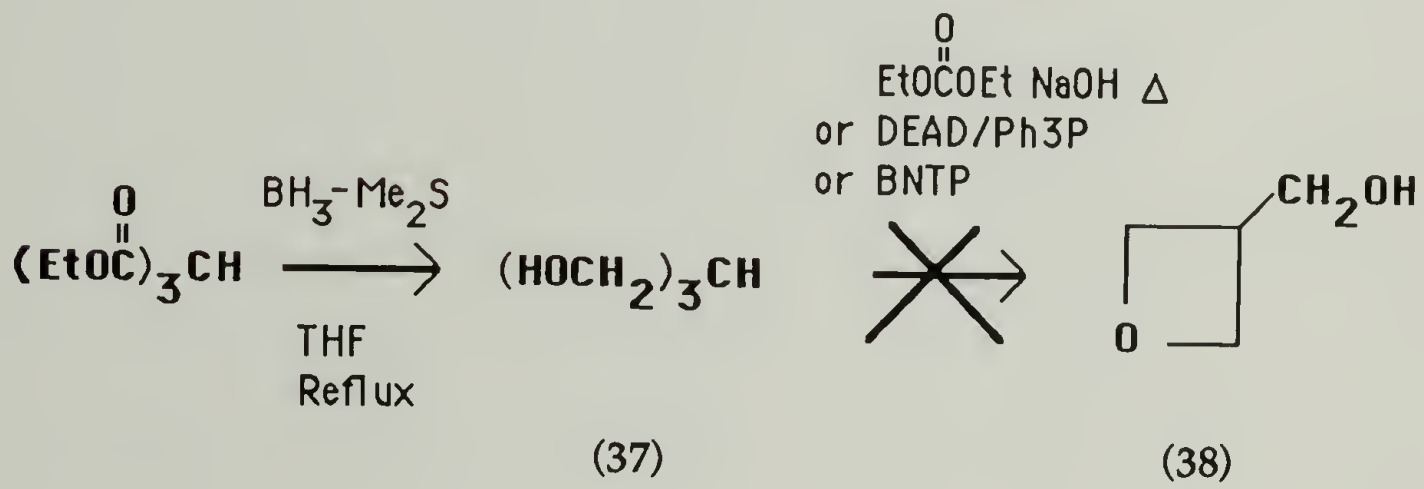
reaction on 3-chloro-2-chloromethyl-1-propene. All attempts to cyclize this haloalcohol failed. The addition of any base (NaOH in refluxing water, NaH in tetraglyme and BuLi in dioxane) appears to have led to dehydrobromination as the primary reaction.

**d. Attempted cyclization of 2-(hydroxymethyl)-1,3-propanediol.**

Once it became apparent that the above cyclization would not work, an attempt was made to perform a cyclization in the absence of reactive bromo groups to give 3-(hydroxymethyl)oxetane (38) which could then be converted to bromo derivative (Scheme III.4). 2-(Hydroxymethyl)-1,3-propanediol (37) was synthesized in 90% yield by the reduction of triethyl methanetricarboxylate with $BH_3$-$Me_2S$.[72] All attempts to cyclize this material by published reactions for the formation of oxetanes using diethylcarbonate,[11,73] diethylazodicarboxylate (DEAD)-triphenylphosphine ($Ph_3P$)[74]and bis(neopentyloxy)triphenylphosphorane (BNTP)[75] failed. Once again it appeared that elimination reactions predominated.




Scheme III.4. Attempted Synthesis of 3-(Bromomethyl)oxetane




Scheme III.5. Attempted Synthesis of 3-(Hydroxymethyl)oxetane.

## C. Structural Stability of Polymers.

### 1. Stability of Poly(3-chlorooxetane).

The repeating unit isomerization that interconverts poly[(chloromethyl)thiirane] and poly(3-chlorothietane) is characterized by a rate constant on the order of $10^{-7}$ $s^{-1}$ at 35° C [76], and the isomerization is readily detected by $^{1}H$ or $^{13}C$ NMR spectrometry. Figure III.2 shows a 50 MHz $^{13}C$ NMR spectrum of a 35:65 copolymer of 3CO and epichlorohydrin, which was prepared from an equimolar mixture of the monomers. Strong resonances from each of the isomeric repeating units are apparent, and it is clear that any repeating unit isomerization of poly(3-chlorooxetane) would be easily revealed by changes in the $^{13}C$ NMR spectrum of the homopolymer. As anticipated, however, heating of poly(3-chlorooxetane) at 80° C in bulk or in DMF caused no important spectral changes over periods of weeks to months.

### 2. Stability of Other Polymers.

The physical condition was visually checked and the chemical nature of all the polymers in this study were monitored by NMR . There was never any indication that any form of repeat unit isomerization had taken place in the neat polymers or in the course of the substitution reactions that will be discussed in the following sections. I do not believe that the ether oxygen in the polymer backbone possesses sufficient nucleophilic character to displace the halides.

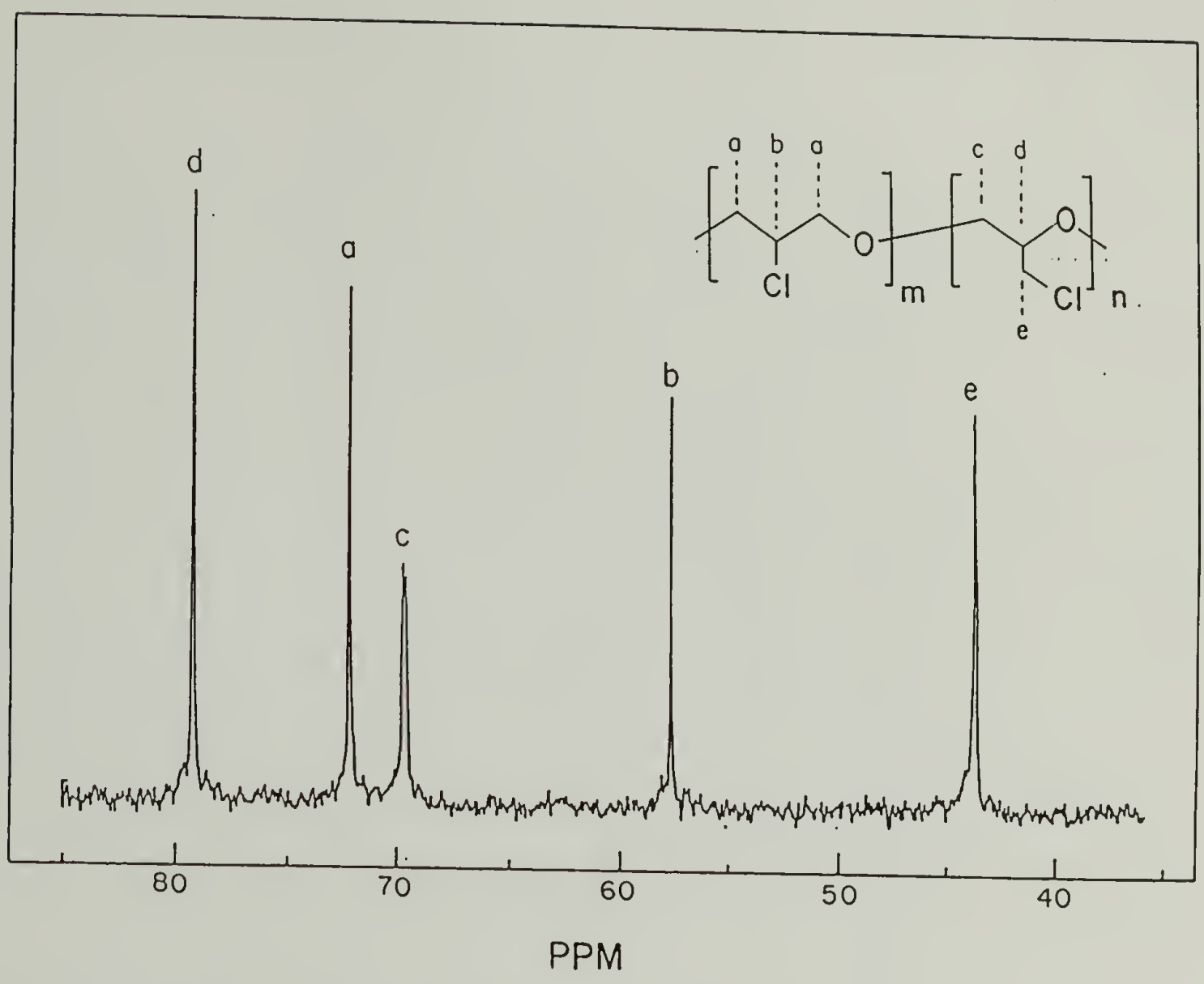



Figure III.2. 50 MHz $^{13}C$ NMR spectrum of a copolymer of 3CO and epichlorohydrin prepared from an equimolar mixture of the monomers.

## D. Polymer Reactions

Previous work in our group[5,66] studied the kinetics of the reaction of tetrabutylammonium benzoate (TBAB) with poly[(ω-chloroalkyl)oxirane]s in dimethylacetamide. The method used required the tedious isolation of the polymer products through the removal of aliquots from the reaction followed by several reprecipitations. The major drawbacks of this method were the use of a relatively large amount of polymer and the possibility of the preferential loss of either reacted or unreacted polymer during isolation.

It was decided that a better method would be to observe directly the progress of the substitution reaction using NMR. This method requires only a small amount of polymer and there is no isolation step. Also this method allows for the easy collection of a large number of data points for each run because the sample could remain in the spectrometer throughout the reaction. TBAB was kept as the kinetic probe because of its demonstrated lack of undesirable side reactions with our polymers and because the signals of the aromatic ring in NMR spectra are far removed from those of the polymer allowing for easy observation.

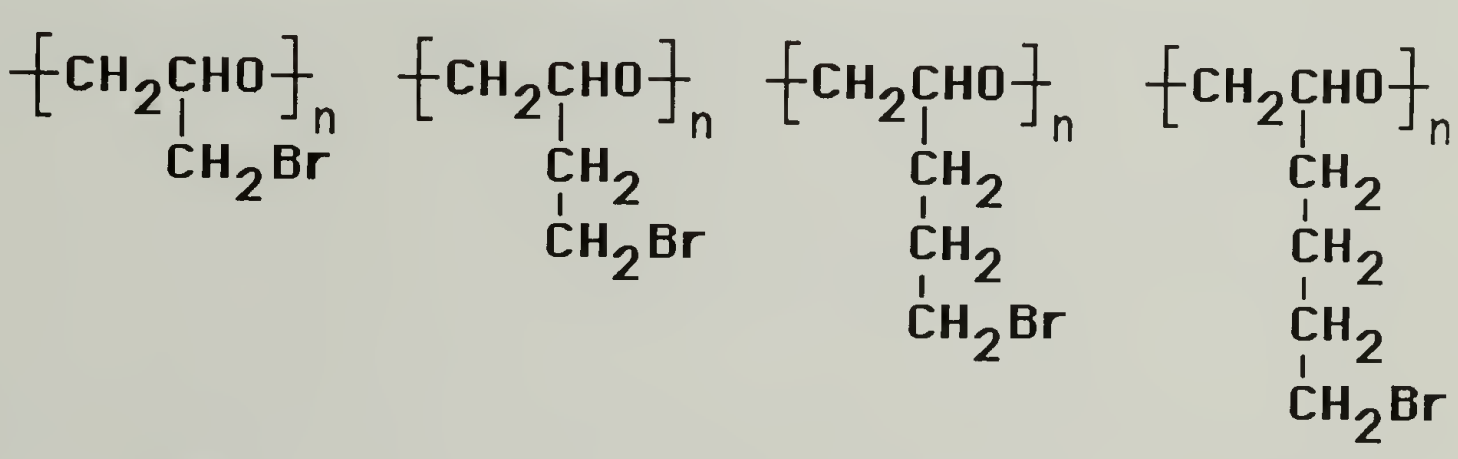
### 1. Kinetics of the Displacement of Bromide by Benzoate Anion in $CDCl_3$.

The method used consists of the separate dissolution of 2 equivalents of TBAB (based on $-CH_2Br$) and the polymer in $CDCl_3$ at 45° C. These solutions are then mixed under $N_2$ and injected into a dry, $N_2$ purged septum capped NMR tube. The tube is immediately placed into the preheated NMR sample probe and spectra are then acquired automatically at prescribed intervals. Individual spectra resulted from the acquisition of 24 transients, each transient comprising a 90° pulse followed by a 2 sec data acquisition period and a 3 sec delay between transients. The resulting spectra are assumed to represent the composition of the system at a time midway through the 2 minute accumulation period. Figure III.3 shows 300 MHz $^1H$ NMR spectra of PBEO (a) and of the same polymer after treatment with TBAB in $CDCl_3$ at 45° C for 30 hr (b). Treatment with benzoate ion introduces new aromatic signals (δ 7.3-8.1) and a strong line at δ 4.4 due to the protons at the point of substitution. The bromomethyl resonance in the spectrum of the starting polymer (δ 3.8) has disappeared and the absence of vinylic resonances

from the spectrum of the product polymer suggests that substitution by benzoate ion is not accompanied by significant dehydrobromination.

Spectra of the reaction mixtures are complicated by strong signals from TBAB. In fact, all of the resonances of the starting polymer are affected, and the most convenient kinetic analysis employs comparative integration of the aromatic signals that arise from TBAB and from polymer-bound benzoate. Figure III.4 shows a series of $^1H$ NMR spectra recorded in situ in the course of the reaction of TBAB with PBBO in $CDCl_3$ over a period of 15 hr. The TBAB-derived signals at δ 7.25 and 8.08 decrease in intensity and are progressively replaced by new resonances from polymer-bound benzoate at δ 7.3-7.6 and 7.9-8.0. The latter resonances shift to higher field with increasing reaction time, perhaps as a result of paramagnetic shielding by adjacent phenyl rings.

Integration of spectra such as those shown in Figure III.4 allows the determination of the extent of displacement of bromide by benzoate ion as a function of time. These results are shown as conversion vs time plots for PBMO (**39**), PBEO (**40**) and PBPO (**41**) in Figure III.5 and as second-order rate plots for these polymers and PBBO (**42**) in Figure III.6. The rate plots in Figure III.6 were used to estimate the rate constants for each of the reactions based on initial slope at low conversion and these values are listed in Table III.5. In addition to observed conversion vs time data Figure III.5 contains calculated second-order conversion curves (solid lines) for the reaction of the polymers that would be expected if the rate constants estimated above were constant throughout the reaction. The reactions of the three high homologues of



(39) (40) (41) (42)

the series, PBEO, PBPO and PBBO show negative deviation from second-order kinetics at high conversion. This phenomenon is thought arise from the steric hindrances about a reaction site when near neighbors have already reacted. Further discussion of this and of the size of the

deviation appears in a later section. For PBMO with TBAB no deviation was noted because the reaction was not followed to high enough conversion.

From this data it can be seen that extension of the side chain from one carbon atom to two ((**40**) → (**41**)) leads to an order-of-magnitude increase in reaction rate. This observation is consistent with known structure-reactivity relations for $S_N2$ reactions on simple alkyl halides. The oxygen atom β to bromide in PBMO (**39**) would be expected to be mildly deactivating,[42] and extension of the side chain removes the β-branch point. In general, the reactivity of β-branched (e.g. isobutyl) halides toward nucleophilic reagents is depressed in comparison with that of primary, straight-chain analogues. For example, Streitwieser lists comparative data for nine reactions of isobutyl and 1-propyl halides;[40] within this set, $k_{propyl}/k_{isobutyl}$ varies from 4.3 (for RBr + $Cl^-$ in acetone) to 33.8 (RI + $Br^-$ in acetone).

Extension of the side chain by another carbon, as in the case of PBPO (**41**), yields an additional 40 % increase in reactivity over the ethyl side chain. This observation is also consistent with observations made for small molecules where removal of δ branch point leads to higher reactivity. Looking again to Streitwieser's text we find that the rate of reaction with KI in acetone for 1-bromo-4,4-dimethylpentane is approximately 25 times that of 1-bromo-3,3-dimethylbutane. These compounds have the branch point on a quarternary carbon thus making direct comparison to the polymers with a tertiary branch difficult but it may be inferred that there will still be an effect of δ tertiary branch point, though to a lesser degree.

The one puzzling result is the low reactivity of PBBO (**42**). One would expect that PBBO should be of the same reactivity as PBPO and not the same as PBEO. In the literature there are no reports of the branch point affecting reactivity this far out, and it is unlikely that the ether linkages could be causing any change in reactivity.

Direct comparison of these results with the previously studied poly[(chloroalkyl)-oxiranes][66] is not possible due to the different reaction conditions used ($CDCl_3$, 45°C for the bromo derivatives, DMAc, 50°C for the chloro derivatives), but despite the less favorable $S_N2$ conditions, lower temperature and poor $S_N2$ solvent, the bromides were found to be more reactive than the chlorides. This can be seen by comparing the rate constants listed in Table III.5 with those in the next section. In fact attempts to study the reactions of the chloride polymers in $CDCl_3$ by this method were thwarted by the low reactivity of polymers in $CDCl_3$. After 24 hr of reaction at 45° C less than 3% conversion was obtained.

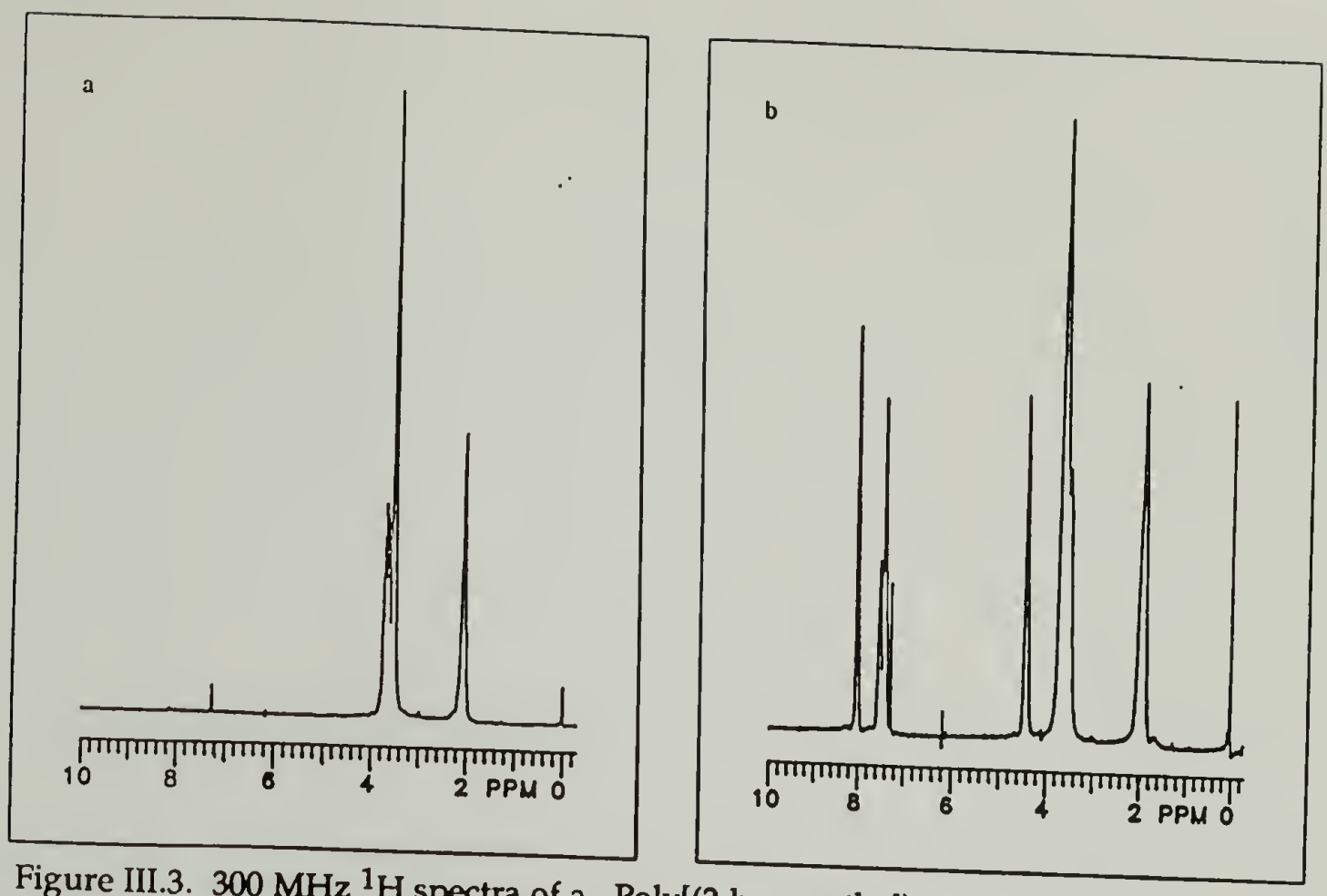



Figure III.3. 300 MHz $^1H$ spectra of a. Poly[(2-bromoethyl)oxirane]. b. Poly[2-(benzoyloxyethyl)oxirane] in $CDCl_3$.

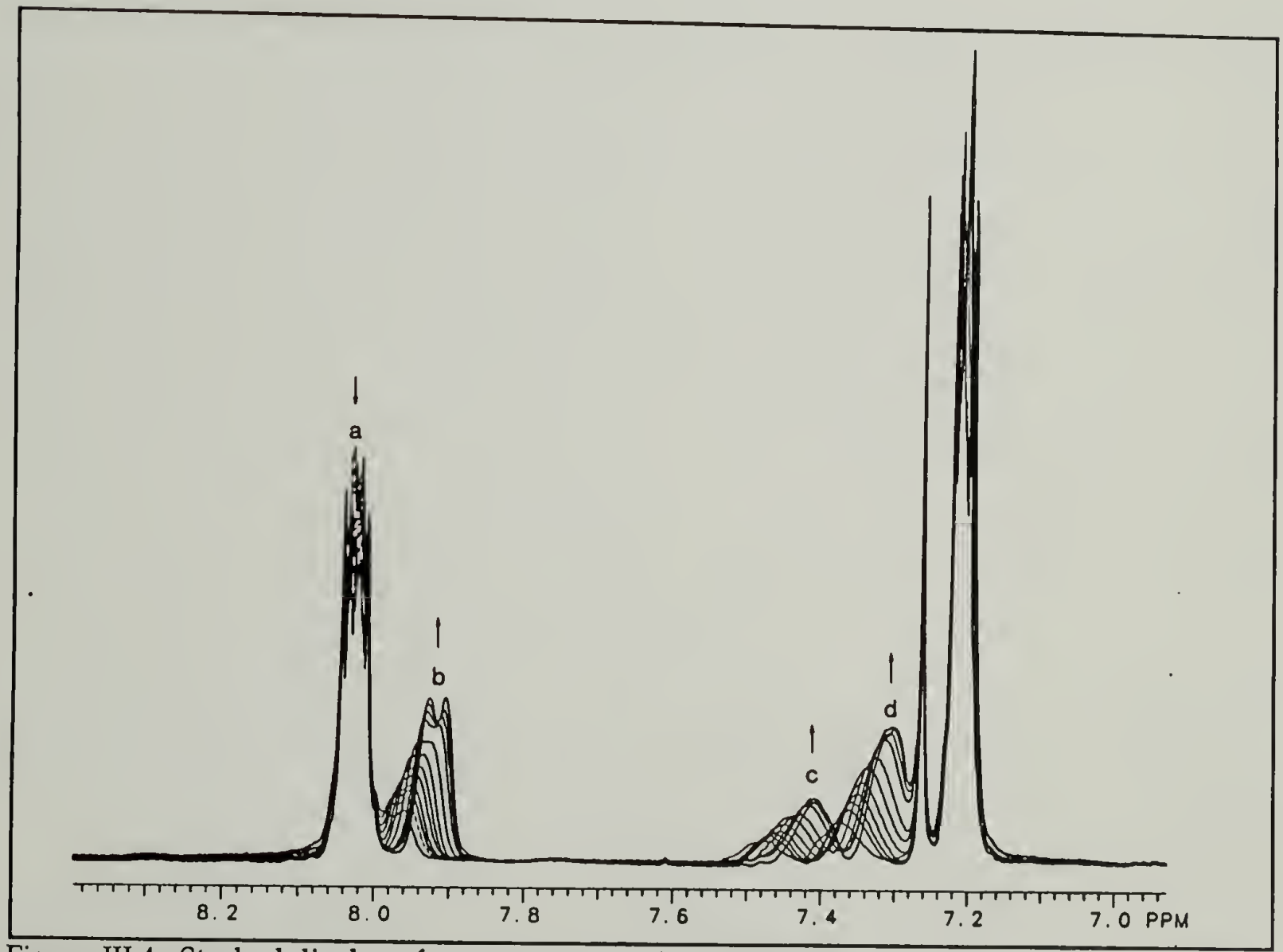



Figure III.4. Stacked display of spectra representing 10 to 60% conversion in reaction of TBAB and PBPO in $CDCl_3$ at 45°C.

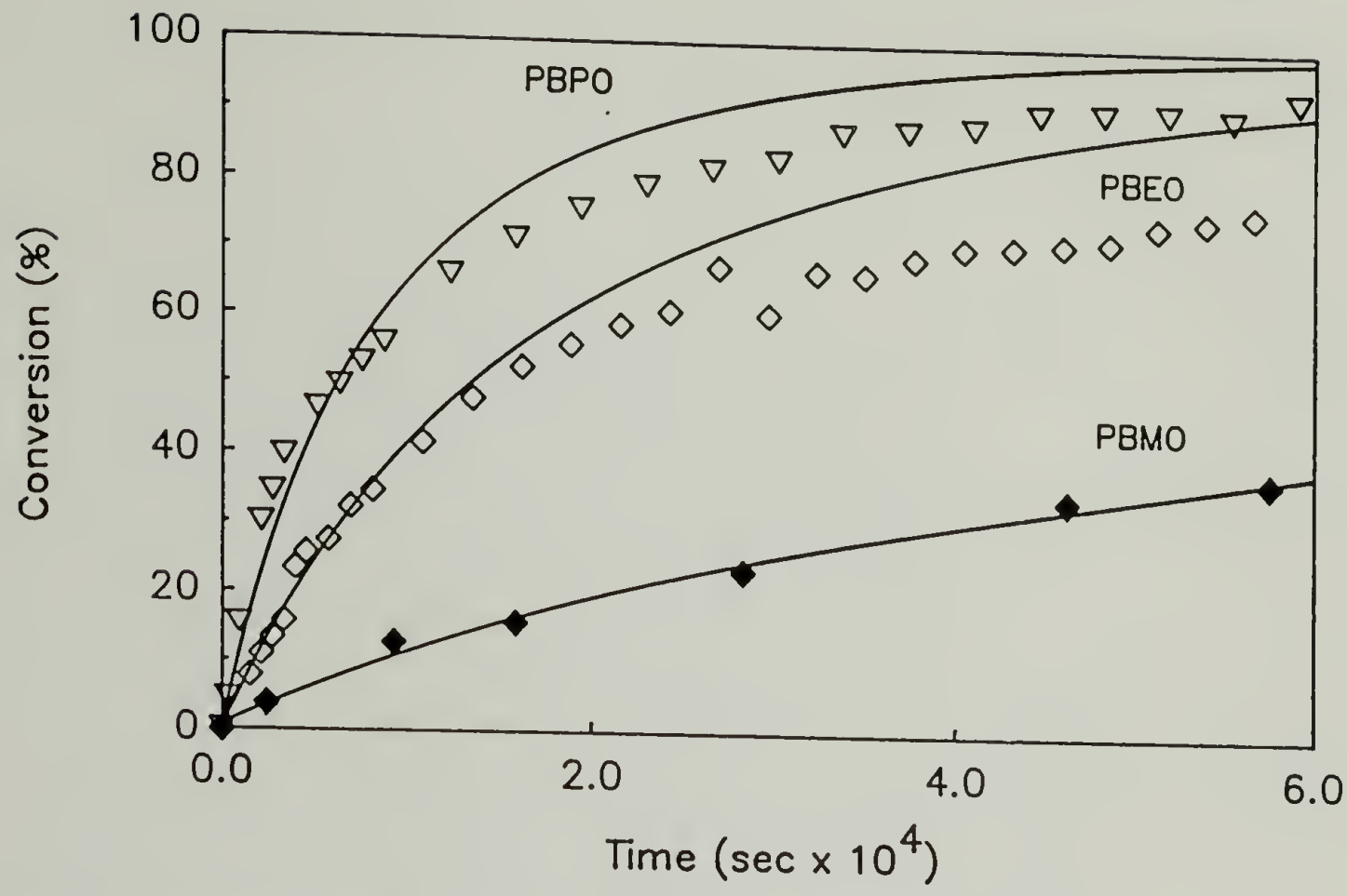



Figure III.5. % Conversion vs time for the reaction of PBMO (◆), PBEO (◊) and PBPO (▽) with TBAB at 45° C in $CDCl_3$. Solid lines represent anticipated % conversion for each polymer based on rate constants derived at low conversion.

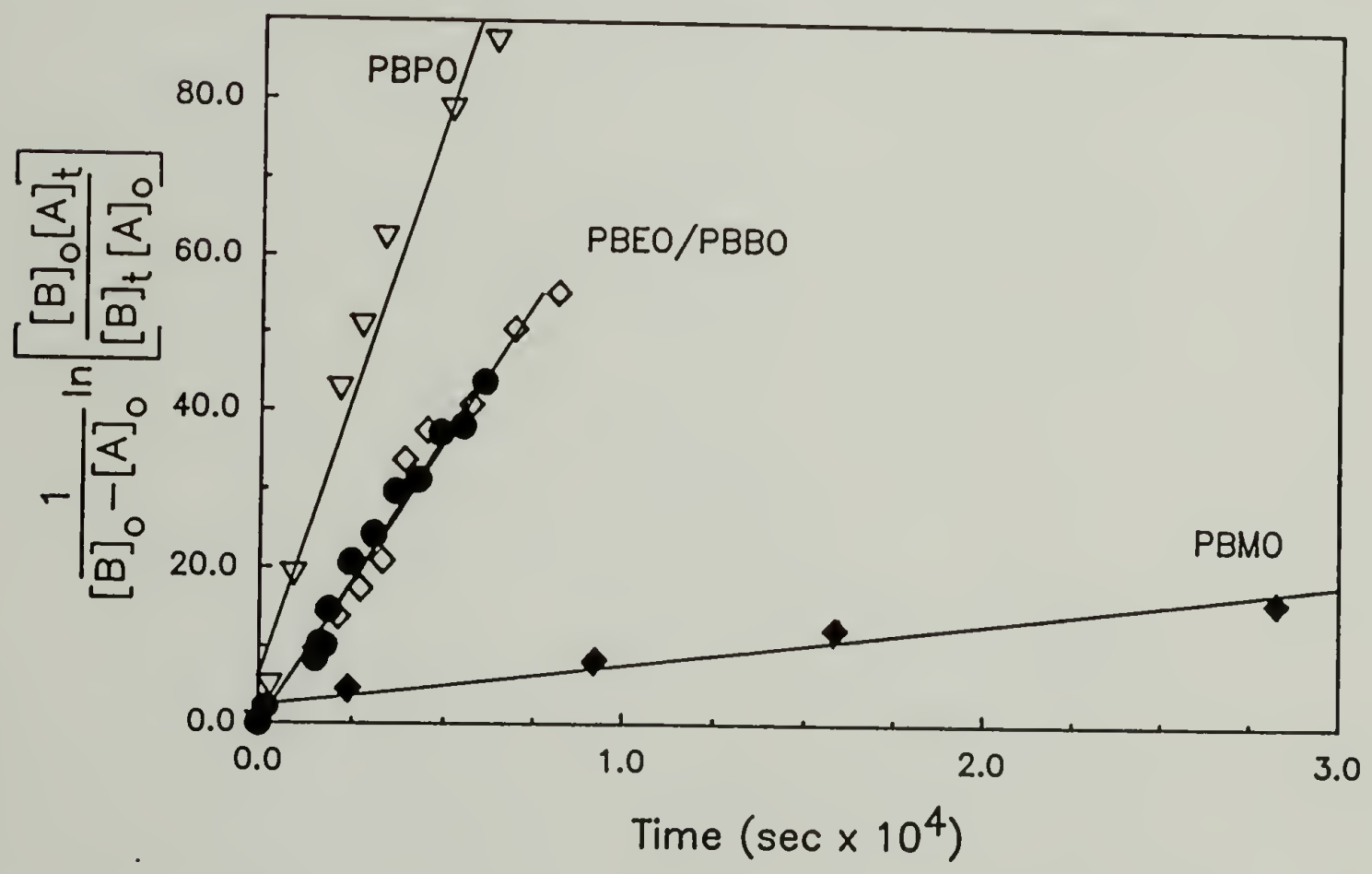



Figure III.6. Second order plot of the kinetics of reaction of ω-bromoalkyloxirane polymers with TBAB at 45° C in $CDCl_3$. PBMO (◆), PBEO (◊), PBPO (▽) and PBBO (●).

Table III.5. Second Order Rate Constants for the Reaction of Poly[(ω-bromoalkyl)oxirane]s with TBAB at 45° C in $CDCl_3$.

| Polymer | $[-CH_2Br]_0$ (equiv/L) | $[TBAB]_0$ (M) | $k^a$ ($M^{-1}$ $s^{-1}$) |
|---|---|---|---|
| PBMO | $8.57 \times 10^{-2}$ | 0.174 | $(7.0 \pm 1.2) \times 10^{-4}$ |
| PBEO | $6.97 \times 10^{-2}$ | 0.140 | $(7.1 \pm 0.8) \times 10^{-3}$ |
| PBPO | $4.53 \times 10^{-2}$ | $9.11 \times 10^{-2}$ | $(1.1 \pm 0.3) \times 10^{-2}$ |
| PBBO | $3.88 \times 10^{-2}$ | $8.10 \times 10^{-2}$ | $(6.6 \pm 0.7) \times 10^{-3}$ |

a. Rate constants estimated from linear portions of second-order rate plots at conversions of less than 55%. Errors represent one standard deviation of slopes of origin-to-point lines.

**2. Kinetics of the Displacement of Halides by Benzoate Anion in DMAc.**

Preparation of the (ω-bromoalkyl)oxirane polymers was motivated in large part by the expectation that these polymers would be more reactive toward nucleophilic substitution than the chloride analogs that were reported some time ago.[66] As indicated previously, direct comparison of the reactivities of the chlorides and bromides in $CDCl_3$ was not accomplished. However, such a comparison was found to be possible in DMAc where the reactions of both polymers take place on convenient time scales.

The prior study of the reaction of TBAB with the poly[(ω-chloroalkyl)oxirane]s[5,66] in DMAc was limited to one experiment at 50° C with more than a two fold excess of TBAB with respect to bound reactive group for each polymer. The first reaction of equimolar amounts TBAB and PECH in the current study at 50° C in DMAc yielded a rate constant more than 5 times that of the previously reported method ($3.5 \times 10^{-4}$ $M^{-1}$ $s^{-1}$ vs a value of $6.3 \times 10^{-5}$ $M^{-1}$ $s^{-1}$ ), thus it was decided that further investigation of the (ω-chloroalkyl)oxirane polymers was needed to clarify the source of this difference and to get a more accurate picture of the substitution kinetics in general.

In the following sections the reactions of PCEO with TBAB will be used to illustrate the method employed to monitor the reaction with $^{13}C$ NMR and prove the reliability of the technique. A short discussion will follow about the other chloride containing systems that were studied and finally there will be some discussion about the reactions of (ω-bromoalkyl)oxiranes. To avoid lengthy repetition, discussion of some systems will be covered only in a comparative manner. In Appendix C there is a full listing of all data obtained from the $^{13}C$ experiments in tabular form in addition to examples of spectra used for the determinations of reaction conversion, $T_1$'s and NOE factors.

**a. Description and justification of the method of data acquisition.**

The reaction of PCEO with TBAB in DMAc was studied by measuring the extent of conversion by $^{13}C$ NMR. A typical reaction preparation is detailed in the experimental section and in brief consisted of the predissolution of the required amount of polymer and TBAB in separate DMAc solutions with preequilibration of each component to the planned reaction temperature. The components were then mixed and injected into a 10 mm NMR tube which was

then placed into the preheated NMR sample probe. $^{13}C$ NMR spectra were then obtained at specified intervals, with continuous broad band $^{1}H$ decoupling, a 50° pulse width, 1 sec acquisition time and a 1 sec pulse delay following the acquisition time. Each spectrum required 10 min to acquire and resulted from the accumulation of 300 transients using this pulse sequence. Upon the completion of acquisition the resulting FID was zero filled to 64,000 points and Fourier transformed using 5 Hz of line broadening . The spectra obtained were assumed to represent the composition of the mixture half way through the acquisition period.

In Figure III.7 are shown 75 MHz $^{13}C$ spectra of: a) PCEO alone in DMAc at 50° C and b) an equimolar mixture of PCEO and TBAB (based on reactant groups) in DMAc at 50° C after 7 hr of reaction. It can be clearly seen in spectrum b that a peak arising from benzoyloxymethyl carbons (60.7 ppm) has grown into the spectrum while there has been a corresponding decrease in the chloromethyl carbon signal at 40.6 ppm. Careful examination of these two lines as the reaction progresses shows that the peak widths at half height of the two signals are essentially equal throughout the reaction thereby allowing the use of their relative peak heights after adjustment for differing Nuclear Overhauser Enhancements (NOE), to judge the relative concentrations of the reactants in solution. Additionally the parameters of the spectral acquisition were such that the 2 sec between pulses is the greater than 2.5 times the maximum $T_1$'s of peaks of interest (0.618 sec for the chloromethyl and 0.220 sec for the benzoyloxymethyl) and the use of a 50° pulse allows for the full relaxation of the signals between pulses resulting in the acquisition of quantitative data.

The measured peak heights for each spectrum were converted into degree of reaction data by first dividing the peak height by the measured NOE enhancement factor to obtained unenhanced values and then dividing the benzoyloxymethyl peak height by the sum of the heights of the benzoyloxy- and chloromethyls. This measurement of the degree of reaction was verified by isolating partially reacted polymers and comparing the extent of reaction measured by integration of $^{1}H$ NMR spectra with those obtained using the $^{13}C$ method detailed herein. The results of these comparisons for two polymers, PCEO and PECH, are shown in Table III.6, and the values obtained by the two methods do not differ significantly. Additional

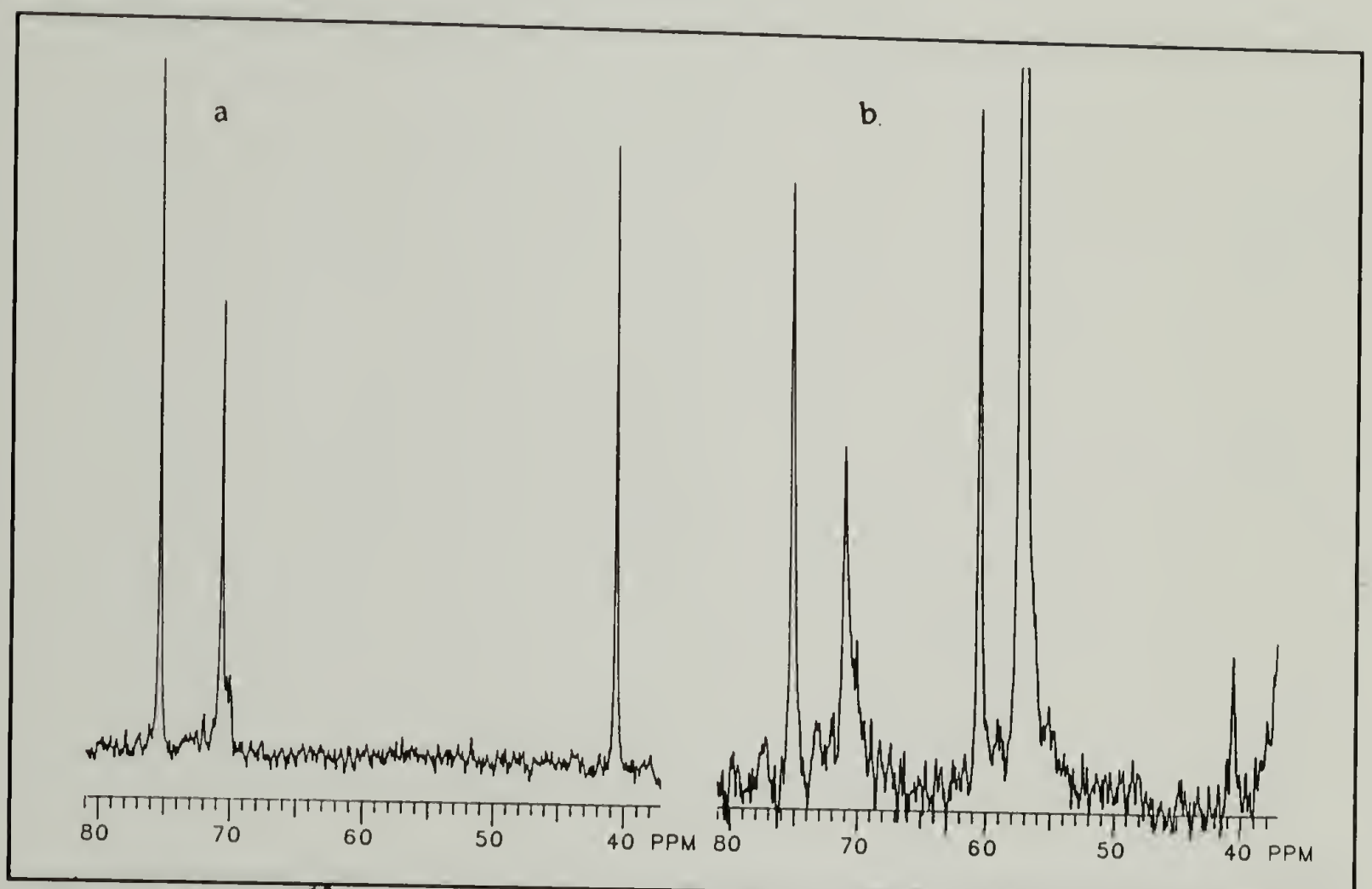



Figure III.7. 75 MHz $^{13}C$ NMR spectra of a) PCEO in DMAC at 50° C and b) a mixture of PCEO and TBAB after 7 hr at 50° C in DMAc.

verification of the method can be inferred in a qualitative sense from the observations that: 1) the extent of reaction never exceeded 100% for all systems studied and 2) unreacted starting materials could always be observed even when the reaction appeared to stop at lower than quantitative conversion.

Table III.6. Comparison of the Extent of Reaction as Determined by $^{1}H$ and $^{13}C$ NMR .

| Polymer | % Conv $^{13}C$[a] | % Conv $^{1}H$[b] |
|---|---|---|
| PCEO | 58.7 (58.5)[c] | 59.3 |
| PCEO | 84.6 (83.2)[c] | 83.2 |
| PECH | 37.4[d] | 40.2 |
| PECH | 68.5[d] | 67.0 |

a. Numbers in brackets indicate values obtained with NOE suppression a 90° pulse width and an preacquisition delay time of 8 sec.
b. $^{1}H$ NMR spectra taken on isolated polymer samples.
c. Spectra taken after complete consumption of TBAB.
d. Last value obtained in a kinetics experiment, polymers were then immediately precipitated into water.

**b. Reactions of poly[(2-chloroethyl)oxirane].**

The substitution reaction on PCEO was run at a series of temperatures ranging from 5° C to 50° C, and monitored using $^{13}C$ NMR. In Figure III.8 is shown the conversion as a function of time for reactions of PCEO with TBAB at 5, 25, 40 and 50° C. Upon first inspection the conversion vs time curve looked to be of classical second order type. The curves in Figure III.8 are calculated conversions as function of time based on the initial second-order plots in Figure III.9. The calculated conversion curves for the reactions at 5 and 25° C fit the observed data very well. However, if we look at the curves drawn for the reactions at 40 and 50° C, which were followed to higher conversion, there is a distinct negative deviation of the observed values from the calculated curve at high conversion. This is again, as in the $^{1}H$ studies discussed previously, viewed as a depression of reaction rate due to the reaction of nearest neighbors.

Though the maximum conversion shown here for these reactions is 89% it should be noted that complete conversion to PBeEO was obtained by using longer reaction times and an excess of TBAB. The reactions studied were terminated before full conversion to save time and it is not believed that anything of great interest could be gained from observations at longer times.

In Table III.7 are listed the rate constants (k) obtained at each of several temperatures. An Arrhenius plot (Figure III.10) from these data gives the activation energy ($E_A$) for the reaction and the intercept with the log k axis gives the Arrhenius prefactor (A). The value obtained for $E_A$ (14.9 Kcal/mol) is in the range of what would be expected for small molecule $S_N2$ reactions in solution and the value for log A (7.4) though somewhat small is not outside of the range of values reported in the literature[77] for small molecule $S_N2$ reactions. Values of a similar size were also obtained from temperature studies of the reactions of PECH, PCPO and 1-chloropentane by this method and are listed in Table III.8.

One of the causes of the observed higher reactivity found in our study than was found earlier,[5] might have been the differences in reactant concentrations. The previous work had a polymer concentration 1.5 times that used here and utilized 2.35 equivalents of TBAB for each reactive site on the polymer. It can be envisioned that there could be a reactant concentration dependence of the rate of reaction if the reaction does not have a first order dependence on both polymer and TBAB. There are two possible forms this could take 1) If the active nucleophilic species arises from a separated ion pair of benzoate anion and quarternary ammonium cation, then it is conceivable that an increase TBAB will actually result in a lower fraction of the TBAB being present as separated ion pairs. This would result in a smaller increase in the rate of reaction. 2) An increase in the concentration of polymer could lower the reactivity of attached functional groups through conformational changes brought on by increased polymer-polymer hard sphere interactions. If there is a collapse of the polymer coil this would most likely lead to increased steric crowding about the reaction site.

In order to insure that the system was in fact first order in both polymer reactant sites and nucleophile, reactions were run at a variety of reactant concentrations at 40° C in DMAc. In Figure III.11 are shown the second order rate plots for reactions of 0.68, 0.82 and 1.0 equivalents of PCEO reactive groups with 1 equivalent (constant 0.22M) of TBAB. The three best fit lines in

this plot are essentially indistinguishable, leading one to conclude that the reaction is first order with respect to polymer substrate concentration. In Table III.9 are shown the reactant concentrations for the three above reactions and two additional ones that contained (-$CH_2Cl$) : TBAB in 1.0:0.5 and 1.0:1.3 ratios along with the rate constants (k) for the reactions. The rate constants are identical within experimental error, affirming that the reaction is first order in both polymer reactive groups and nucleophile.

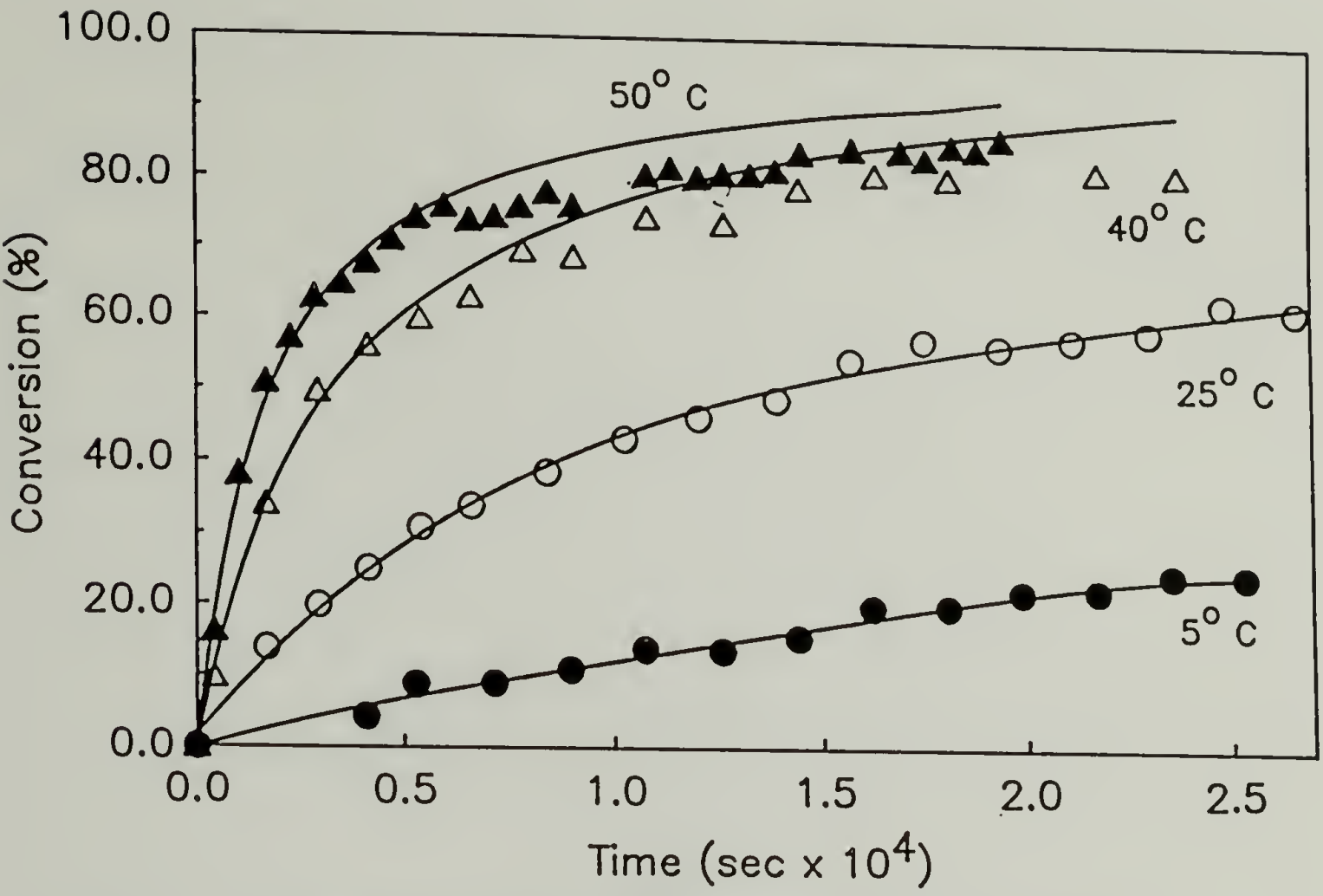



Figure III.8. % Conversion of PCEO to PBeEO in reactions with 1 equiv TBAB at T=5 (●), 25 (O), 40 (Δ) and 50°C (▲), as a function of time. Solid lines indicate expected conversion based on initial rate constants.

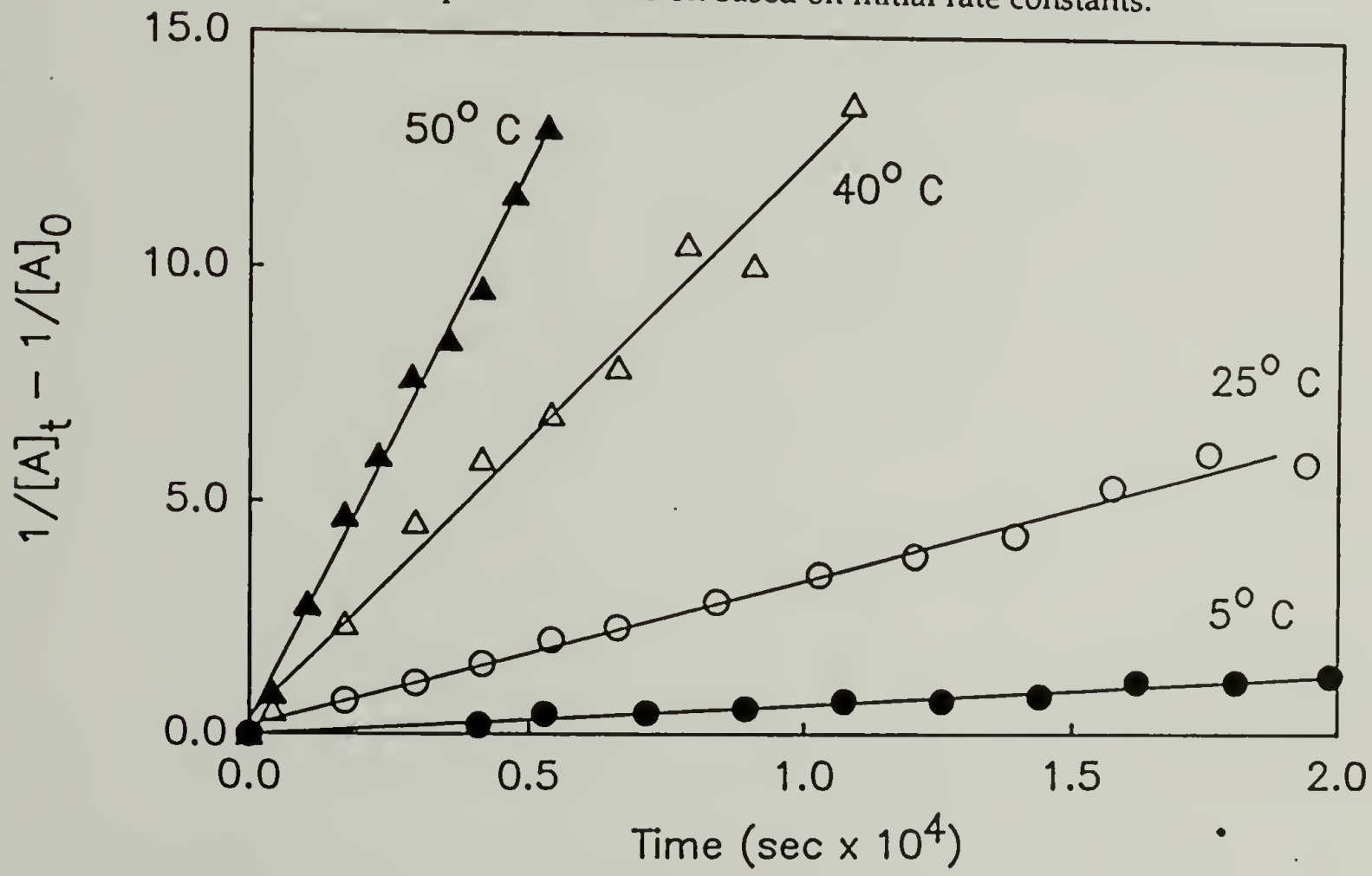



Figure III.9. Second order plot of the reactions of 1 equiv PCEO with 1 equiv TBAB at T=5 (●), 25 (O), 40 (Δ) and 50°C (▲).

Table III.7. Rate Constants for the Reaction of TBAB and PCEO in DMAc at Different Temperatures.

| Reaction | Temperature (° C) | [-$CH_2Cl$] (equiv/L) | [TBAB] (M) | k [a] ($M^{-1}$ $s^{-1}$) |
|---|---|---|---|---|
| CR6 | 5 | 0.220 | 0.220 | $(6.1 \pm 0.8) \times 10^{-5}$ |
| CR7 | 25 | 0.220 | 0.220 | $(3.5 \pm 0.3) \times 10^{-4}$ |
| CR8 | 40 | 0.219 | 0.219 | $(1.3 \pm 0.1) \times 10^{-3}$ |
| CR9 | 50 | 0.220 | 0.220 | $(2.5 \pm 0.2) \times 10^{-3}$ |

a. Rate constants estimated from linear portions of second-order rate plots at conversions of less than 55%. Errors represent one standard deviation of the slopes of origin-to-point lines.

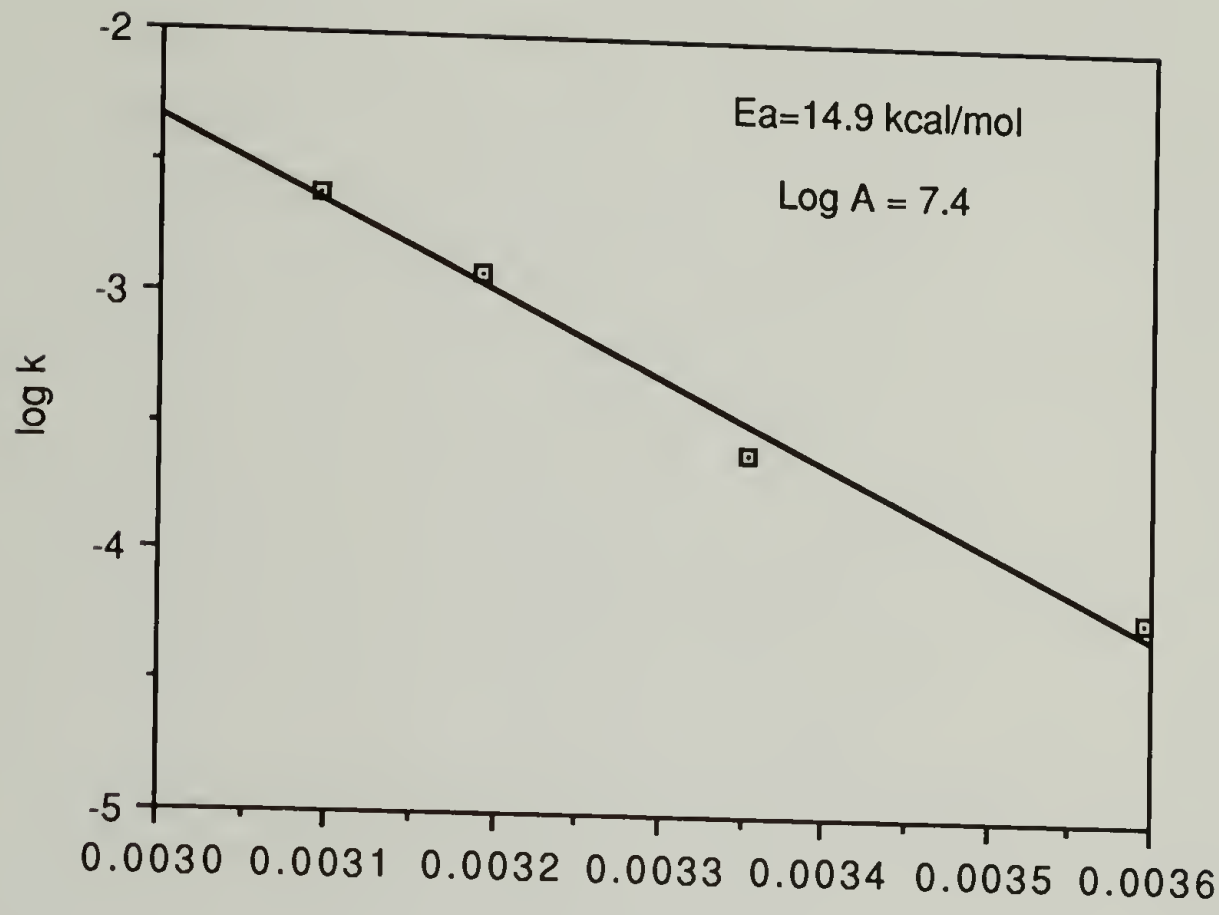



Figure III.10. Arrhenius plot for the reaction of PCEO and TBAB, from rates obtained at T=5, 25, 40 and 50° C.

Table III.8. Arrhenius Constants for the Reaction of TBAB with PECH, PCEO, PCPO and 1-Chloropentane in DMAc.

| Compound | $E_a$ (Kcal/mol) | Log (A/sec) |
|---|---|---|
| PECH | 15.1 | 6.8 |
| PCEO | 14.9 | 7.4 |
| PCPO | 14.7 | 7.5 |
| 1-Chloropentane | 14.3 | 7.6 |

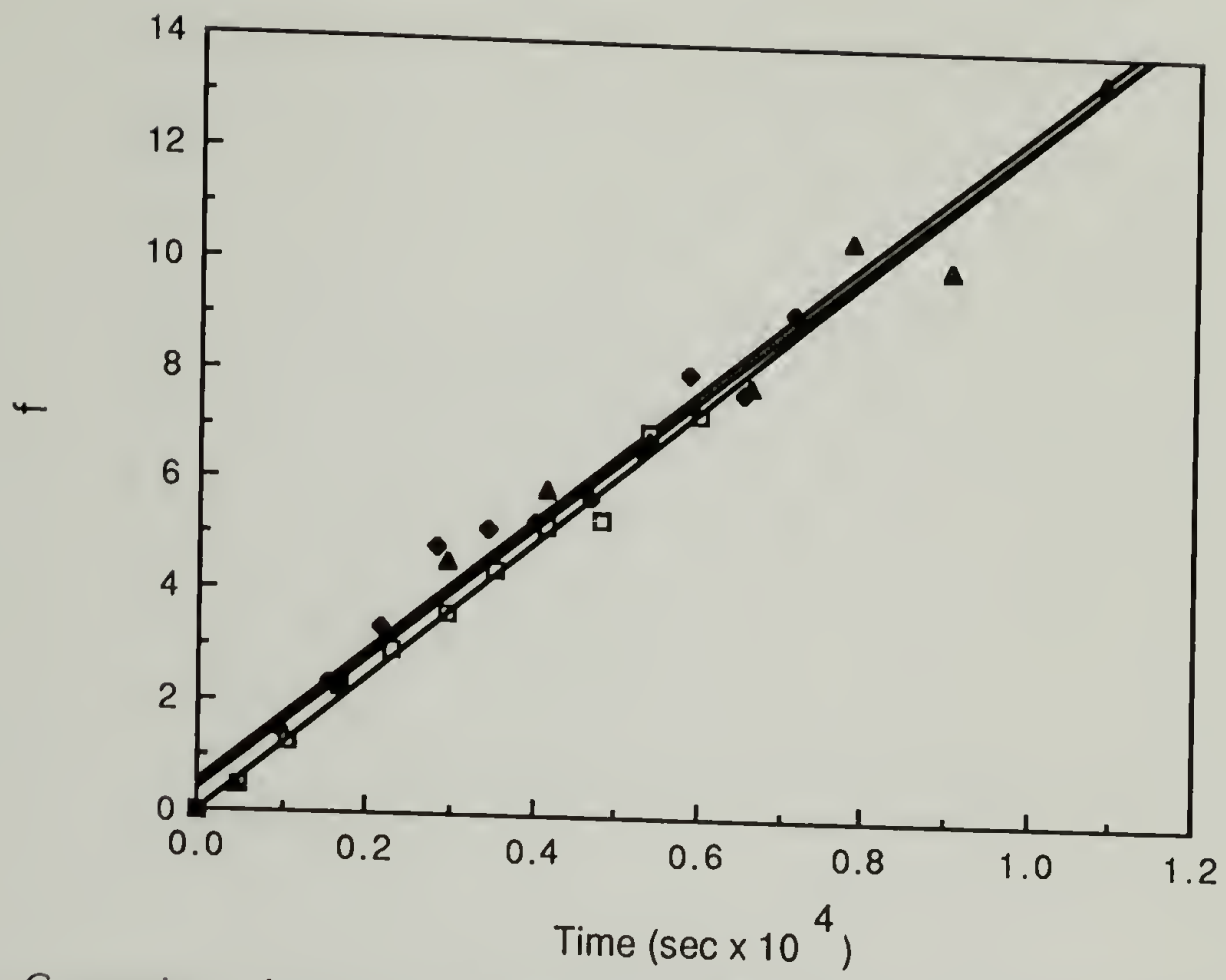



Figure III.11. Comparison of second order rate plots for reactions at 40° C containing different concentrations of PCEO. $[TBAB]_0$ = 0.22 M. $[\text{-}CH_2Cl]_0$ = 0.22 M (□); 0.18 M (◆); 0.15 M (▲).

Table III.9. Reaction Rate Constants for Systems Containing Different Concentrations of PCEO and TBAB at 40° C in DMAc.

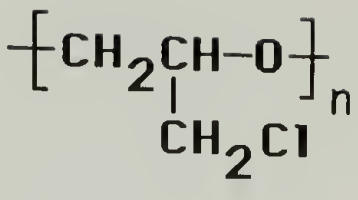
| Reaction | $[CH_2Cl]_0$ (equiv/L) | $[TBAB]_0$ (M) | k ($M^{-1}$ $s^{-1}$) a |
|---|---|---|---|
| CR8 | 0.22 | 0.22 | $(1.3 \pm 0.1) \times 10^{-3}$ |
| CR13 | 0.18 | 0.22 | $(1.4 \pm 0.2) \times 10^{-3}$ |
| CR12 | 0.15 | 0.22 | $(1.4 \pm 0.2) \times 10^{-3}$ |
| CR11 | 0.22 | 0.11 | $(1.3 \pm 0.2) \times 10^{-3}$ |
| CR10 | 0.22 | 0.28 | $(1.4 \pm 0.1) \times 10^{-3}$ |

a. Rate constants estimated from linear portions of second-order rate plots at conversions of less than 55%. Errors represent one standard deviation of slopes of origin-to-point lines.

**c. Reactions of other chlorinated polyethers.**

The reactions of other polymers with TBAB in this study were performed and analyzed in much the same manner as in the above case, but with adjustments to the delay times and number of transients in the spectra acquisition. Pulse sequence parameters and reactant concentrations are listed in the Experimental Section and measured values for $T_1$'s and NOE's for all polymers used in this work are listed in Appendix C. An additional step was used for studying the conversion of 1-chloropentane to 1-benzoyloxypentane. The long $T_1$'s of the carbons of interest, 11 sec for the chloromethyl and 3.3 sec for the benzoyloxymethyl, precluded the use of delay times necessary for complete relaxation of the nuclei. These reactions were monitored using a 3 sec pulse recycle time (AT=1, D=2) and the heights of the resulting peaks were adjusted to correct for saturation of the spin system. The correction factors used were determined by comparing the heights of the peaks of each component in a spectrum obtained using a 75 sec recycle time (complete relaxation) with those in a spectrum obtained with the 3 sec recycle time.

The order of reactivity of these materials is for the most part, what one would expect given the precedents of small molecule studies and previous work done in this laboratory.[66] Figure III.12 shows the conversion of (ω-chloroalkyl)oxirane polymers (**1**, **43-45**)to the corresponding poly[(ω-benzoyloxyalkyl)oxirane]s at 40° C in DMAc. The reactions went to high conversion for the higher members of the series in 10 hr. Once again, it appears that the methyl derivative, PECH(**1**), is being converted at a much slower rate. The second order rate plots shown in Figure III.13 are analyzed to give the rate constants at low conversion that are listed in Table III.10. The ordering of reactivity once again depends on separation from the branch point. The rate constant jumps an order of magnitude going from PECH (**1**) to PCEO (**43**) reflecting the removal of the β–branch point and loss of the inhibiting inductive effects of the β-ether linkage. There is also an increase in rate constant as we move further out on the chain and lose the effects of the branch point with PCPO (**44**) and PCBO (**45**) which have almost identical rates of reaction.



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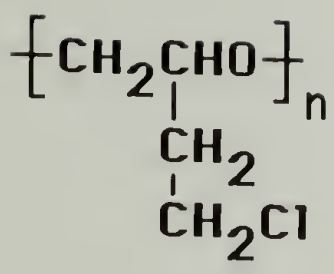

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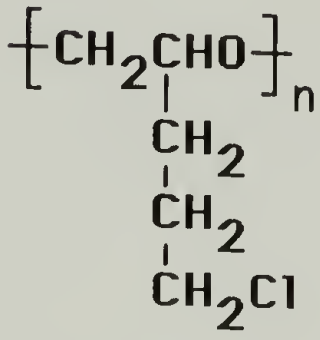

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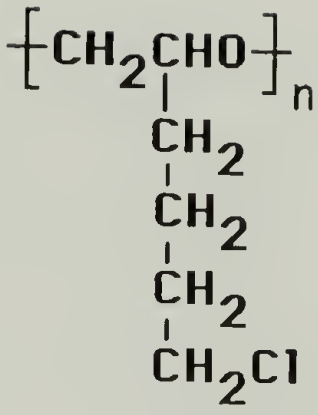

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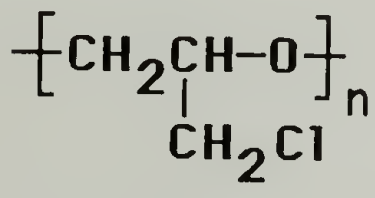
The one surprising feature to come out of the data at 40° C, is that 1-chloropentane ($C_5H_{11}Cl$) had a rate constant approximately 3 times that of PCPO and PCBO. The pendant chloro groups in PCPO and PCBO are far enough removed from the polymer backbone so as to diminish the effects of branching and the ether linkage and should therefore be as reactive as straight chain halides. This expectation was reinforced by the fact that Boucher[58] had found that the reactivities of the polymers in his systems were comparable with structurally analogous small molecules, and by Flory's work describing the equal reactivity of polymer end groups.[45] There are several possible sources of this difference in reactivity. First it might be a manifestation of ponderal effects; where the absolute mass of the molecule on which the functional group is attached affects reactivity in addition to any steric interactions,[78] this probably is not so and proof against this possibility can be found in the examples given by Flory[45] which showed that increases in chain size beyond propyl did not affect reactivity. Secondly the polymer could be changing the environment around the reaction site, possibly by varying solution polarity within the polymer coil. Morawetz[79] used changes in solution polarity around reactive sites to explain the differences in the rates of aminolysis of nitrophenyl isobutyrate and several copolymers of nitrophenyl acrylate as detailed in Table III.11. The relative rates were found to increase with the polarity of the copolymer (copoly(styrene) having the lowest polarity and copoly(dimethylacrylamide) the highest). It

appears that the polymer groups displace solvent molecules from around the reaction site and if the polymer-bound groups are less polar than the displaced solvent there is a resulting drop in $S_N2$ reaction rate. For reactions taking place in my systems the displacement of solvent from around the reaction site would modify reactivity in a different fashion. In the aminolysis the reaction is between two uncharged species and it proceeds through a charged transition state. The reaction proceeds at a faster rate in more polar solvents due to the ability of these solvents to assist in the stabilization of the charges. In reactions involving the reaction of an ionic nucleophile, such benzoate anion, with a neutral substrate reaction rates can be depressed slightly by increasing polarity,[39] so it is unlikely that polymer induced changes in polarity would account for the difference in reactivity. However, one must also consider the solubilization of the benzoate-tetrabutyl ammonium ion pair by the reaction media. DMAc is one of the best solvents for solubilizing ions,[80] so the displacement of DMAc molecules from the vicinity of the reaction could result in the TBAB being present as a tighter ion pair which could be assumed to be less reactive.

In Figure III.14 and Table III.12 are presented data similar to that above for reactions at 50° C. Again the same ordering in reactivity can be seen for the systems listed above and additionally they present data for the reactions of poly[3-(chloromethyl)oxetane] (P3CMO) (46) and poly[2-(chloromethyl)oxetane] (P2CMO) (47) with TBAB. The absence of a β-ether oxygen should make P3CMO more reactive than PECH or P2CMO toward attacking nucleophiles . Analysis of second order kinetic plots at low conversion gives rate constants of $8.2 \times 10^{-4}\ M^{-1}\ s^{-1}$, $3.6 \times 10^{-4}\ M^{-1}\ s^{-1}$ and $4.0 \times 10^{-4}\ M^{-1}s^{-1}$ for P3CMO, PECH and P2CMO respectively showing that the inductive influence of the β-ether lowers reaction rate by 50%. It is also of interest to note that the reactivities of PECH and P2CMO are the same, within experimental error, even though the spacing between functional groups has been increased.



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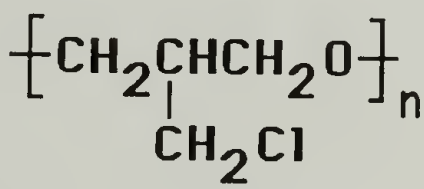

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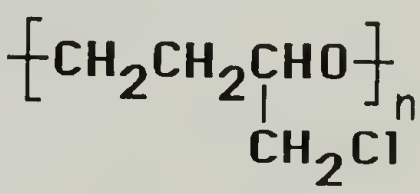

(47)

The reactivity of another oxetane polymer (P3CO) was also tested. It was found to be essentially inert towards the substitution reaction at 50° C, and it was not until the reaction was run at 90° C with a four fold excess of TBAB that reliable conversion measurements could be obtained in a 12 hr period. Under these conditions a rate constant of $9.4 \times 10^{-6}$ $M^{-1}$ $s^{-1}$ was measured and represented the lowest value measured for any reaction. Though direct comparison with PECH was not possible at 90° C, we can estimate that k would be approximately $4 \times 10^{-3}$ $M^{-1}s^{-1}$ at 90° C for PECH by extrapolating from data obtained at 5 temperatures between 30 and 70° C. This 1000 fold decrease in reactivity can be attributed to the reaction taking place on a secondary carbon which is β to two ether linkages, situation which can as described in the Introduction lead to much lower reactivity.

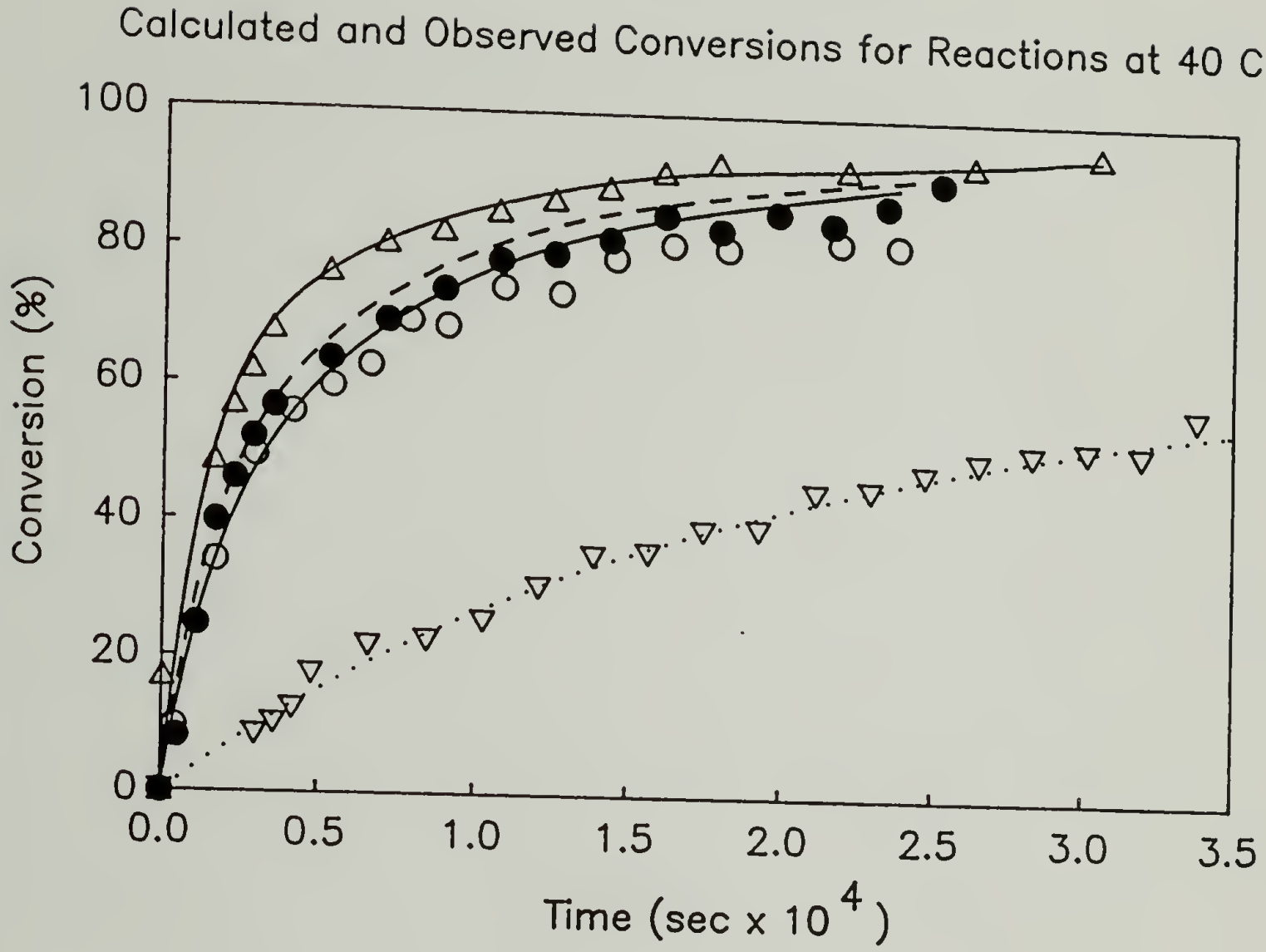


Figure III.12. Conversion of (ω-chloroalkyl)oxirane polymers to the corresponding poly[(ω-benzoyloxyalkyl)oxirane]s by reaction with TBAB at 40° C. PECH (∇), PCEO (O), PCPO (●) and PCBO (Δ).

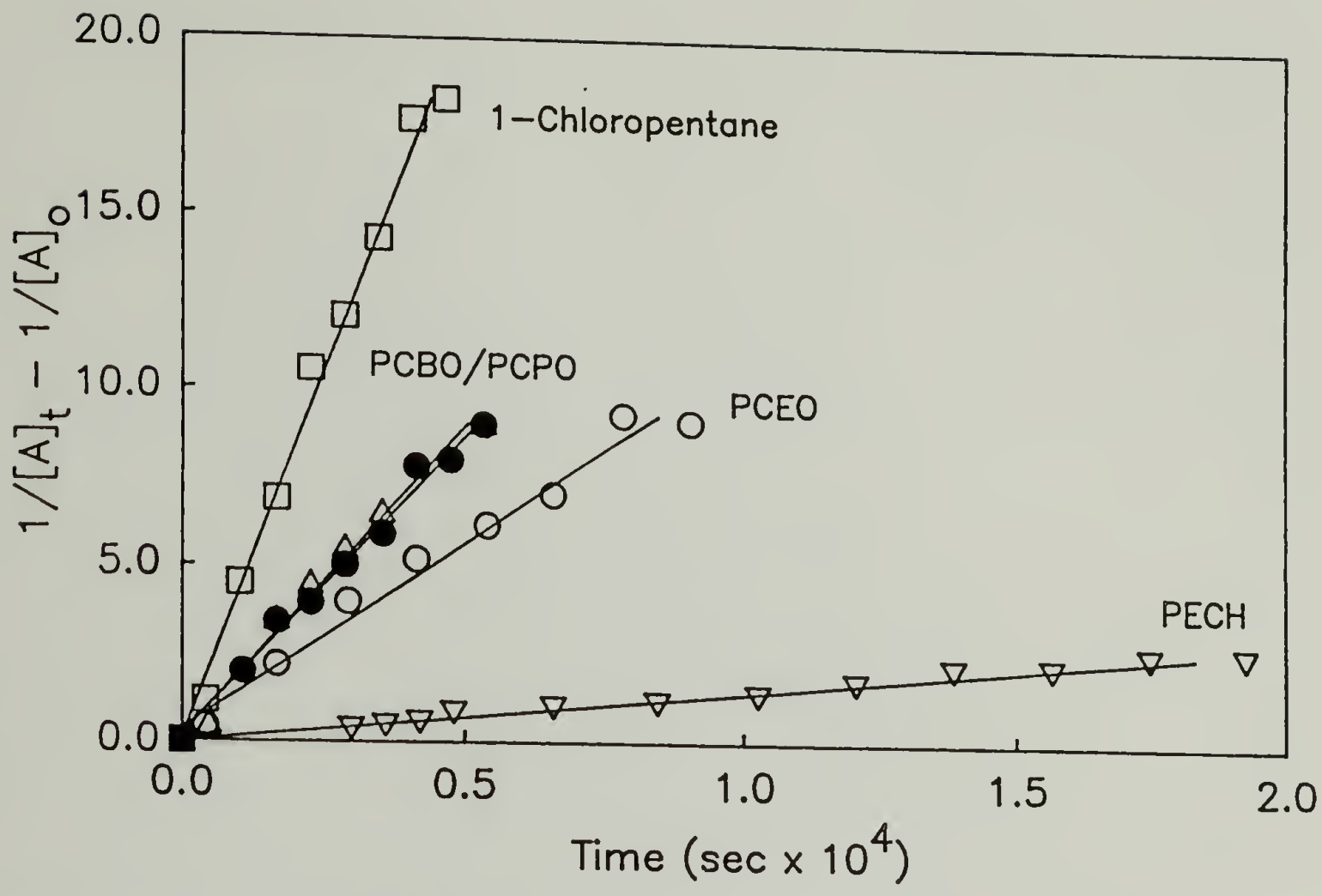


Figure III.13. Second order rate plots for the reactions of (ω-chloroalkyl)oxirane polymers and 1-chloropentane with TBAB at 40° C. PECH (▽), PCEO (○), PCPO (●), PCBO (△) and 1-Chloropentane (□).

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Table III.10. Rate Constants for the Reaction of TBAB with Poly[(ω-chloroalkyl)oxirane]s and 1-Chloropentane at 40° C in DMAc.

| Polymer | $[-CH_2Cl]_0$(equiv/l) | $[TBAB]_0$(M) | k ($M^{-1}$ $s^{-1}$) [a] |
|---|---|---|---|
| PECH | 0.25 | 0.25 | $(1.4 \pm 0.1) \times 10^{-4}$ |
| PCEO | 0.22 | 0.22 | $(1.3 \pm 0.1) \times 10^{-3}$ |
| PCPO | 0.19 | 0.20 | $(1.9 \pm 0.1) \times 10^{-3}$ |
| PCBO | 0.28 | 0.30 | $(1.8 \pm 0.1) \times 10^{-3}$ |
| $C_5H_{11}Cl$ | 0.16 | 0.16 | $(4.3 \pm 0.2) \times 10^{-3}$ |

a. Rate constants estimated from linear portions of second-order rate plots at conversions of less than 55%. Errors represent one standard deviation of the slopes of origin-to-point lines.

Table III.11. Ratio of the Second-Order Rate Constants for the Aminolysis of Nitrophenyl Acrylate Copolymers and Nitrophenyl Isobutyrate in Dioxane at 50° C.[a]

| Comonomer | (k/k°) [a] | |
|---|---|---|
| | $n\text{-}C_4H_9NH_2$ | $n\text{-}C_{10}H_{21}NH_2$ |
| Styrene | 0.0353 | 0.0305 |
| Methylacrylate | 0.296 | 0.320 |
| Dimethylacrylamide | 5.68 | 4.98 |

a. k is the second-order rate constant for polymer-bound ester and k° rate constant for nitrophenyl isobutyrate.

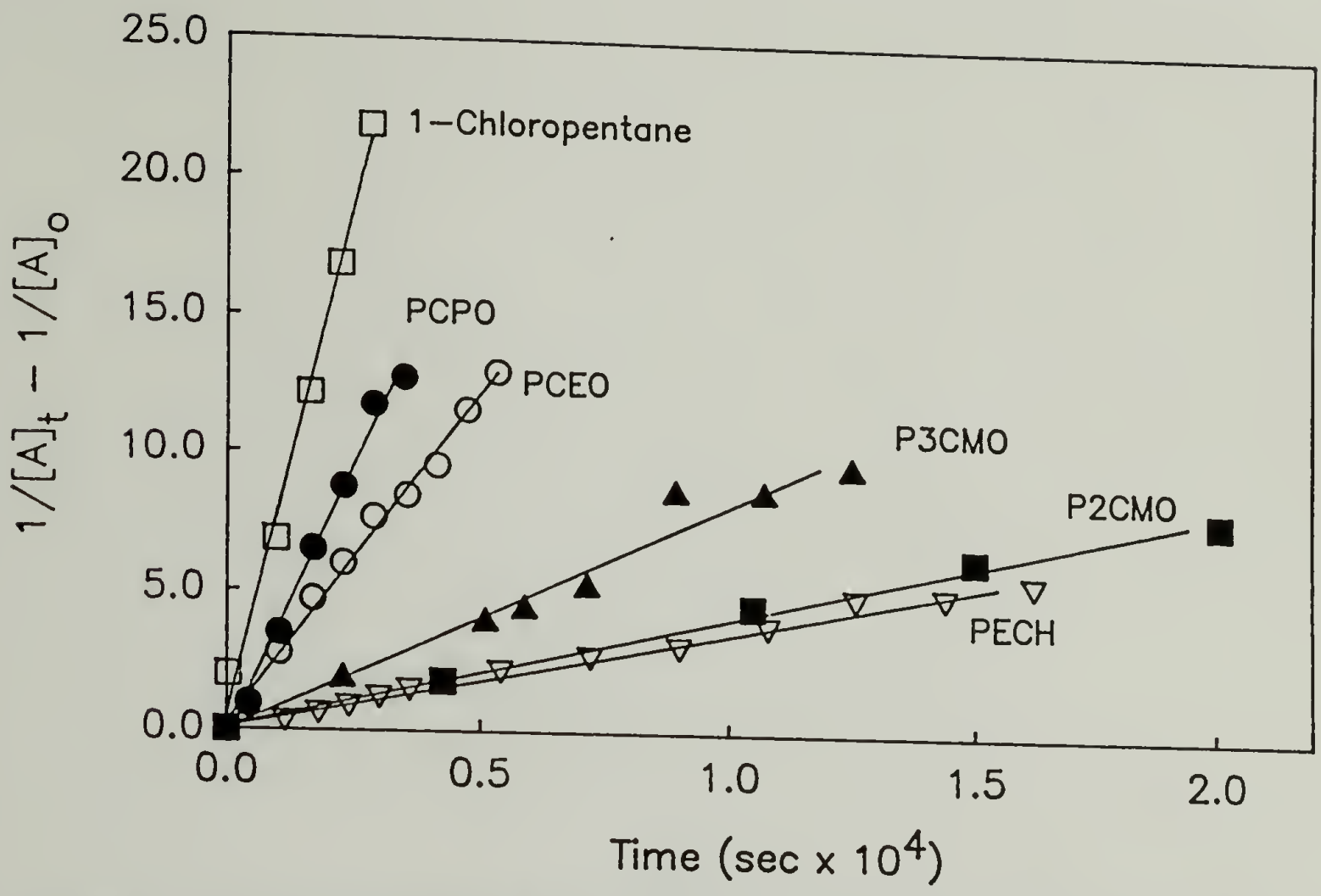


Figure III.14. Second order rate plots for the reactions of PECH (▽), PCEO (○), PCPO (●), P2CMO (■), P3CMO (▲) and 1-chloropentane(□) with TBAB at 50° C in DMAc.

Table III.12. Rate Constants for the Reaction of TBAB with Chloroalkyl Polyethers and 1-Chloropentane at 50° C in DMAc.

| Polymer | $[-CH_2Cl]_0$ (equiv/l) | $[TBAB]_0$ (M) | $k(M^{-1} s^{-1})$ [a] |
|---|---|---|---|
| PECH | 0.25 | 0.25 | $(3.6 \pm 0.4) \times 10^{-4}$ |
| P2CMO | 0.15 | 0.15 | $(4.0 \pm 0.3) \times 10^{-4}$ |
| P3CMO | 0.22 | 0.22 | $(8.2 \pm 0.8) \times 10^{-4}$ |
| PCEO | 0.22 | 0.22 | $(2.5 \pm 0.2) \times 10^{-3}$ |
| PCPO | 0.19 | 0.20 | $(3.9 \pm 0.6) \times 10^{-3}$ |
| $C_5H_{11}Cl$ | 0.16 | 0.17 | $(8.1 \pm 0.2) \times 10^{-3}$ |

a. Rate constants estimated from linear portions of second-order rate plots at conversions of less than 55%. Errors represent one standard deviation of the slopes of origin-to-point lines.

**d. Reactions of poly[(2-bromoethyl)oxirane] and poly[(bromomethyl)oxirane].**

The reactions of PBEO and PBMO with TBAB in DMAc were studied in much the same manner as the chlorides except the backbone methine resonances were utilized to follow the reaction instead of the terminal methylenes used in chloride reactions. This was necessary because the bromomethyl resonance is obscured by solvent peaks in $^{13}C$ NMR spectra. Figure III.15 shows spectra of PBEO in DMAc at 50° C (a) and a mixture of PBEO and TBAB in DMAc after 30 minutes of reaction at -5° C. The latter spectrum shows the development of a new backbone methine signal at 74.6 ppm due to repeating units carrying benzoate residues as well as the benzoyloxymethyl resonance at 60.4 ppm. The degree of reaction was determined by comparison of the relative peak heights of the methine resonances at 74.6 and 75.6 ppm, peaks that corresponding to reacted and unreacted repeat units.

The reactions of the brominated polymers are, as expected, much faster than those of the equivalent chloride containing substrates. At 50° C conversion of PBEO to PBeEO, in DMAc with 1 equiv of TBAB, takes about 10 min and cannot be followed using our standard NMR methods. If the temperature is lowered to 5° C the reaction takes place on a reasonable time scale. A direct comparison of the reactivity of PBEO and PBMO with PCEO can be seen in Figure III.16. It is obvious that the bromo polymers are much more reactive; the rate constants derived from the slopes show that PBEO has a rate constant at 5° C that is 60 times that of PCEO ($3.8 \times 10^{-3}$ vs $6.1 \times 10^{-5}$ $M^{-1}$ $s^{-1}$). The rate constant for conversion of PBMO ($9.9 \times 10^{-4}$) is more than an order of magnitude greater than that for the reaction of PCEO.

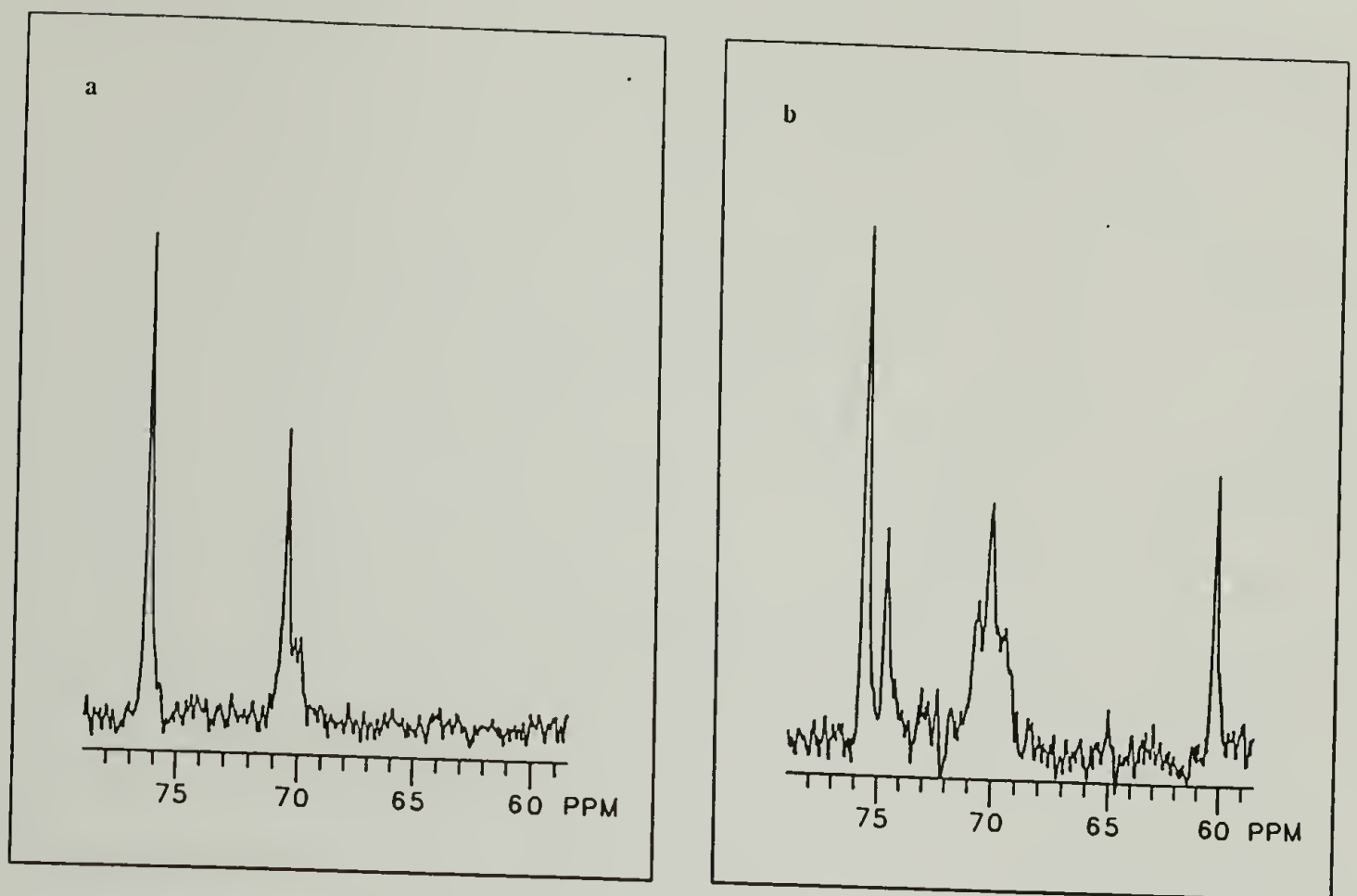


Figure III.15. 75 MHz $^{13}C$ NMR spectra of a: PBEO in DMAc and b: a mixture of TBAB in DMAc after 30 min of reaction at 5° C.

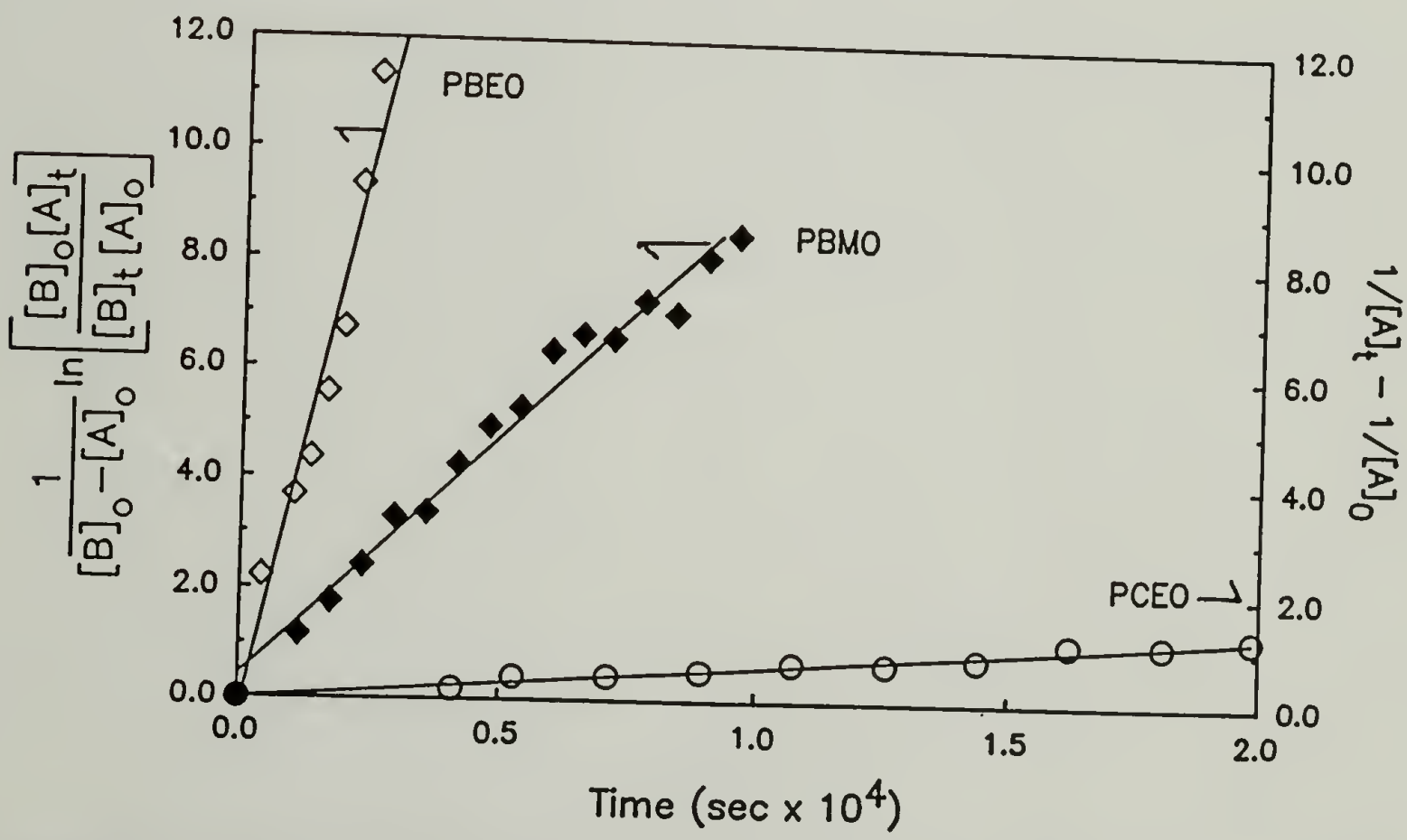


Figure III.16. Second order rate plots for the reactions of PCEO (O), PBMO (◆), and PBEO (◊) with TBAB at 5° C in DMAc.

**3. Discussion of Deviation from Second Order Kinetics .**

The retardation of these displacement reactions at high conversion is of some interest. It was noted earlier that in the reactions of the poly[(ω-bromoalkyl)oxirane]s with TBAB in $CDCl_3$, there was a detectable departure from second order kinetics at about 55% conversion. This was graphically displayed in Figure III.5 where it was shown that the observed conversion of the polymers in the reaction with TBAB did not fit calculated curves for second order reactions based on the rate constants for each polymer obtained at low conversion. A similar observation was made with the reaction of chlorinated polymers with TBAB in DMAc at 40 and 50°C (Figures III.8 and III.12). In small molecules such retardation is not found in $S_N2$ reaction and in fact the studies we did using 1-chloropentane showed no deviation from linearity in the second order rate plots at conversions greater than 85%. As mentioned in the introduction several other groups have noted similar behavior and have attributed the decrease in reaction rate to an increase in local steric or electrostatic interferences to further reaction.[51,50] For the systems studied here one would not expect to see any electrostatic effects, indicating that the most likely sources of retardation would appear to be associated with either conformational differences between the bromide and benzoate forms of the polymer, or with local steric restrictions arising from the bulk of the benzoate substituent. The former suggestion appears unlikely; viscosity measurements over the course of the reaction in general suggest that the polymer coil suffers no conformational collapse. In fact, the inherent viscosities in DMAc after reaction are essentially the same as those of the unreacted polymers for the bromides, and are slightly higher for the chlorides.

A feeling for the change in local steric restrictions can be obtained from $T_1$ measurements of a series of partially reacted polymers representing different degrees of conversion. Tables III.13 and III.14 summarize the spin-lattice relaxation times for several of the carbon nuclei in PBEO and PCEO, respectively, as well as of their partially substituted derivatives. In each of the examples the $T_1$ of each observed carbon decreases steadily with increasing substitution. Since the nature of the groups directly coupled to each of the carbons shown below is the same throughout, what we are seeing is the effect of changing environments about the carbons. It has been shown that such a decrease in $T_1$'s can be attributed to greater restriction in C-H bond

movements allowing for efficient use of relaxation pathways;[81] thus suggesting that there is an increase in steric crowding about each reactive site.[82]

An effort was made to quantify the degree of reduction in the rate constants for several of the reactions. The neighboring group model developed by Boucher seems appropriate to use for this system assuming that there is no effect of the presence of directionality in the polymer backbone. (If the directionality does play a role a more complex model would be required.) A FORTRAN computer program (CONTOUR, listed in Appendix D) was developed to analyze our conversion data based on Boucher's model, and used to obtained some tentative values for the rates of reaction based on number of reacted neighbors. This program generates 400 calculated conversion vs time curves from all combinations of 20 values of K and L (each 0.02 units apart, starting from estimates of minimum K and L values),for a reaction system given the initial reactant concentrations and the rate constant ($k_0$) determined at low conversion. The program then performs a chi-square analysis, comparing each of the calculated curves with the best fit curve through the actual data at 21 equally spaced points. It was assumed that the combination of K and L which gave the smallest chi-square value represented the best approximation for these parameters.

In Figure III.17 is shown a contour plot of the error as measured by chi-square, for the reaction of PCEO with 1 equiv TBAB at 50° C in DMAc . There is a minimum in the error at $K \approx 1.05$ and $L \approx 0.35$-0.4 suggesting that there is no inhibition to substitution if only one neighbor has reacted. However, if both neighbors have reacted, there is approximately a 60% reduction in rate of reaction ($K=k_1/k_0$ and $L=k_2/k_0$ ). The goodness of the fit of a calculated conversion curve can be seen in Figure III.18, where the calculated curve (using K=1.02 and L=0.47) is plotted along with the measured values (the program KINET listed in Appendix D allows for the calculation of single curves). The calculated extent of reaction coincides with the observed values throughout the entire reaction. The second curve (upper) on the graph shows the anticipated conversion based on $k_0$ if there was no inhibition to the reaction

The calculated K and L values for PCEO and other polymers are presented in Table III.15 (contour plots for the other reactions can be found in Appendix C). Though I would hesitate to draw definitive conclusions based on these calculated values, I do believe there are trends in the data that are noteworthy. First of all, all the reactions have L values less than

unity, showing that the reactivity of a functional group drops significantly after both of its neighbors have reacted. Secondly, it appears that the reactions in $CDCl_3$ have smaller K and L values than those in DMAc. This could be indicative that the polymers in $CDCl_3$ are perhaps in a more tightly coiled conformation. The third and most important trend is that L appears to get larger with increased pendant chain length. The clearest evidence for this can be seen in the reactions in DMAc at 40° C where L increases from 0.47 for PCEO to 0.72 for PCPO and finally to 0.93 for PCBO. An increase in chain length should lead to an increased ability of a pendant chain end to move away from its neighbors, thus this increase in L appears to support the supposition that steric factors are the source of the lowering in reactivity.

The polymers studied by Boucher [58] showed no dependance of K and L on temperature. Only those reactions listed in Table III.15 were followed to high enough conversions to get reliable K and L values thus limiting what can be said about reactions run at different temperatures, but the values for L found for PECH and P3CMO seem to fit into the ordering expected. PECH showed a lower value for L than PCEO at either 40 or 50° C and P3CMO was found to yield a larger value for L than either PCEO or PECH.

One of the weak points of this method for evaluating K an d L values is the dependance on the estimated value of the initial rate constant $k_0$ for which we have estimated possible errors (1 standard deviation of the slopes of the origin to point lines at low conversion) of about ±10% in most cases and one must consider the possibility that a small error in $k_0$ could lead to erroneous conclusions. To evaluate the possible effects of this uncertainty the data for the reaction of PCPO with TBAB in DMAc at 40° C was evaluated using 5 different estimates for $k_0$ as listed in Table III.16. These results show that while the values for K depend greatly on the estimate of $k_0$ (K equals 1.20 for $k_0$ + 1 standard deviation and 0.85 for $k_0$ - 1 standard deviation), the obtained values for L seem to be independent allowing one to draw conclusions based on this value.

Table III.13. Spin-Lattice Relaxation Times[a] of Partially Benzoyloxylated PBEO.

| Conversion % | $T_1$(CH Br)[b] sec | $T_1$(CH Benz)[c] sec | $T_1$($CH_2$ Benz)[d] sec | $\eta_{inh}$[e] dl/g |
|---|---|---|---|---|
| 0 | 0.436 | - | - | 1.37 |
| 41 | 0.436 | 0.328 | 0.325 | 1.46 |
| 45 | 0.374 | 0.412 | 0.262 | 1.42 |
| 57 | 0.339 | 0.318 | 0.267 | 1.38 |
| 80 | 0.335 | 0.271 | 0.246 | 1.39 |
| 88 | - | 0.281 | 0.245 | 1.41 |
| 100 | - | 0.256 | 0.220 | 1.36 |

a. Error limits in $T_1$ measurements less than ±12%.
b. $T_1$ of backbone methine signal from bromine containing repeat units
c. $T_1$ of backbone methine signal from benzoate containing repeat units.
d. $T_1$ of benzoyloxylated methylene.
e. 30° C DMAc.

Table III.14. Spin-Lattice Relaxation Times[a] of Partially Benzoyloxylated PCEO.

| Conversion % | $T_1$(CH)[b] sec | $T_1$($CH_2Cl$)[c] sec | $T_1$($CH_2$ Benz)[d] sec |
|---|---|---|---|
| 0 | 0.523 | 0.618 | - |
| 11 | 0.453 | 0.564 | - |
| 19 | 0.452 | 0.572 | 0.320 |
| 28 | 0.396 | 0.542 | 0.293 |
| 37 | 0.369 | 0.519 | 0.272 |
| 41 | 0.377 | 0.516 | 0.260 |
| 45 | 0.335 | 0.497 | 0.247 |
| 53 | 0.337 | 0.457 | 0.254 |
| 59 | 0.333 | 0.469 | 0.253 |
| 83 | 0.293 | 0.421 | 0.239 |
| 100 | 0.256 | - | 0.220 |

a. Error limits in $T_1$ measurements less than ±10%.
b. $T_1$ of backbone methine signal and represents an average of reacted and unreacted repeated units.
c. $T_1$ of ω-chloro-methylene.
d. $T_1$ of benzoyloxylated methylene.

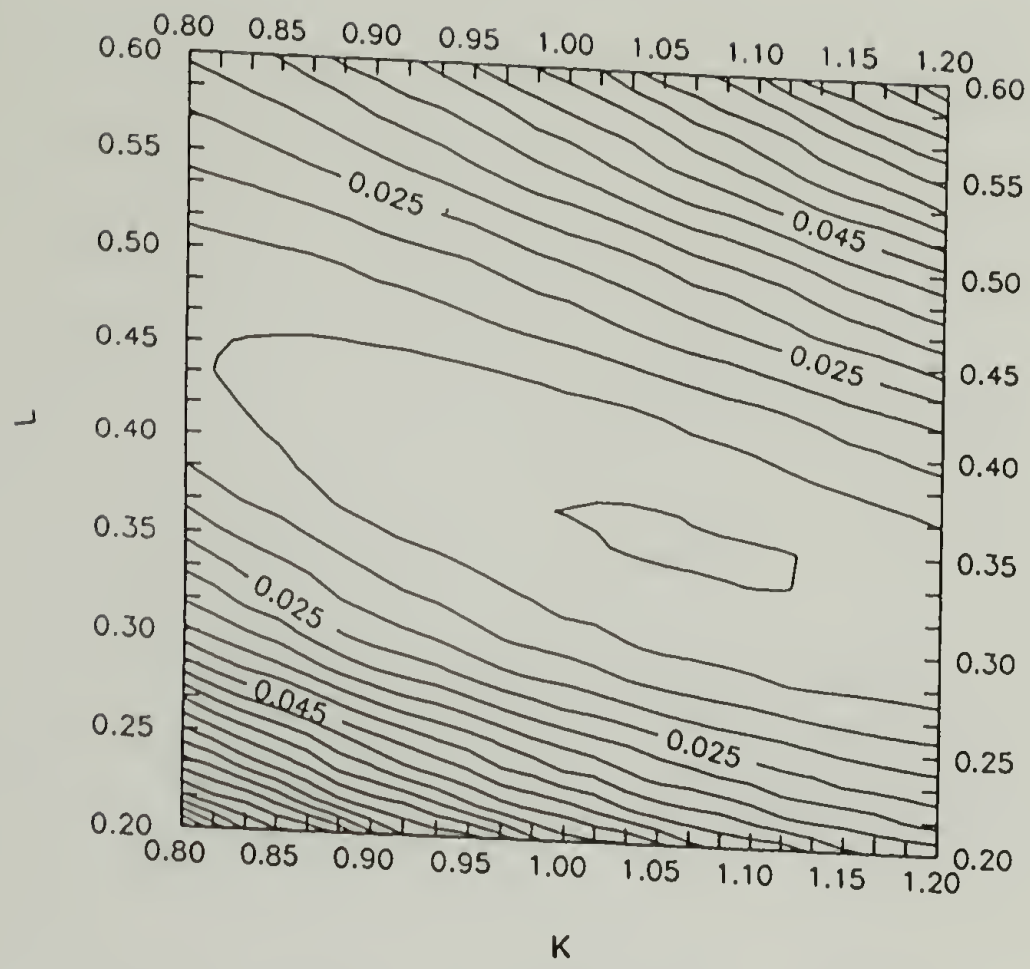


Figure III.17. Contour plot of the error of calculated conversion vs actual conversion as a function of K and L for the reaction of PCEO with TBAB in DMAc at 50° C.

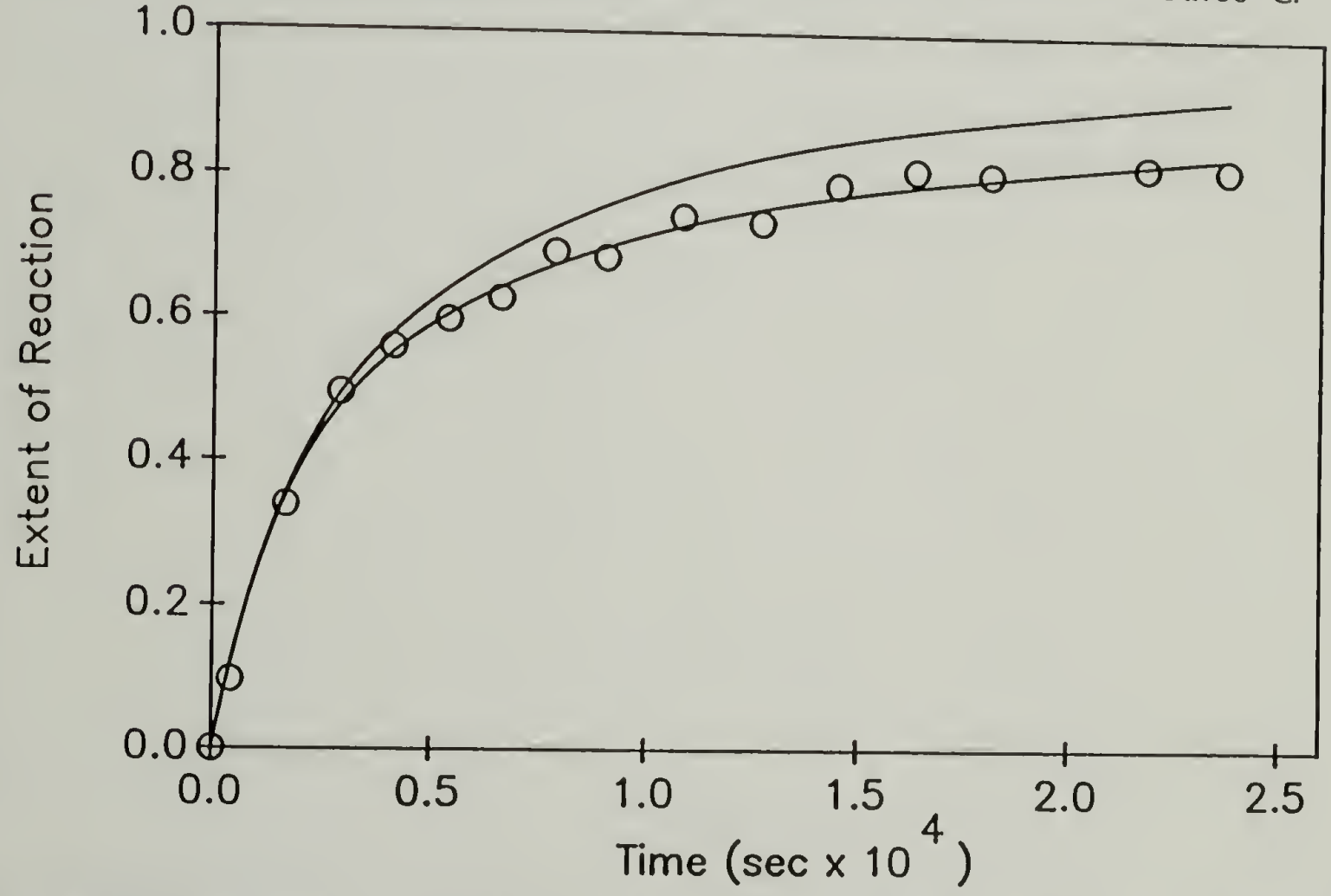


Figure III.18 Comparison of calculated conversion vs time curves vs observed data for reaction of PCEO and TBAB at 40° C in DMAc. Top curve was calculated with K=1, L=1, and the lower curve with K=1.02 and L=0.47.

Table III.15. Calculated K and L Values for Some Reactions of TBAB with Poly(ω-haloalkyl)ethers.

| Polymer | Solvent | Temperature (°C) | K | L |
|---|---|---|---|---|
| PBEO | $CDCl_3$ | 45 | 0.70 | 0.38 |
| PBPO | $CDCl_3$ | 45 | 0.93 | 0.43 |
| PBBO | $CDCl_3$ | 45 | 0.74 | 0.43 |
| PECH | DMAc | 70 | 1.20 | 0.33 |
| PCEO | DMAc | 50 | 1.05 | 0.37 |
| PCEO | DMAc | 40 | 1.02 | 0.47 |
| PCPO | DMAc | 40 | 1.02 | 0.72 |
| PCBO | DMAc | 40 | 0.99 | 0.93 |
| P3CMO | DMAc | 50 | 0.98 | 0.63 |

Table III.16. Calculated K and L Values for the Reaction of TBAB with PCPO in DMAc at 40° C for Different Estimates of Initial Rate Constant.[a]

| Estimate of Initial k | K | L | e[b] |
|---|---|---|---|
| $k_0$ | 1.02 | 0.72 | 0.00482 |
| $k_0$ + 0.5 STD | 0.92 | 0.72 | 0.00630 |
| $k_0$ + 1 STD | 0.85 | 0.72 | 0.00667 |
| $k_0$ - 0.5 STD | 1.07 | 0.73 | 0.00573 |
| $k_0$ - 1 STD | 1.20 | 0.72 | 0.00557 |

a. $k_0$ ($1.9 \times 10^{-3}$ $M^{-1}s^{-1}$) is the average value derived from the slopes of origin-to-point lines for measurements at low conversion. The value STD is one standard deviation of the average slope ($8.6 \times 10^{-5}$ $M^{-1}$ $s^{-1}$).

b. e is the sums of squares of the difference between calculated and observed conversions (chi-square).

## E. Conclusions

The synthetic portion of this work led to the preparation of three new heterocylic monomers: BBO, 3CMO and 2CMO, and four new halogenated polyethers : PBBO, P3CO, P2CMO and P3CMO. It was demonstrated that the polyethers could be prepared in high molecular weight, that they possess elastomeric properties, and that they are subject to clean chemical modification by nucleophilic substitution.

The kinetic studies described represent the first attempt to provide a general set of structure-reactivity relationships for nucleophilic substitutions on halogenated polymers. It was found that the same structure-reactivity relationships that pertain to small molecules carry over for the most part, to the polymeric equivalents. The proximity of the reactive site to a branch point was shown to be a dominant factor in the reactivity of polymers with the same functional group, resulting in a reactivity order for the chloro-polymers of: P3CO « PECH < PCEO < PCPO ≈ PCBO. A similar pattern was established for polymers with bromine as the functional group. The replacement of the chloride with a bromide leads to more than an order-of-magnitude increase in reactivity. It was also found that as with small molecules the presence of a β-ether lowers reactivity toward displacement as evidenced by the higher reactivity of P3CMO at 50° C in DMAc compared to PECH and P2CMO which were found to have essentially equal reaction rates.

The reactions of all of the polyether systems described here, exhibit deviations from second order kinetics at high conversion. It was found that the neighboring group model developed by Boucher to explain deviations from second order kinetics, was applicable to these systems. The best fit values for this model to our data indicated that the reaction of one of a reactive group's neighbors had no effect on its reactivity. However if both neighboring groups had reacted, the reactivity of a functional group can drop by more than 60%.

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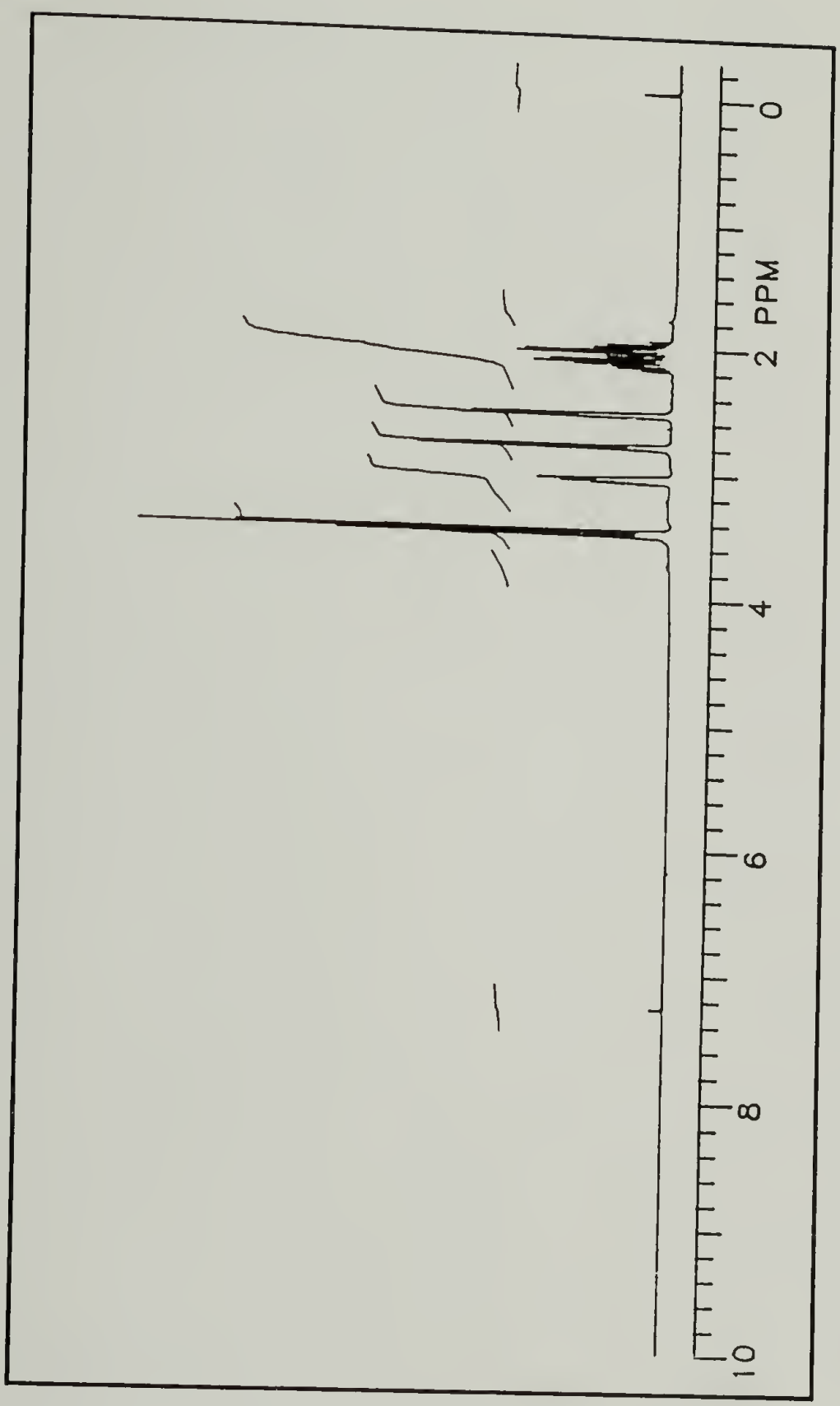
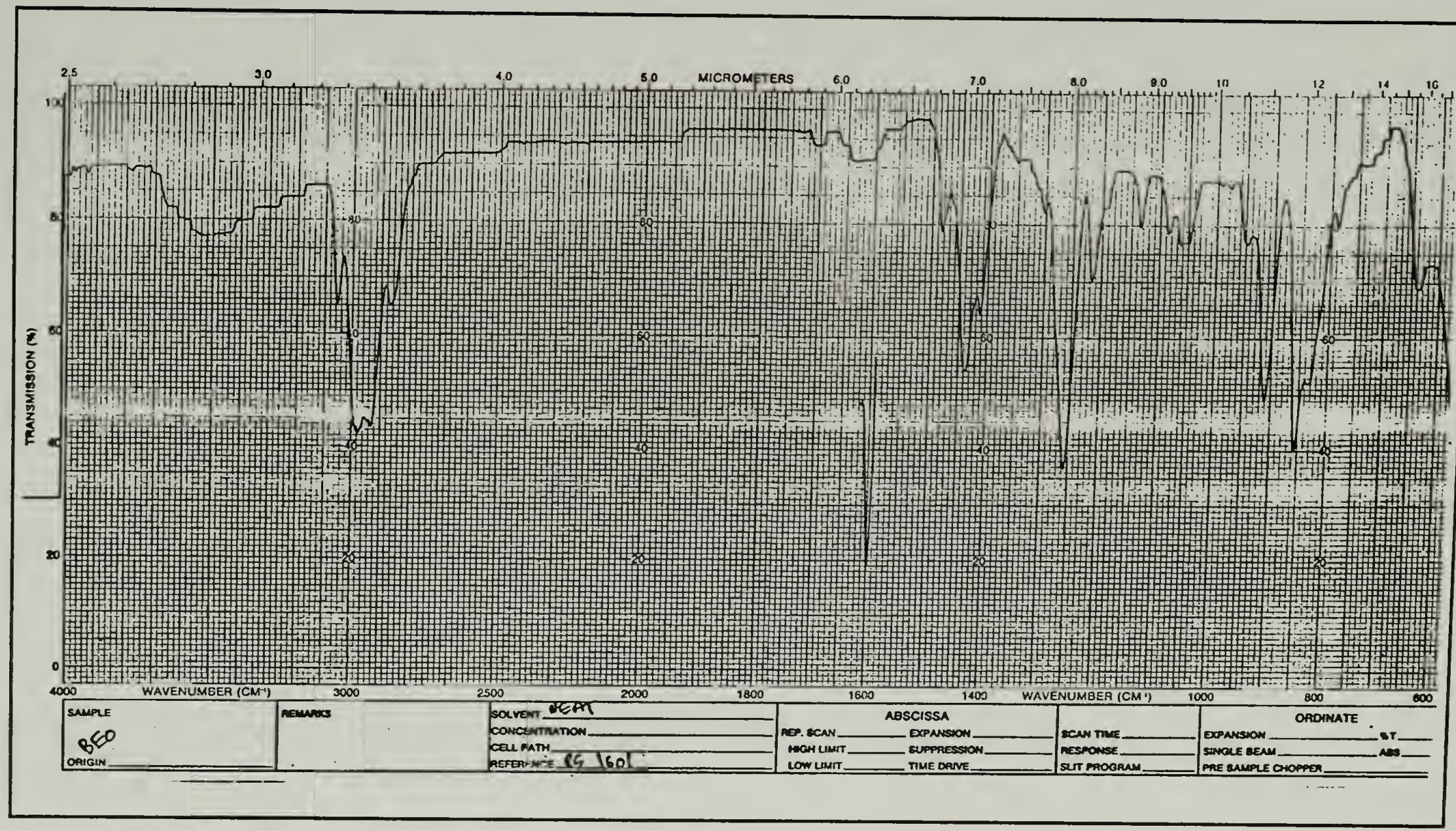
# APPENDIX A.

## Reference Spectra for the Synthesis of Monomers and Intermediates.




(2-BROMOETHYL)OXIRANE

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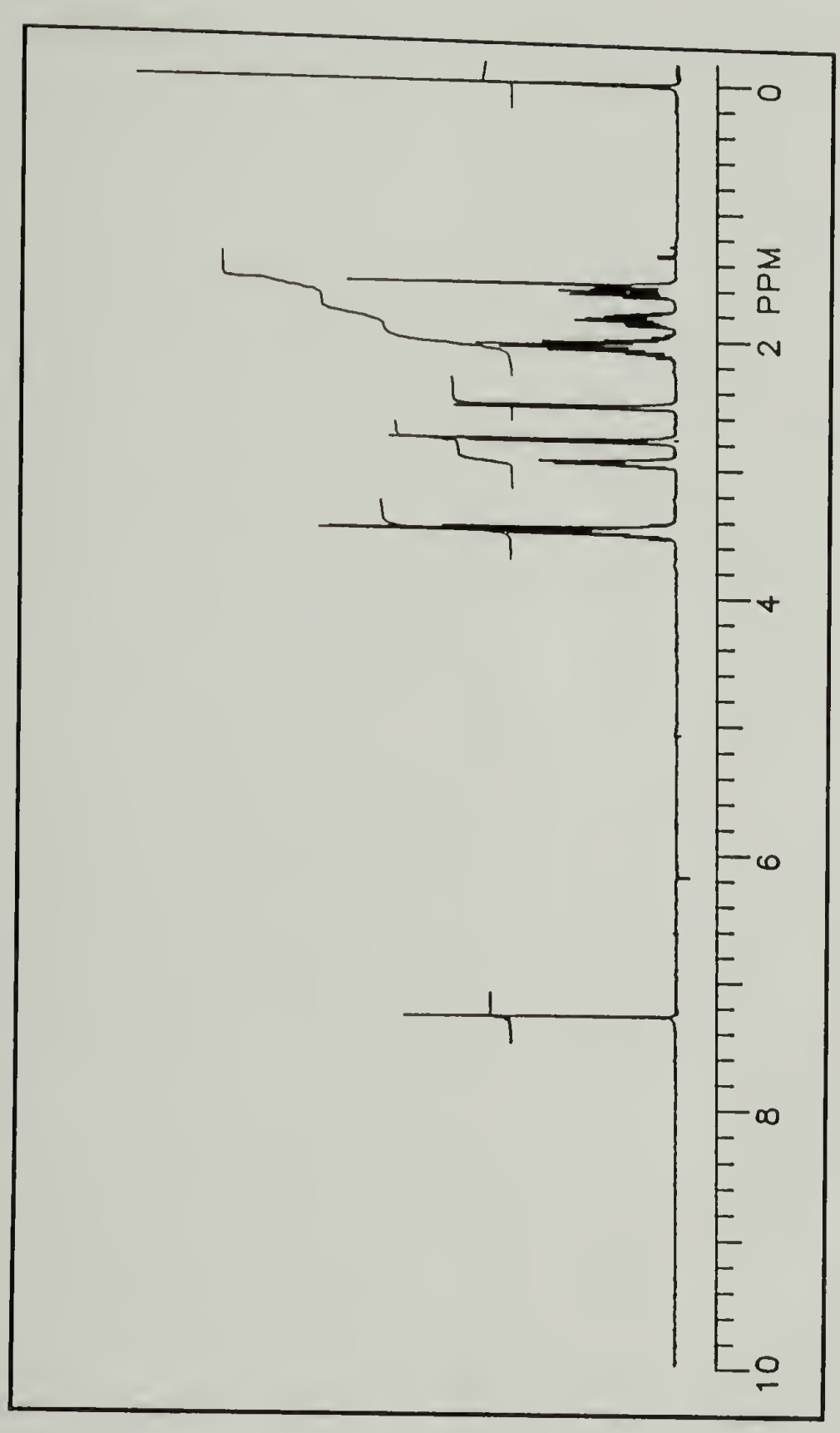


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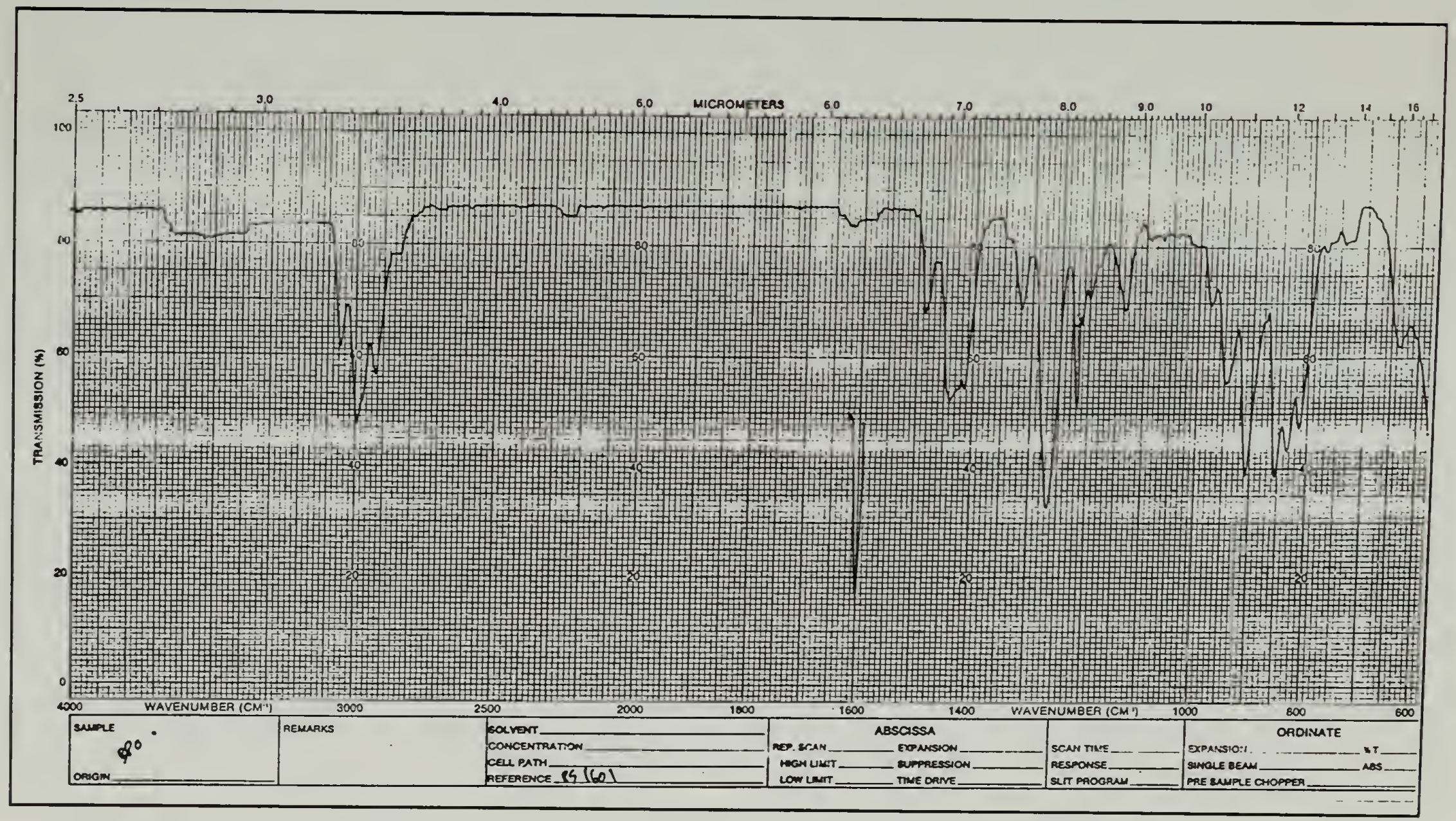


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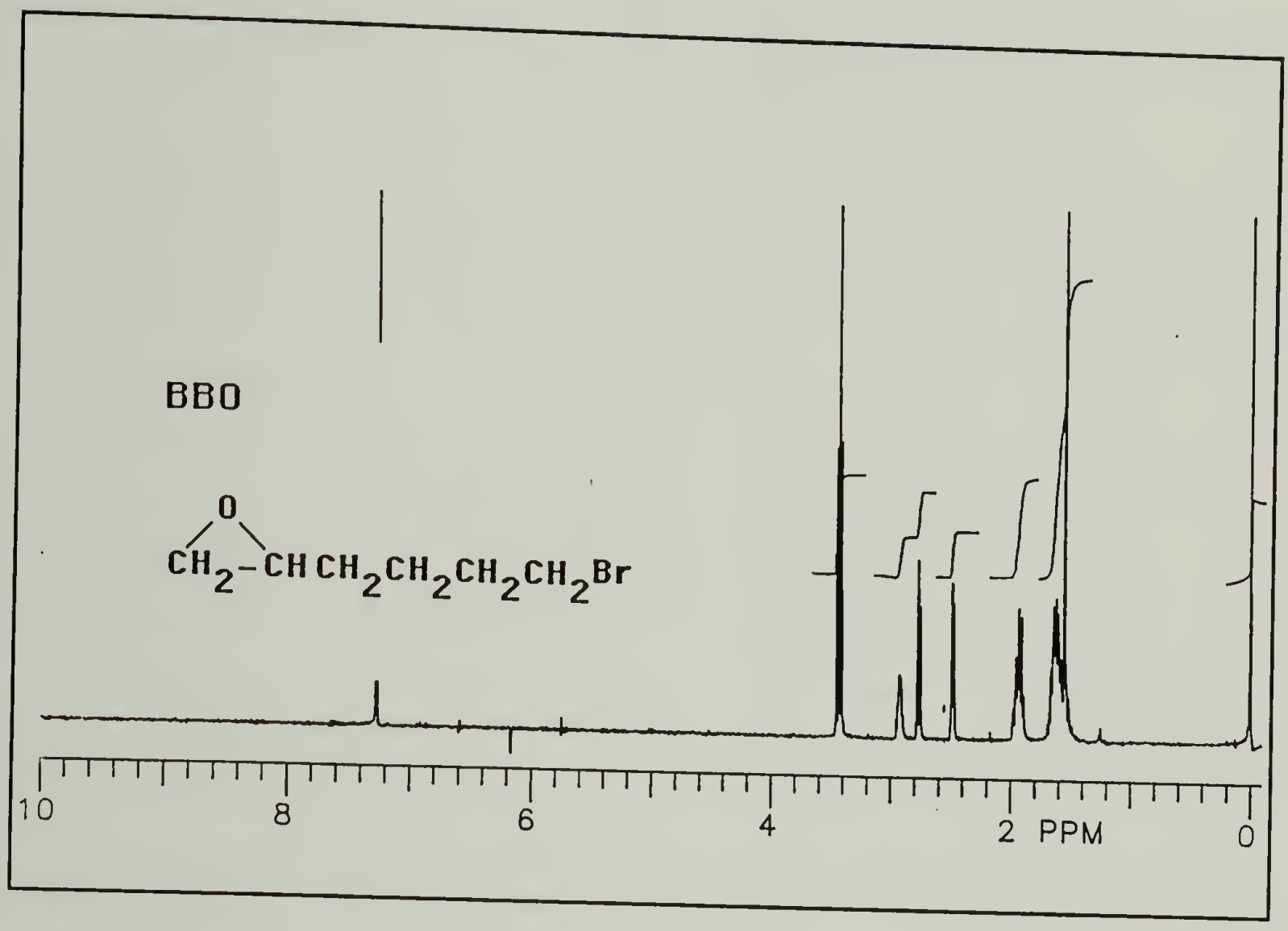
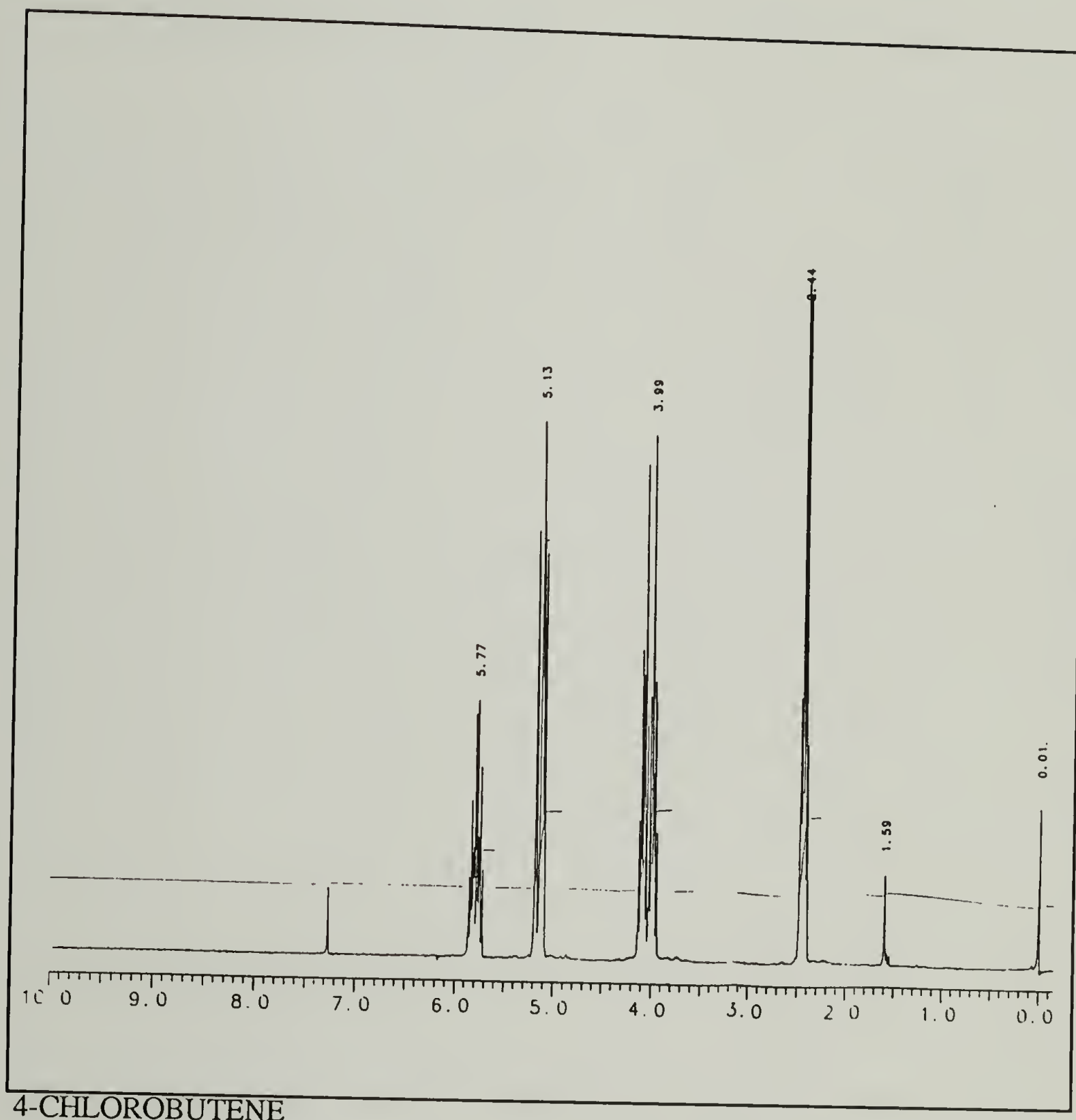
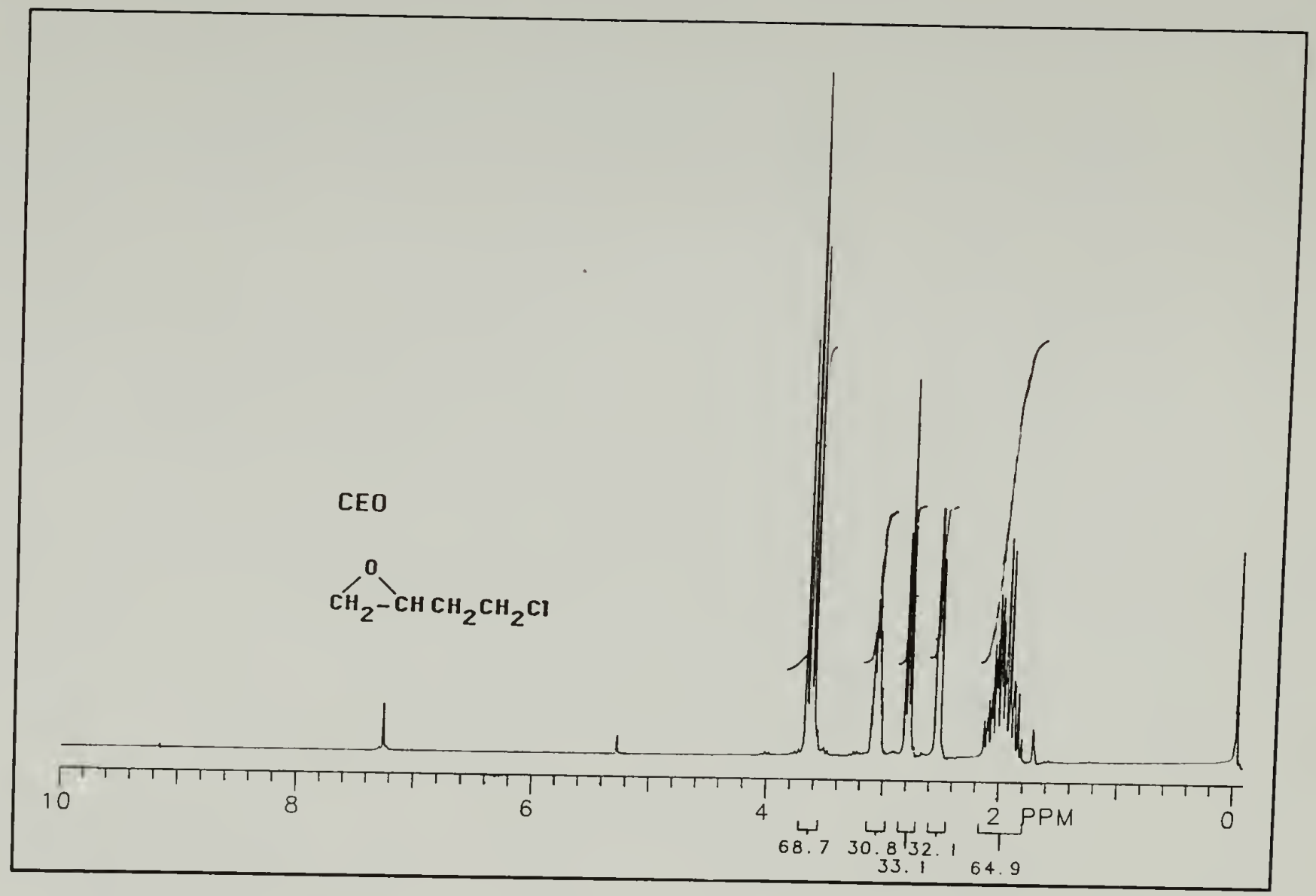

BBO
O
CH2-CH CH2CH2CH2CH2Br
10
8
6
4
2 PPM
0




4-CHLOROBUTENE

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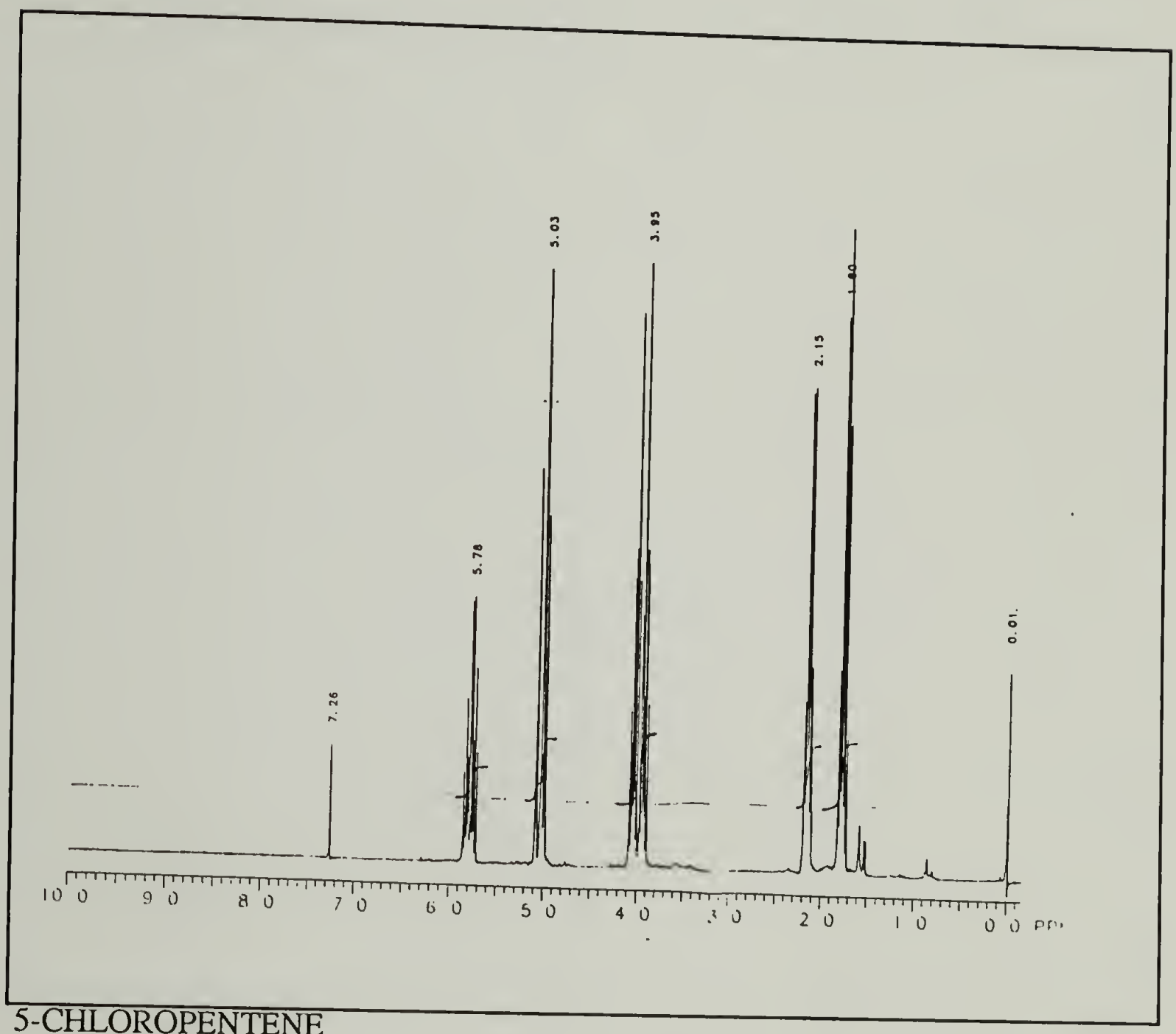


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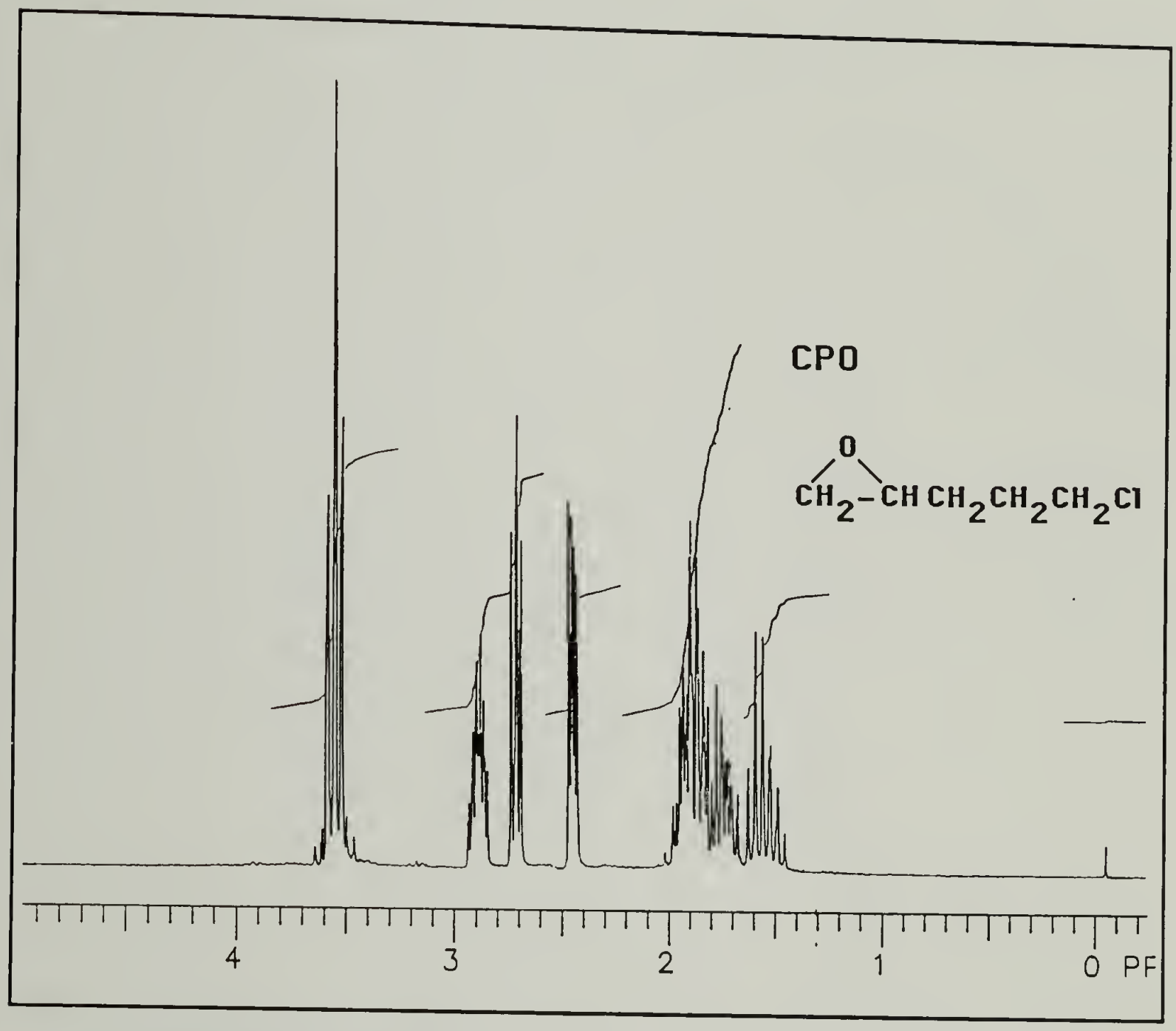


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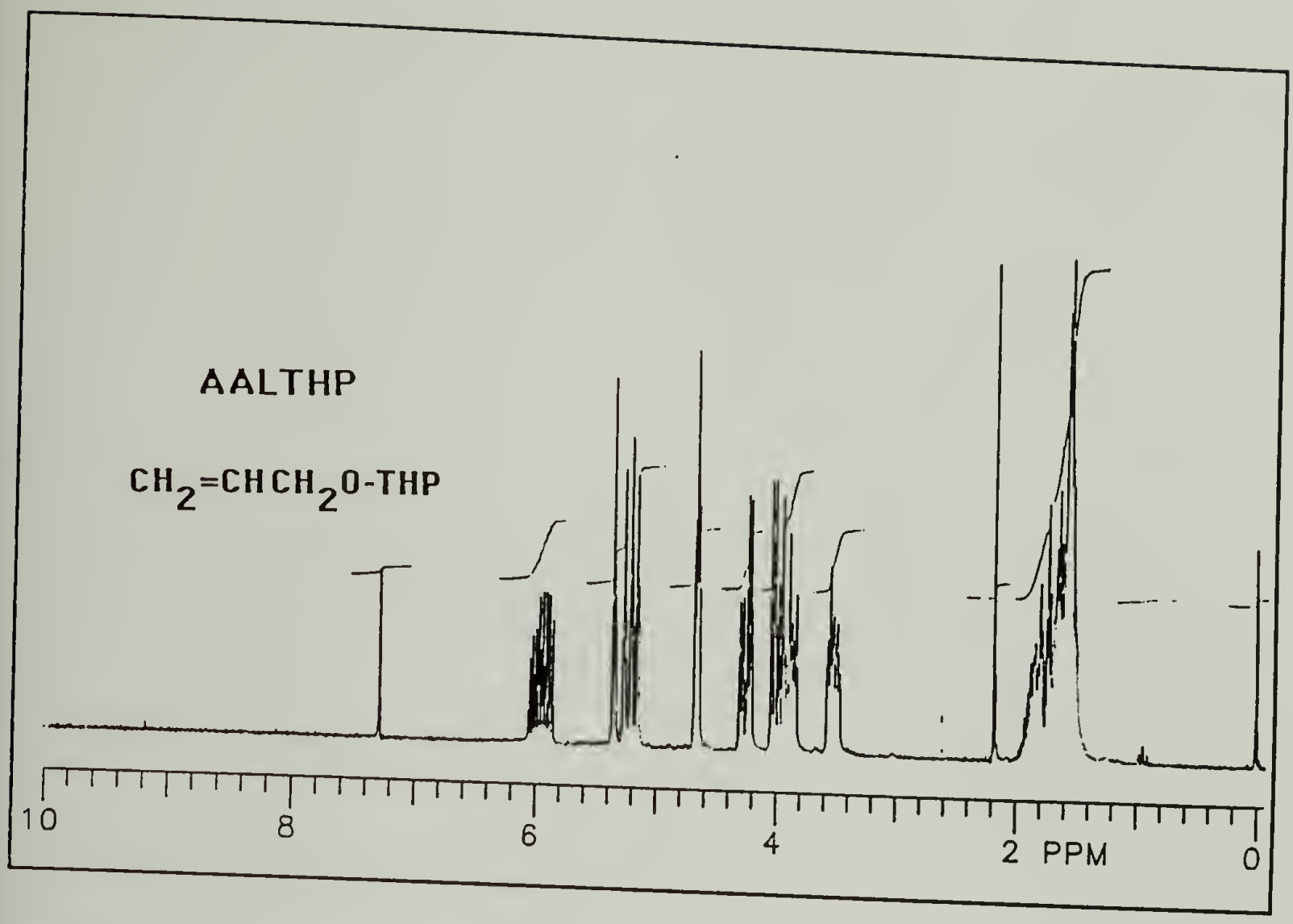
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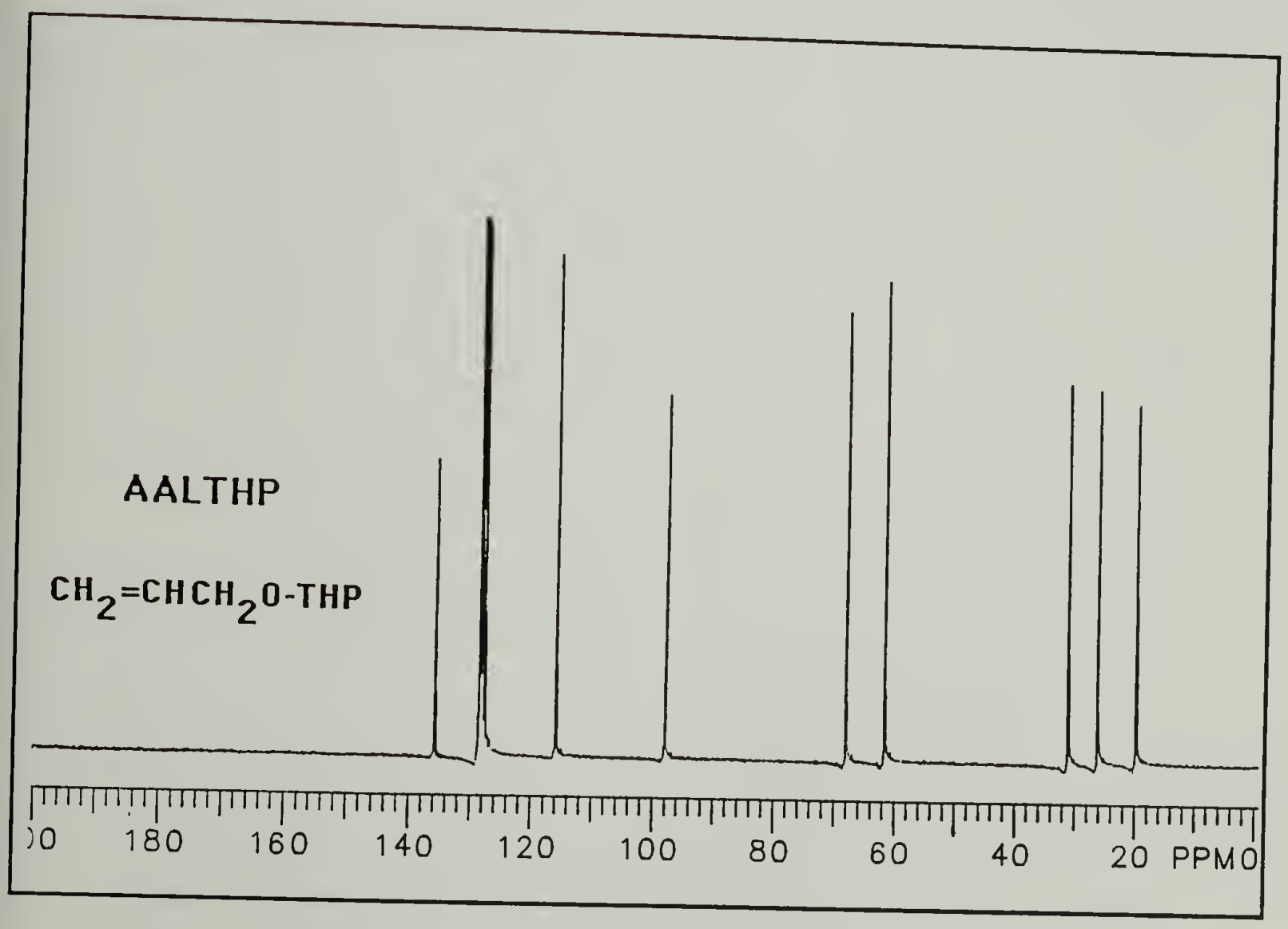
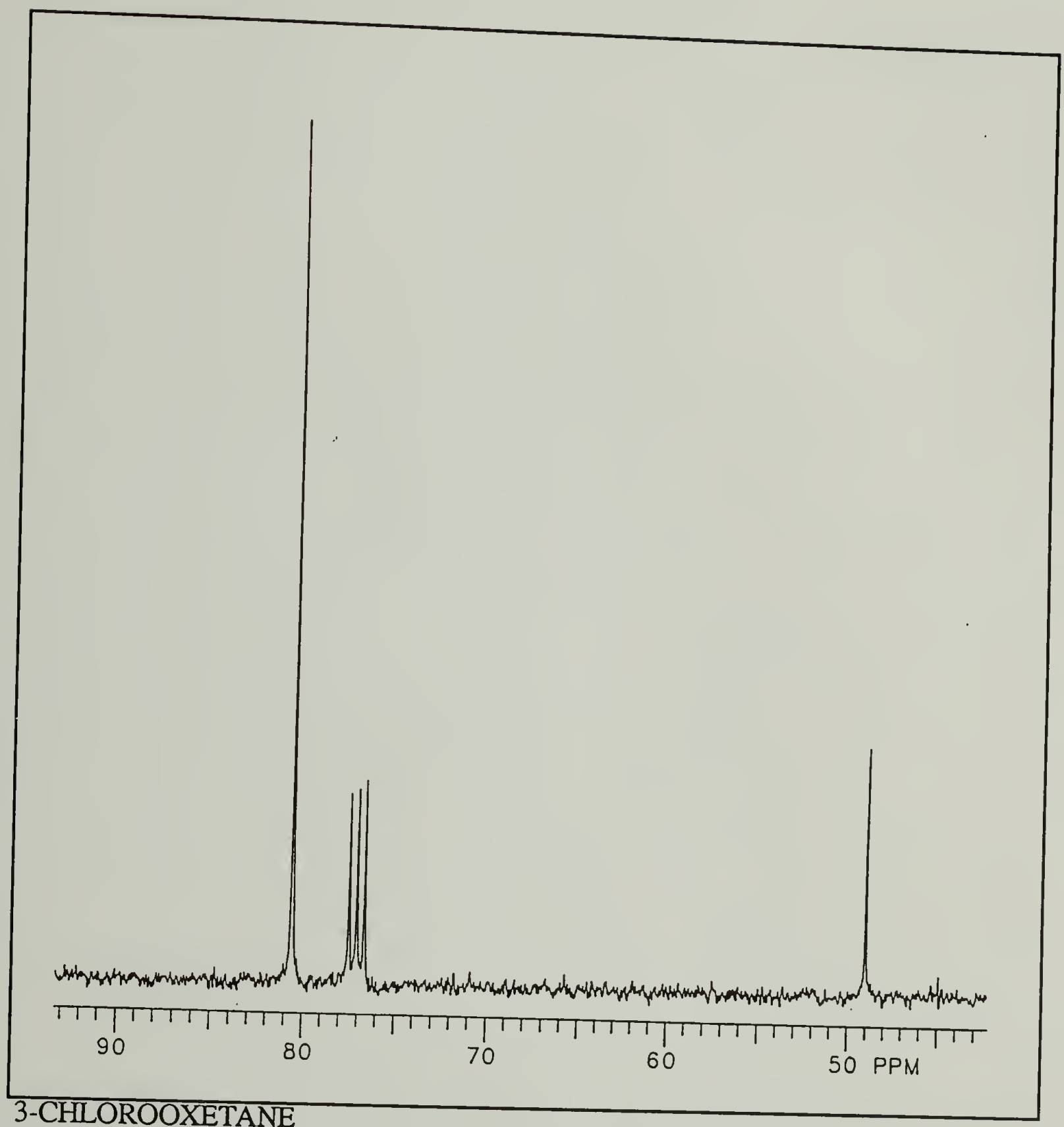
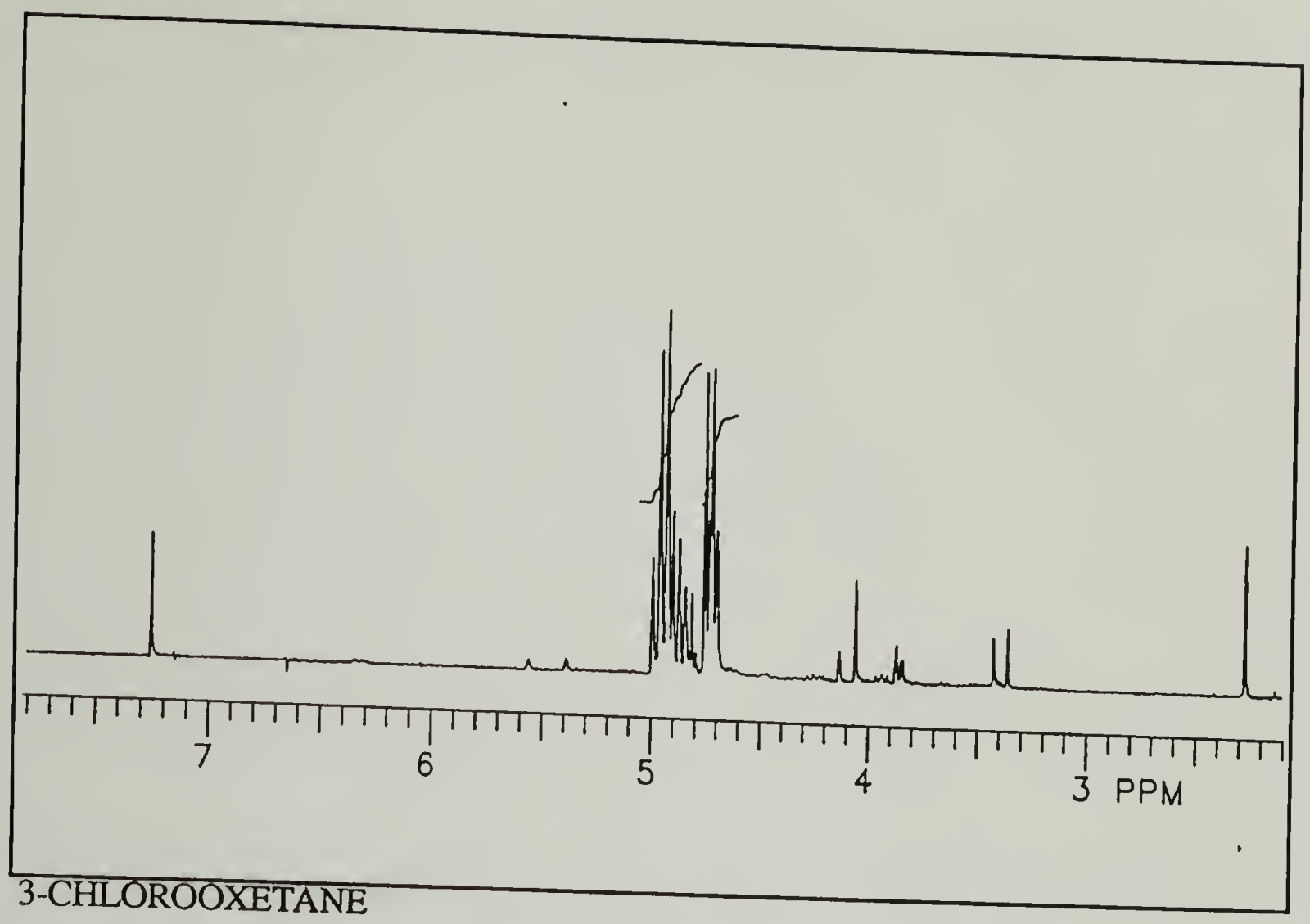
CH2=CHCH2O-THP
10
8
6
4
2 PPM
0


AALTHP
CH2=CHCH2O-THP
180
160
140
120
100
80
60
40
20 PPM0




3-CHLOROOXETANE

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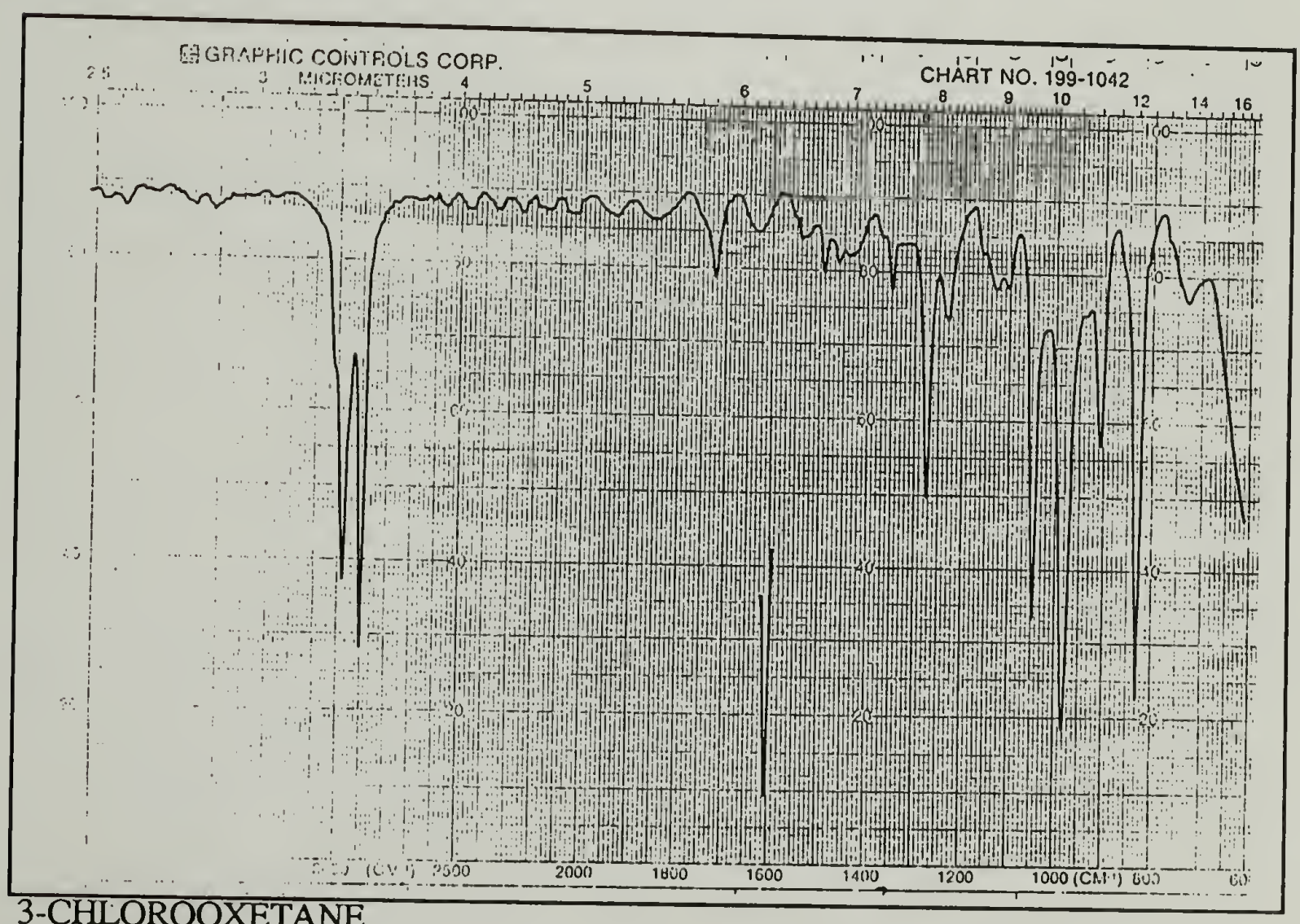


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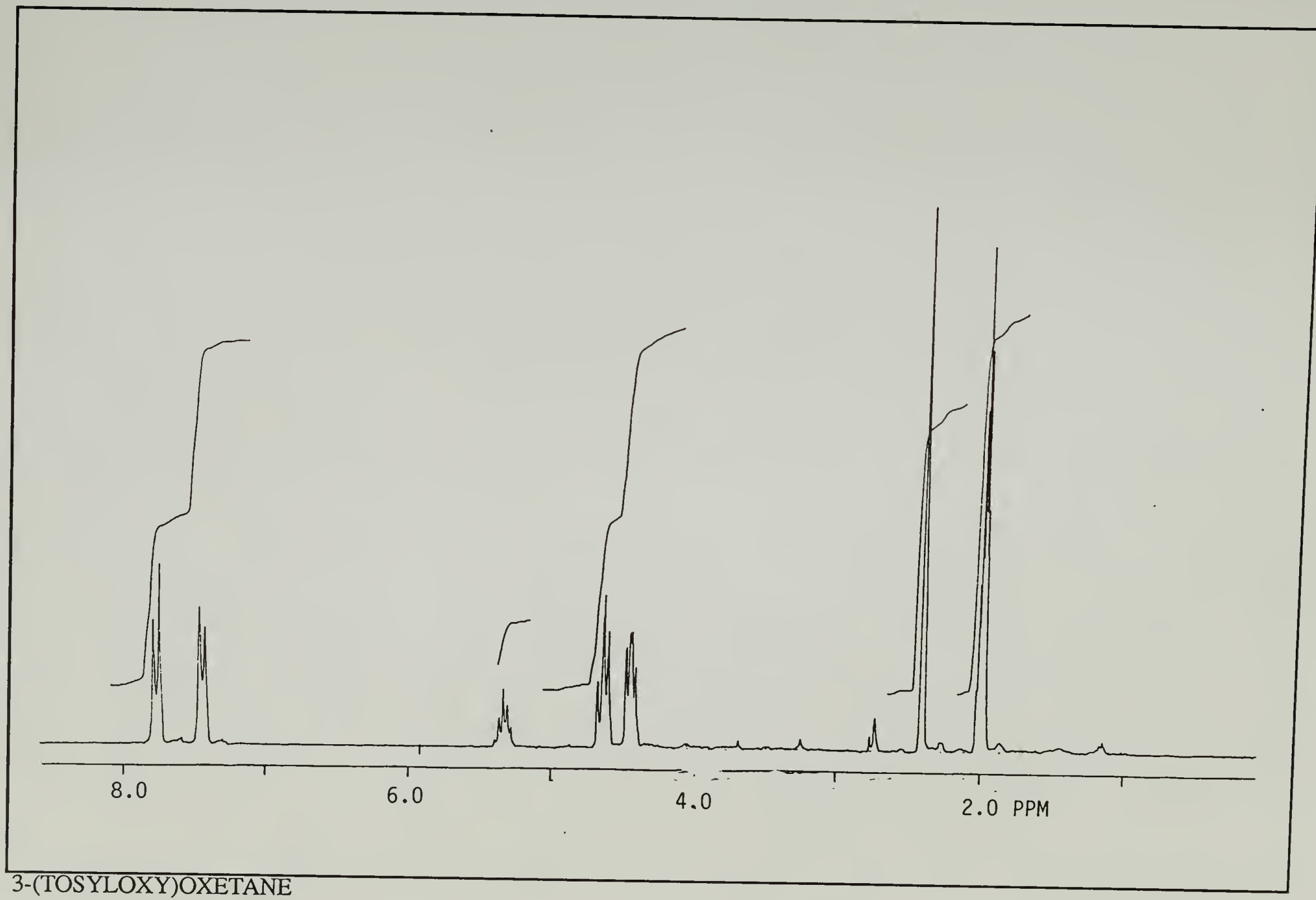
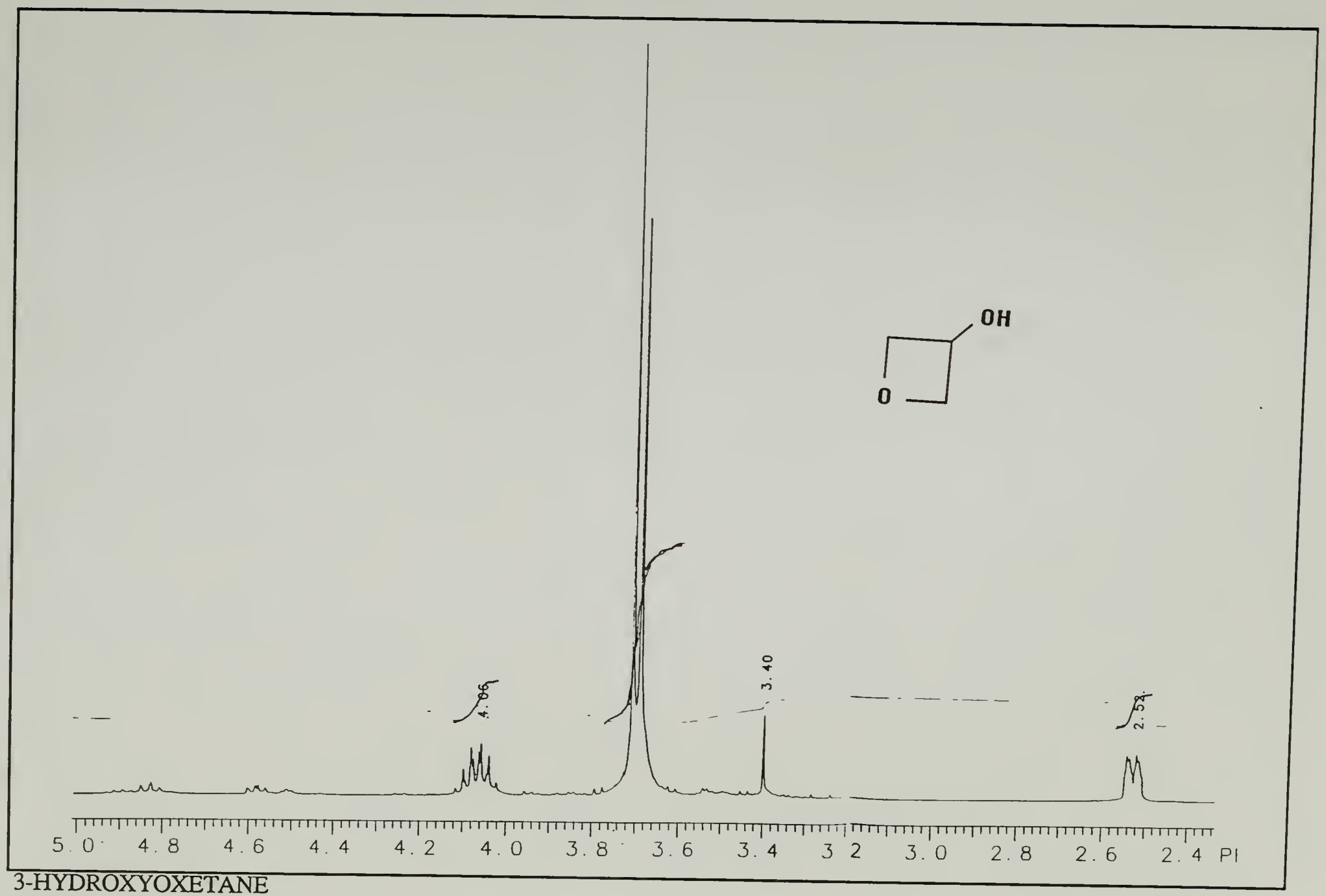



3-(TOSYLOXY)OXETANE

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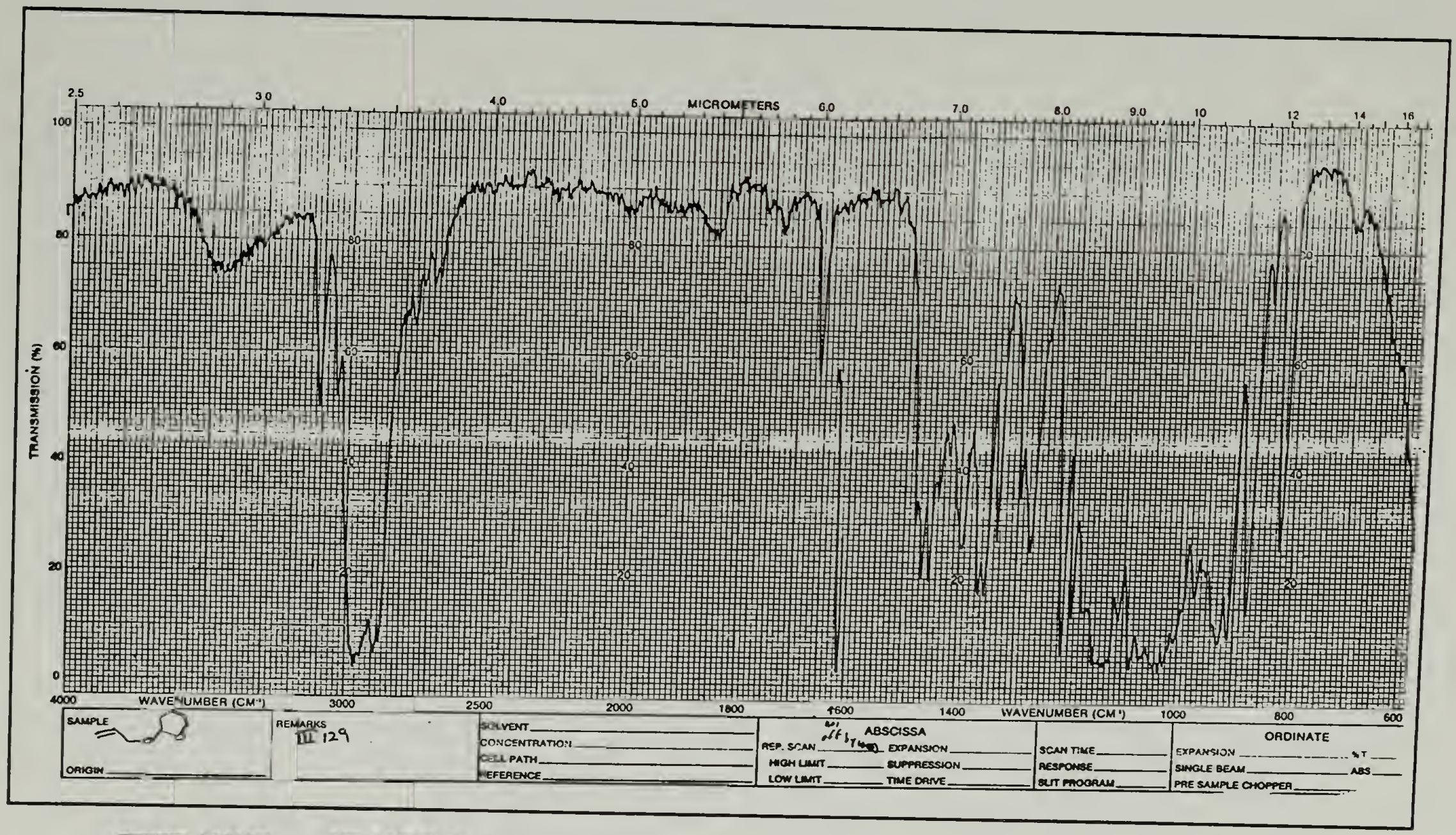
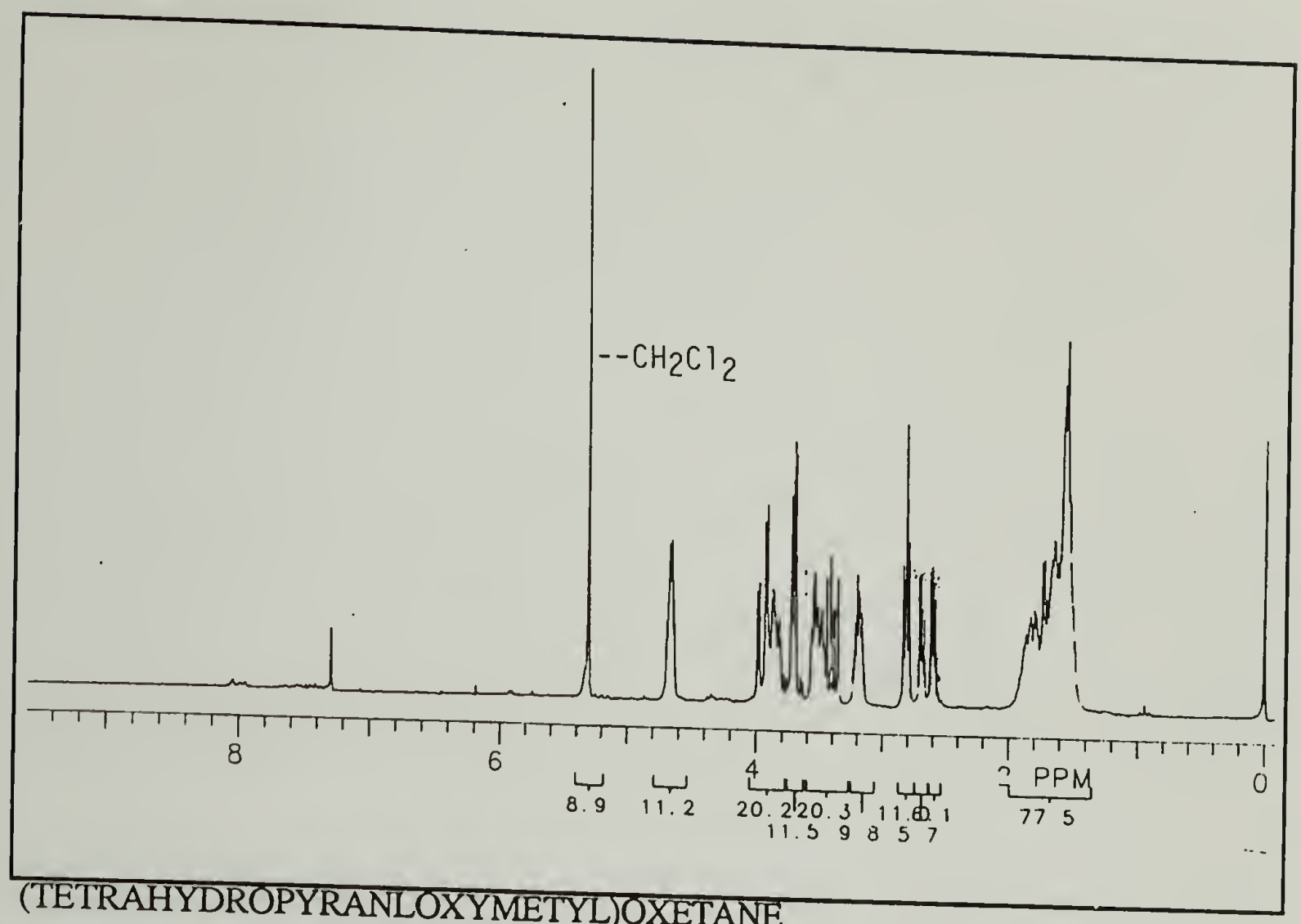
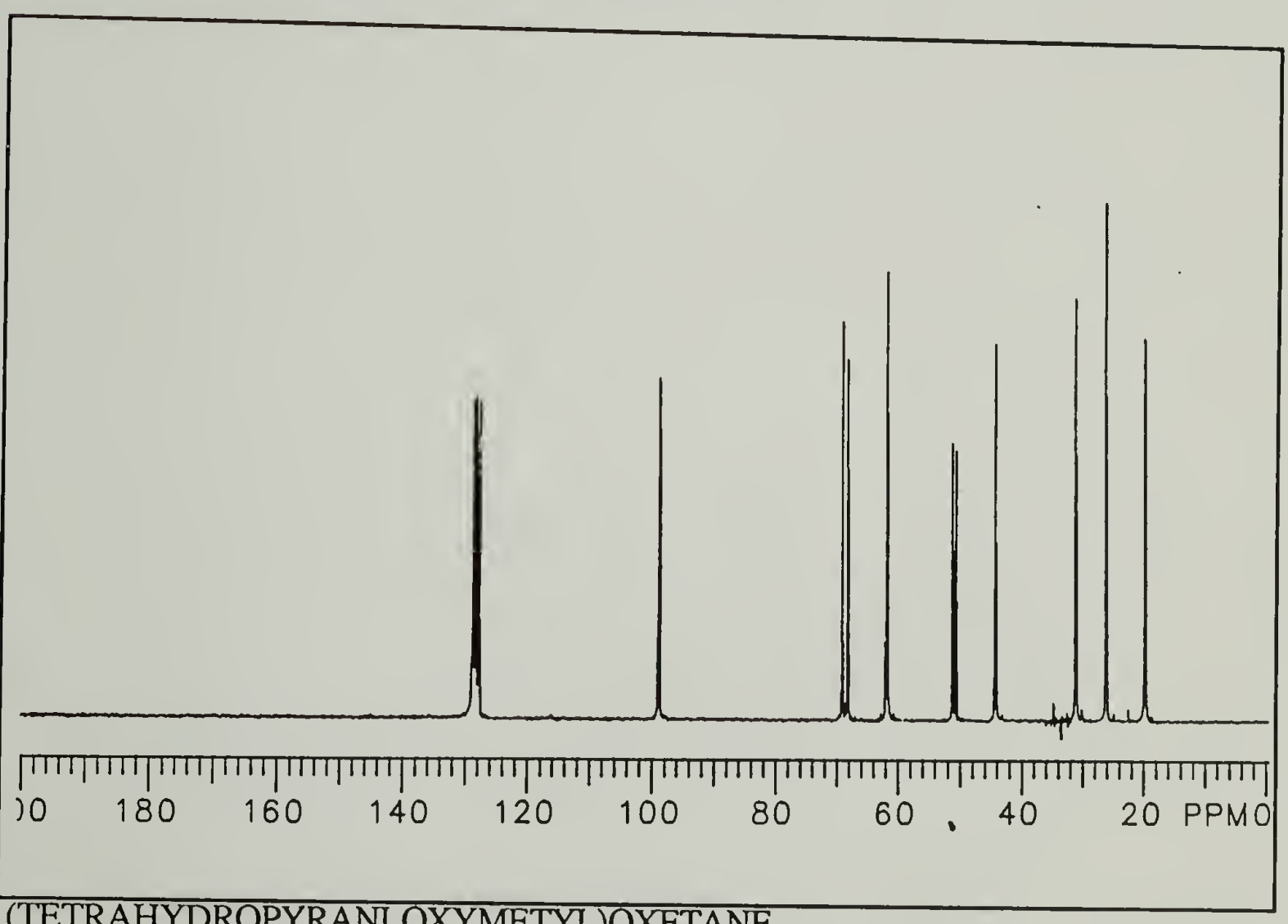


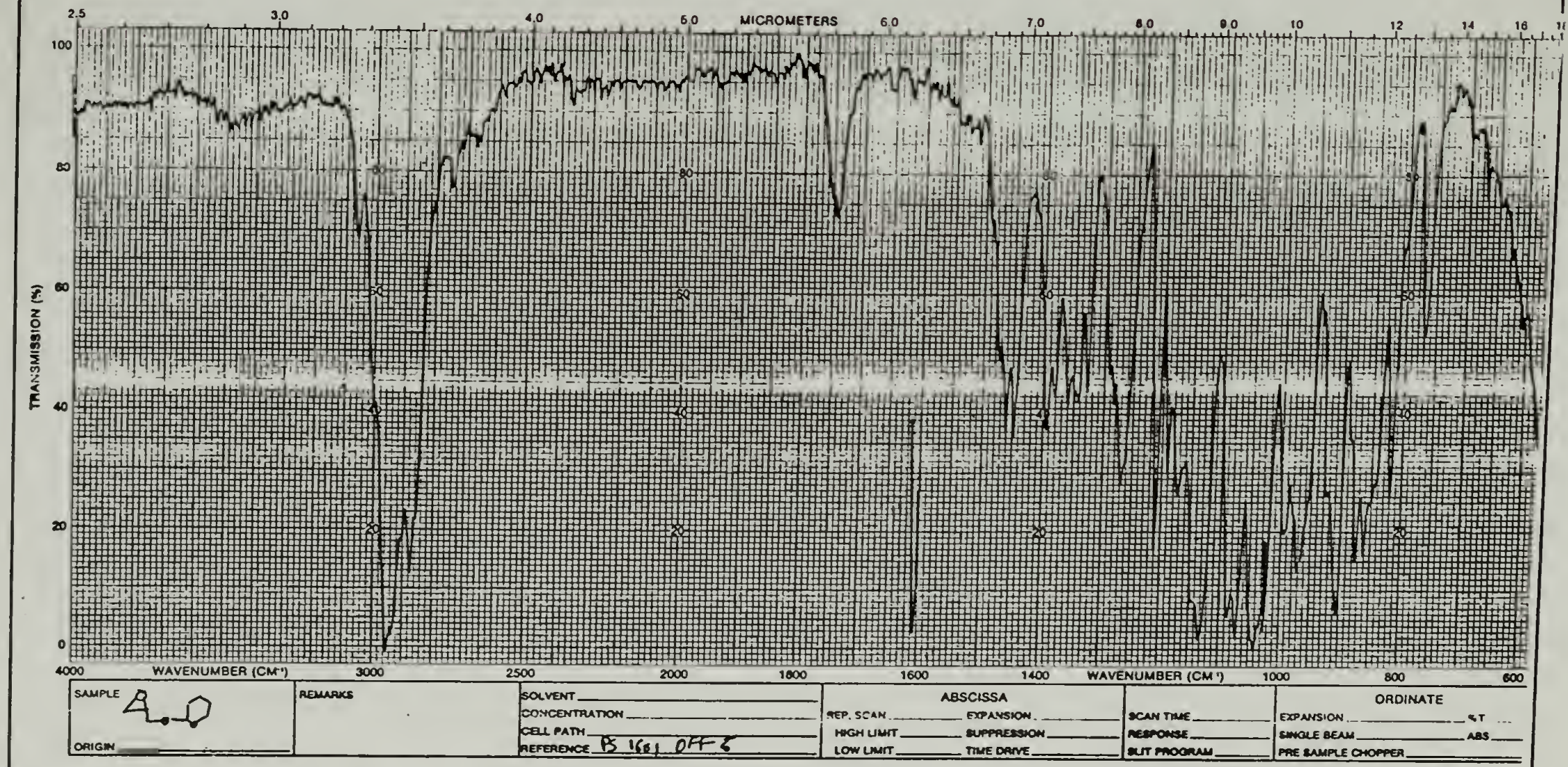

3-(TETRAHYDROPYRANYLOXY)-1-PROPENE




(TETRAHYDROPYRANLOXYMETYL)OXETANE




(TETRAHYDROPYRANLOXYMETYL)OXETANE

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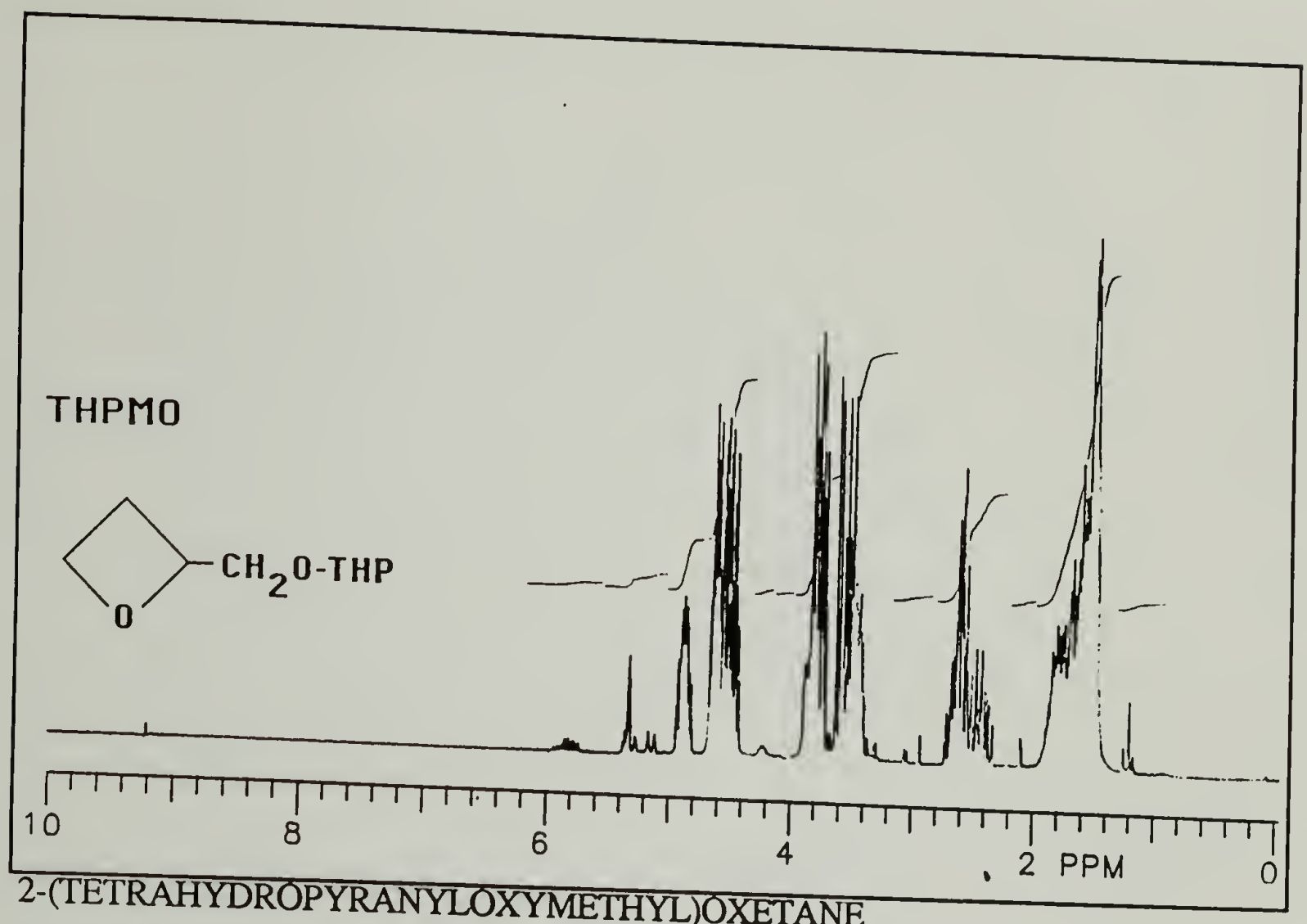


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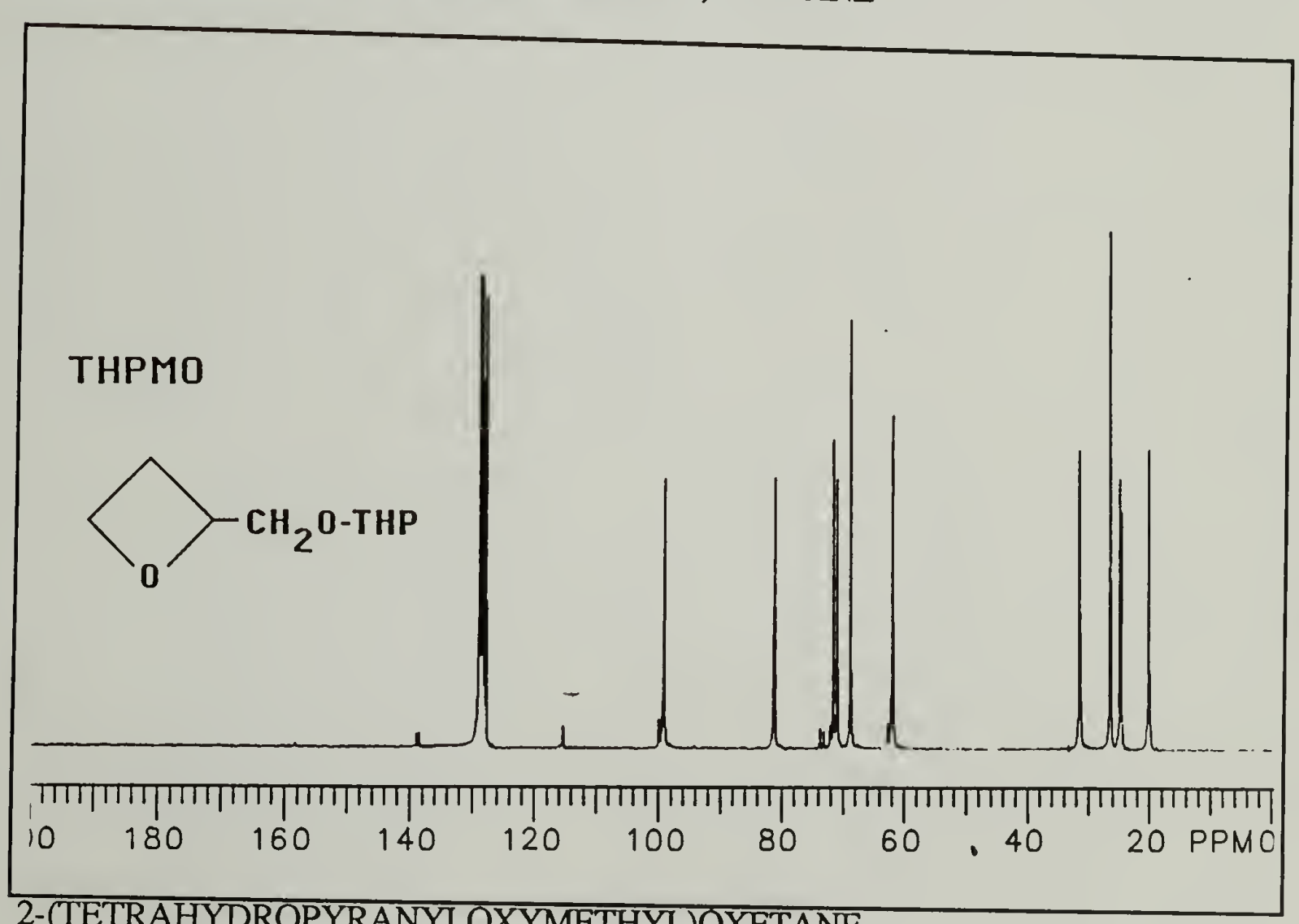


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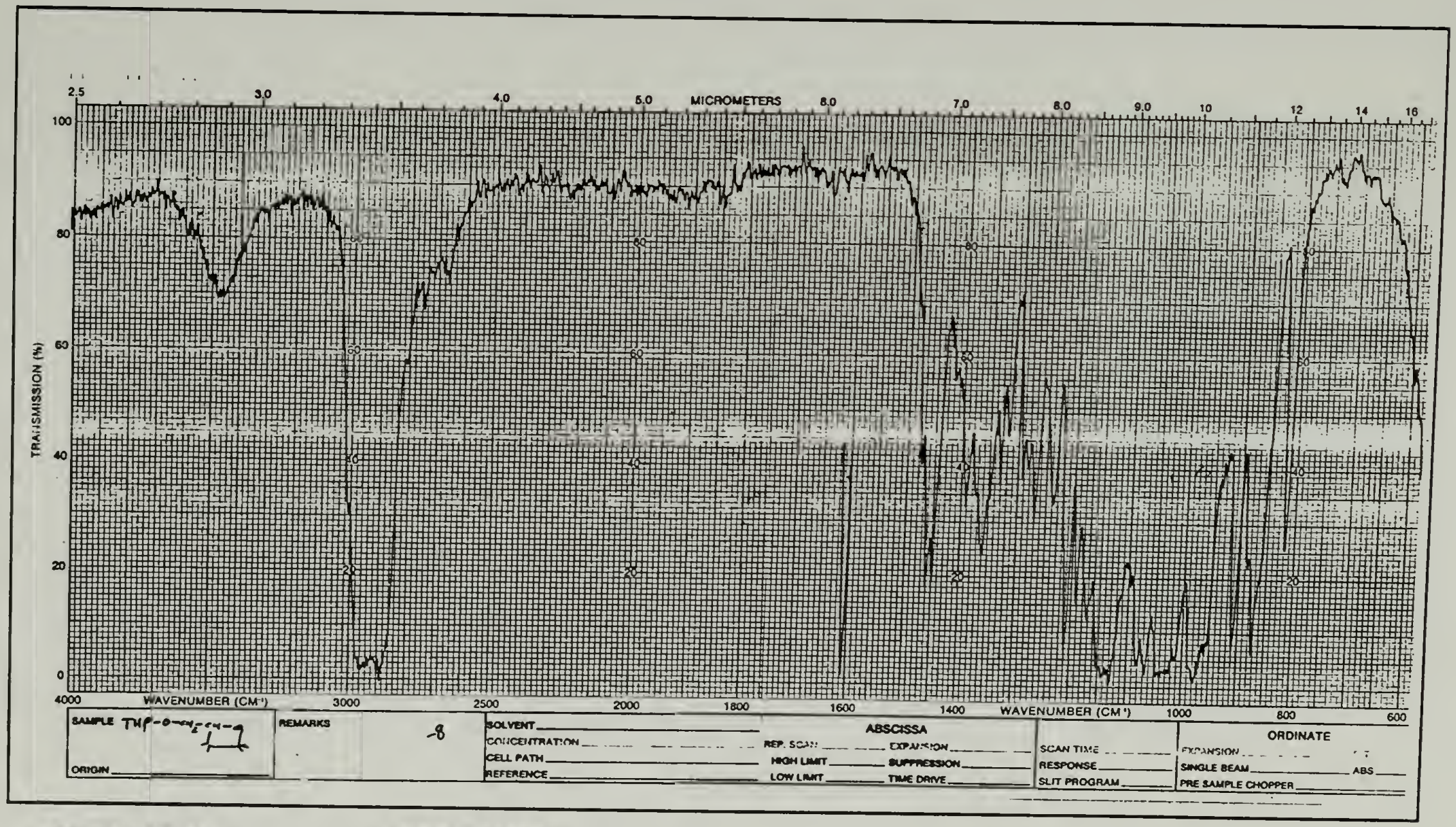


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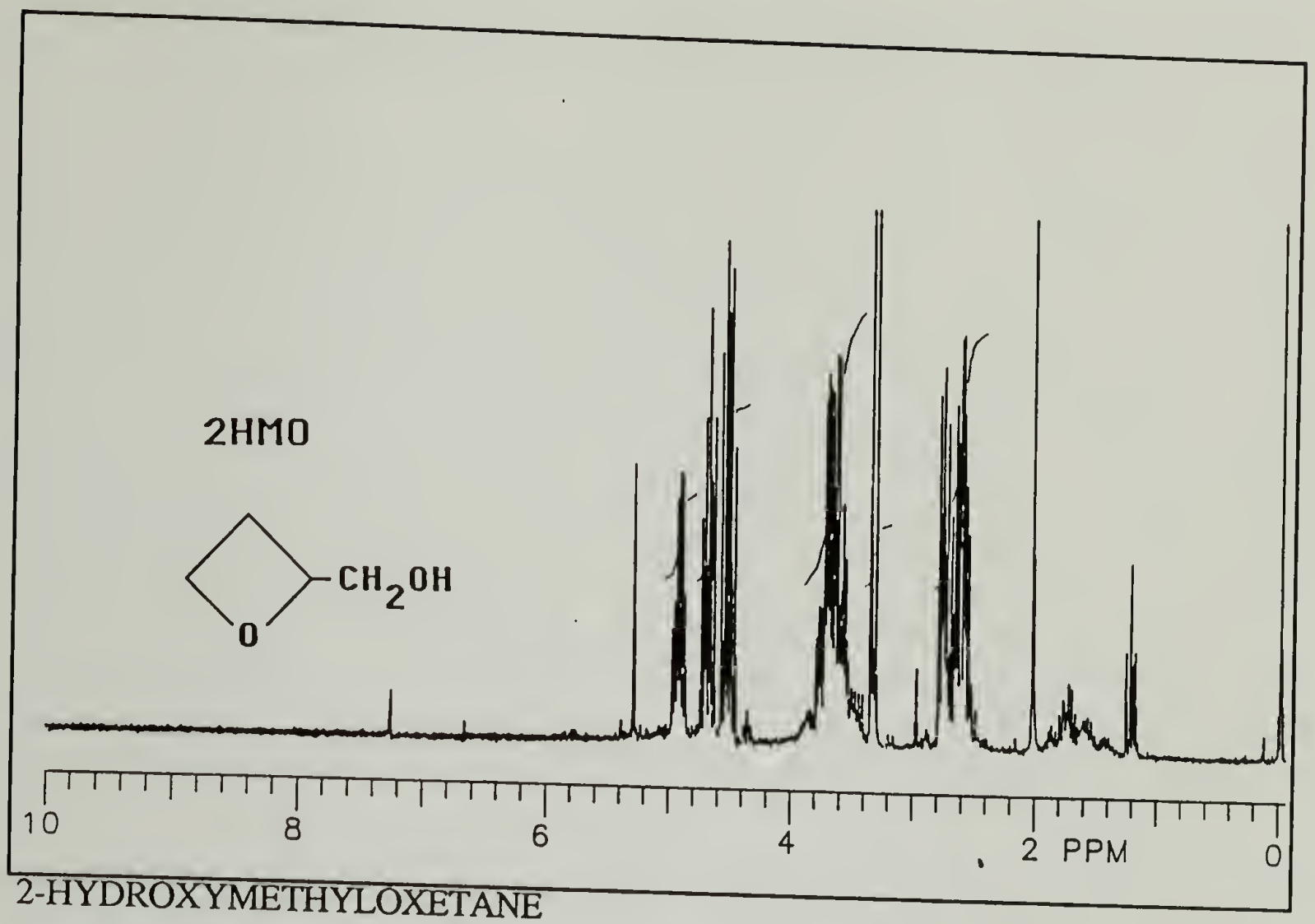


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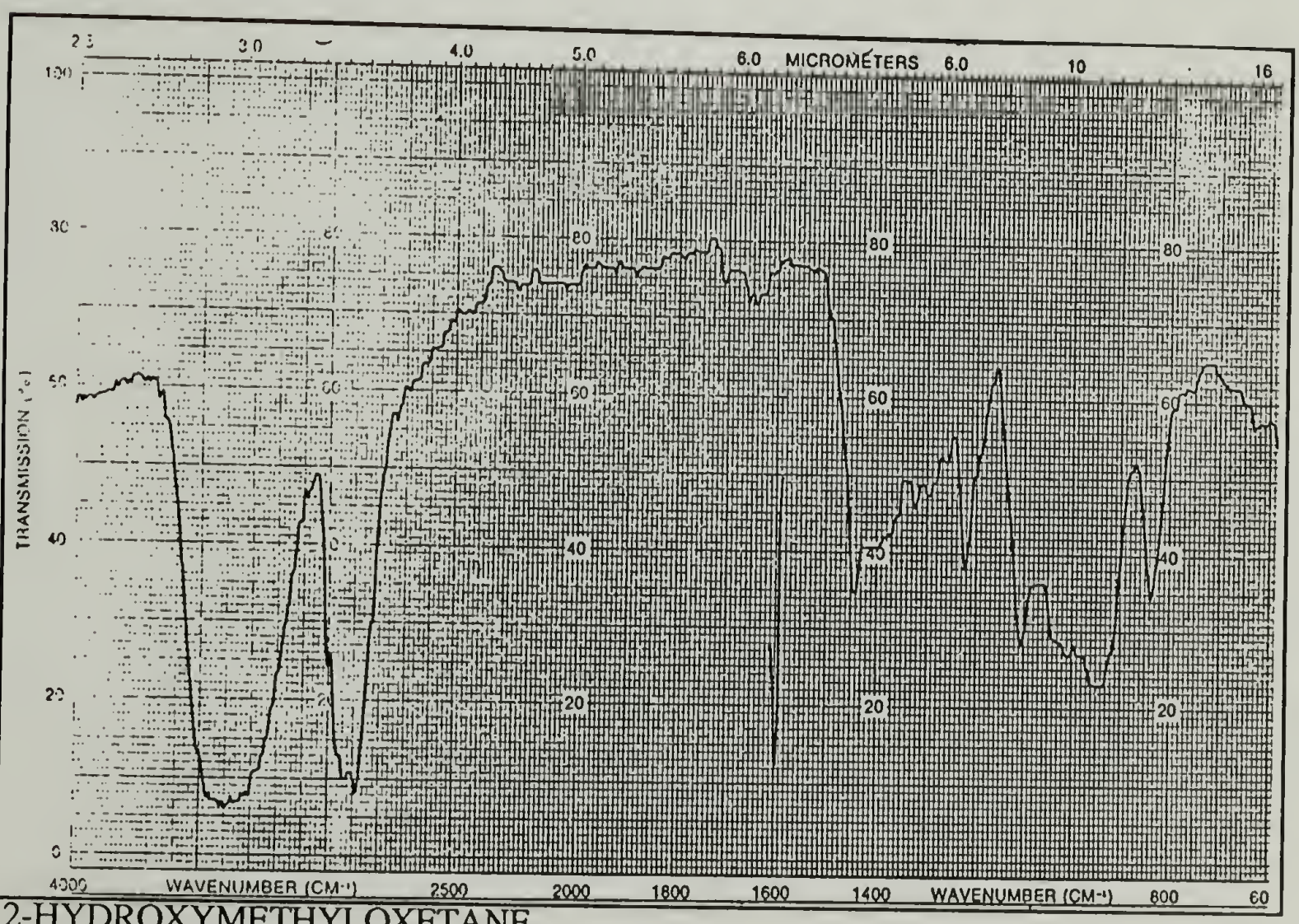


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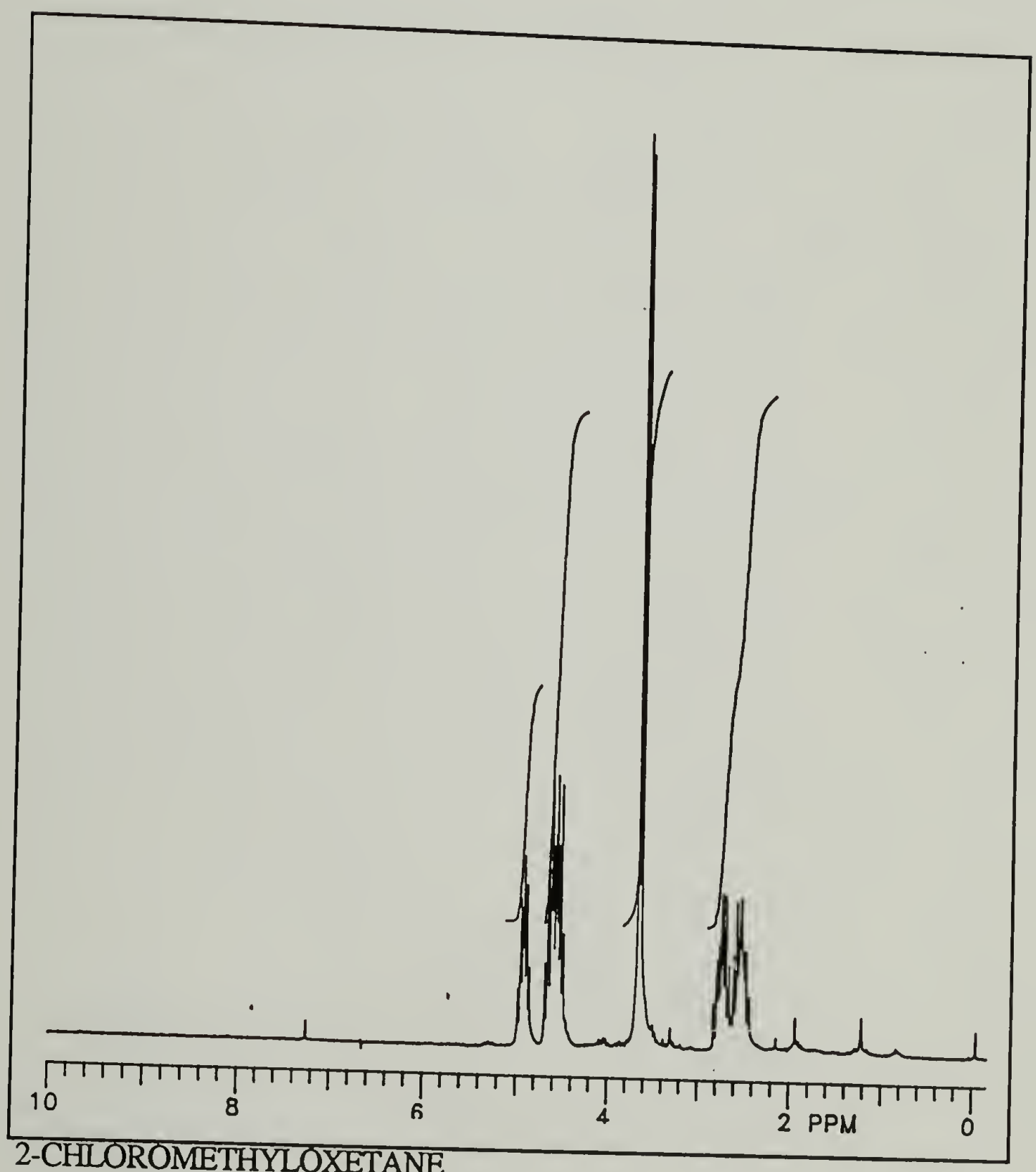


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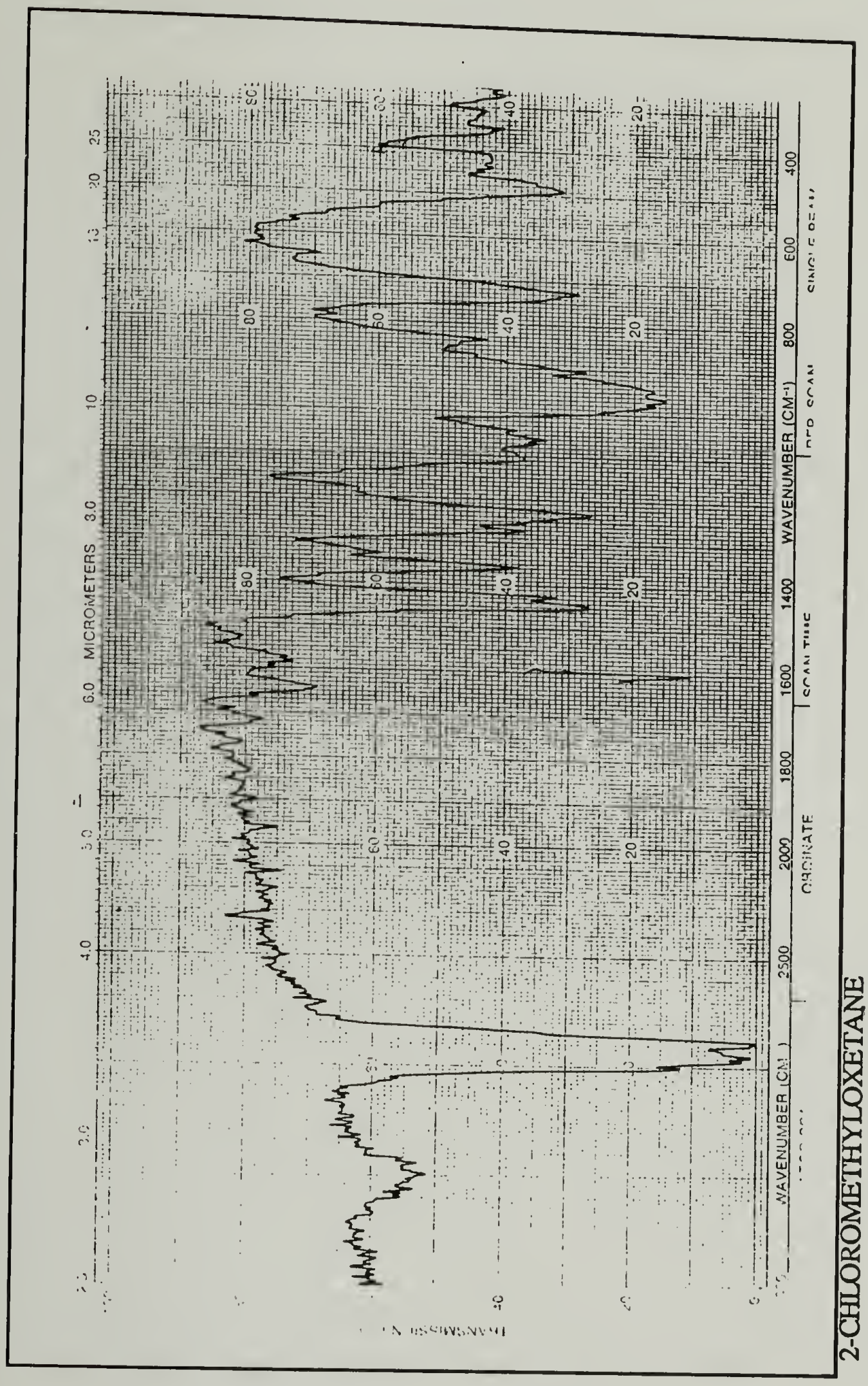


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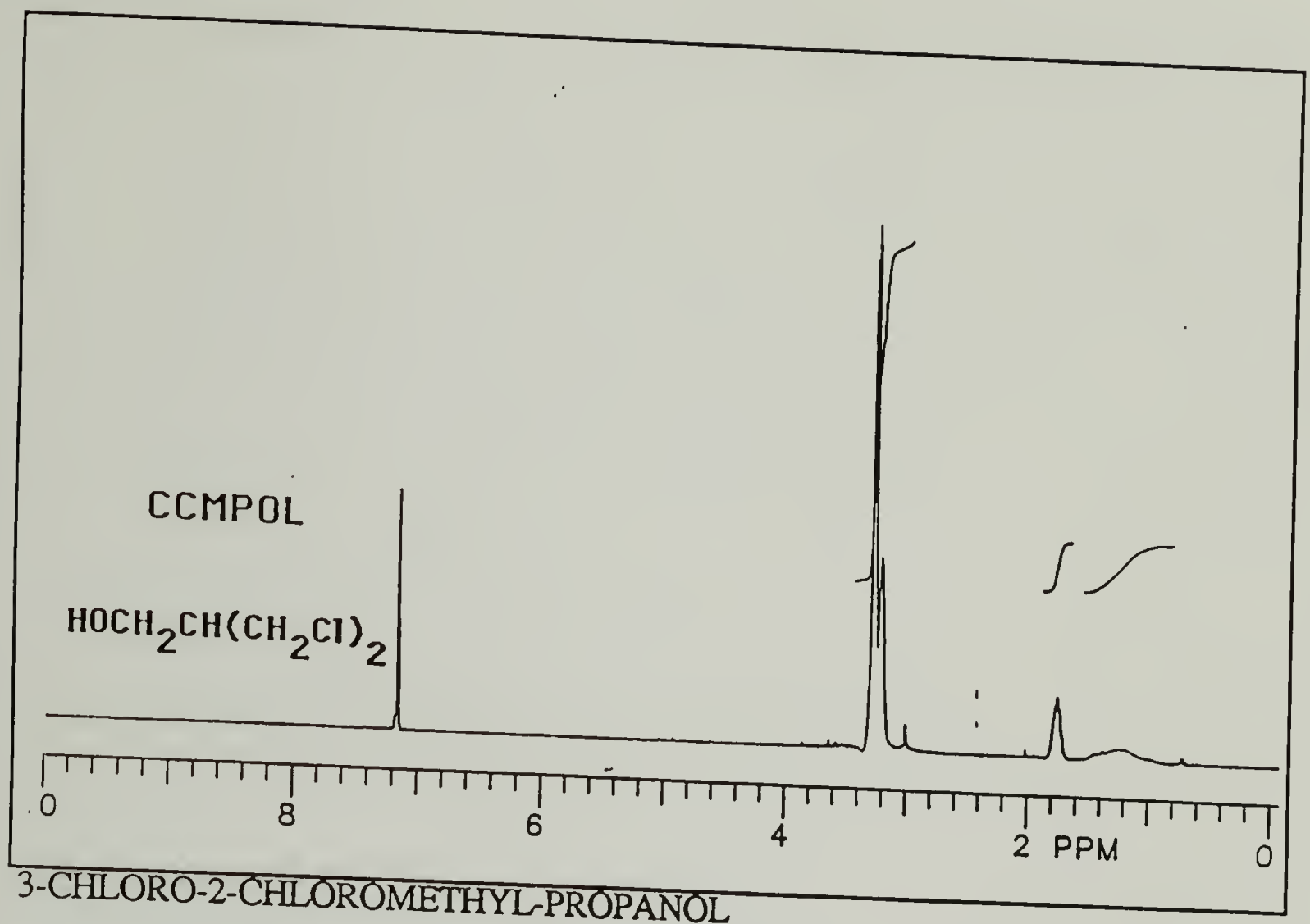


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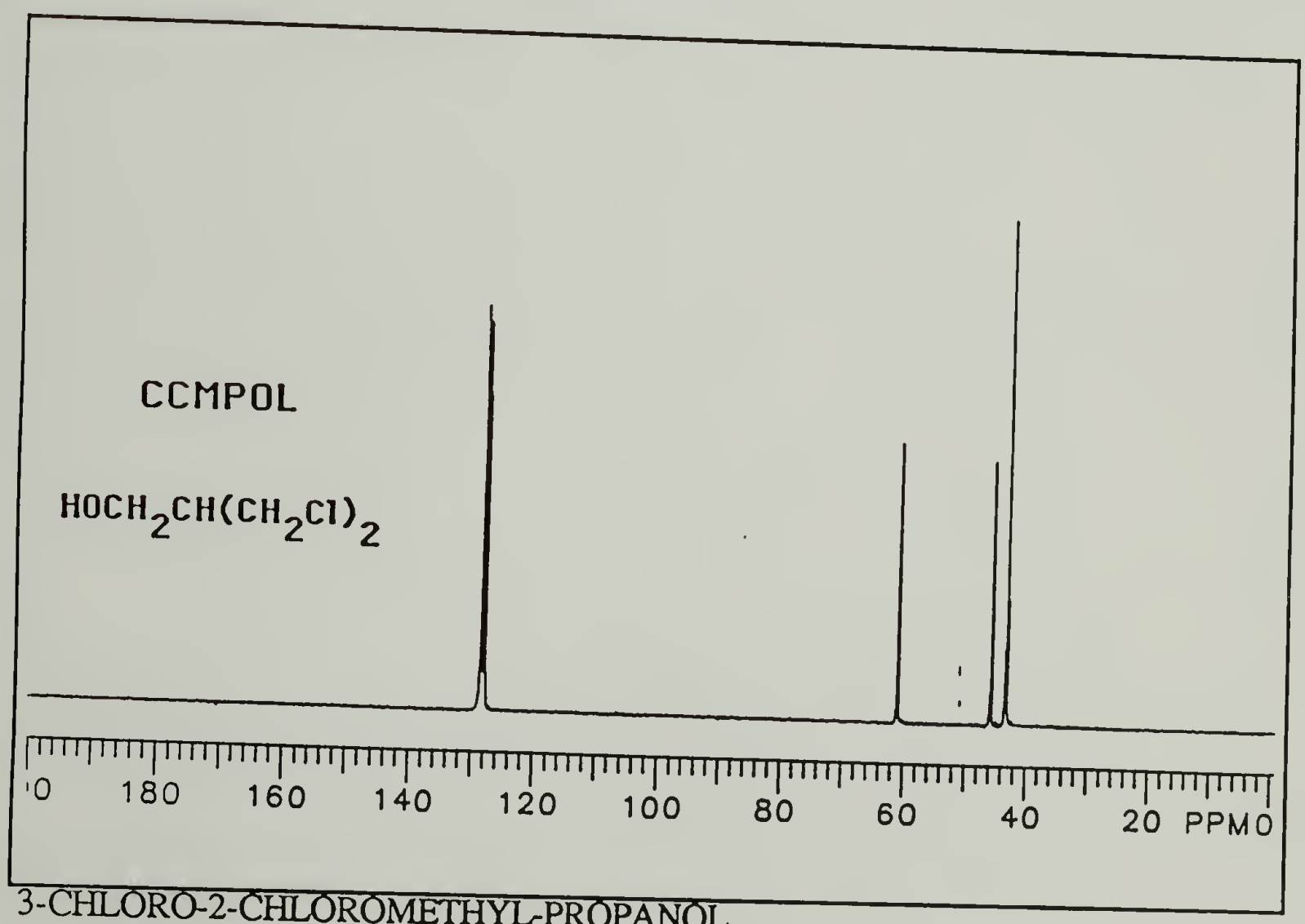


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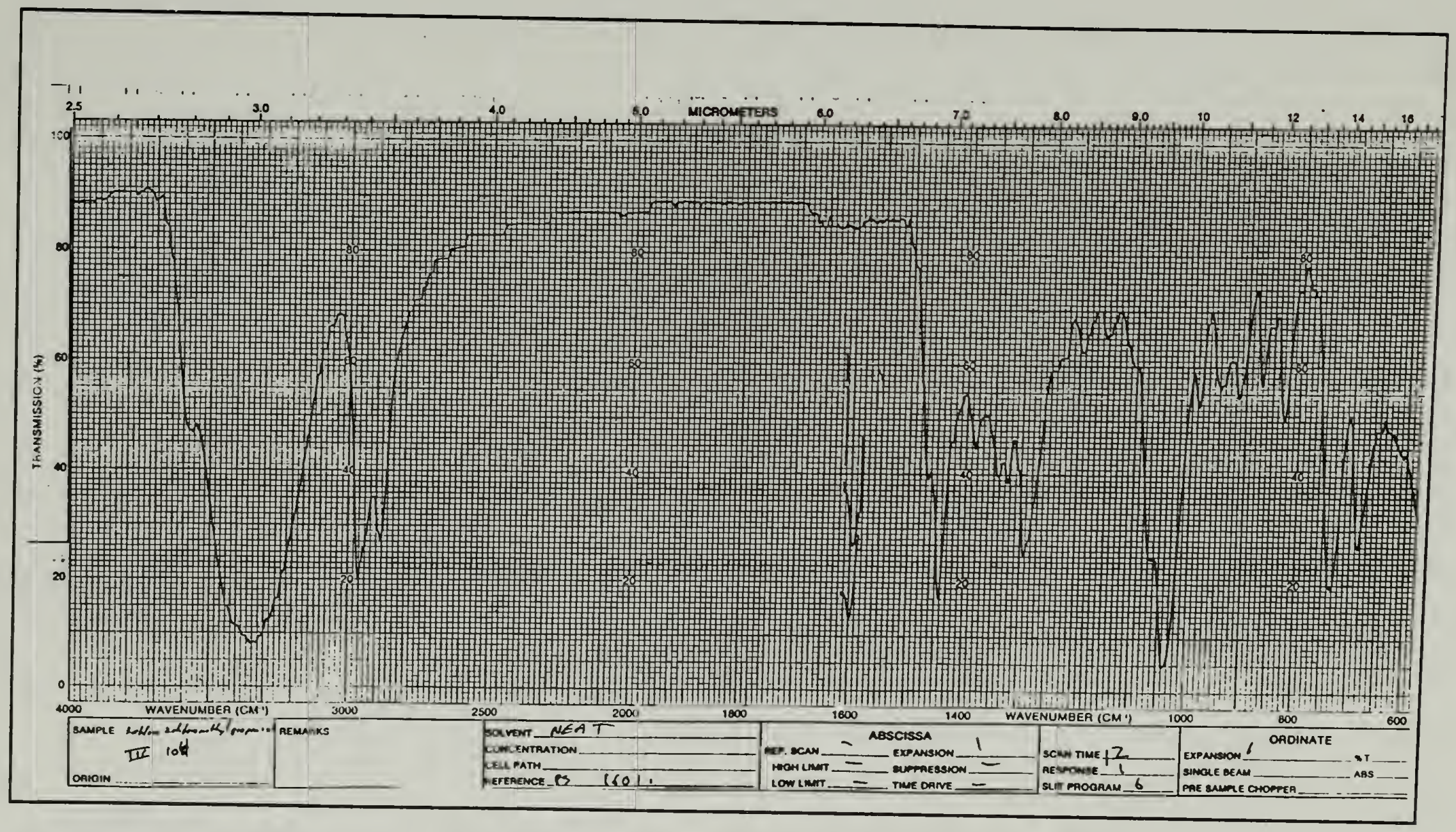


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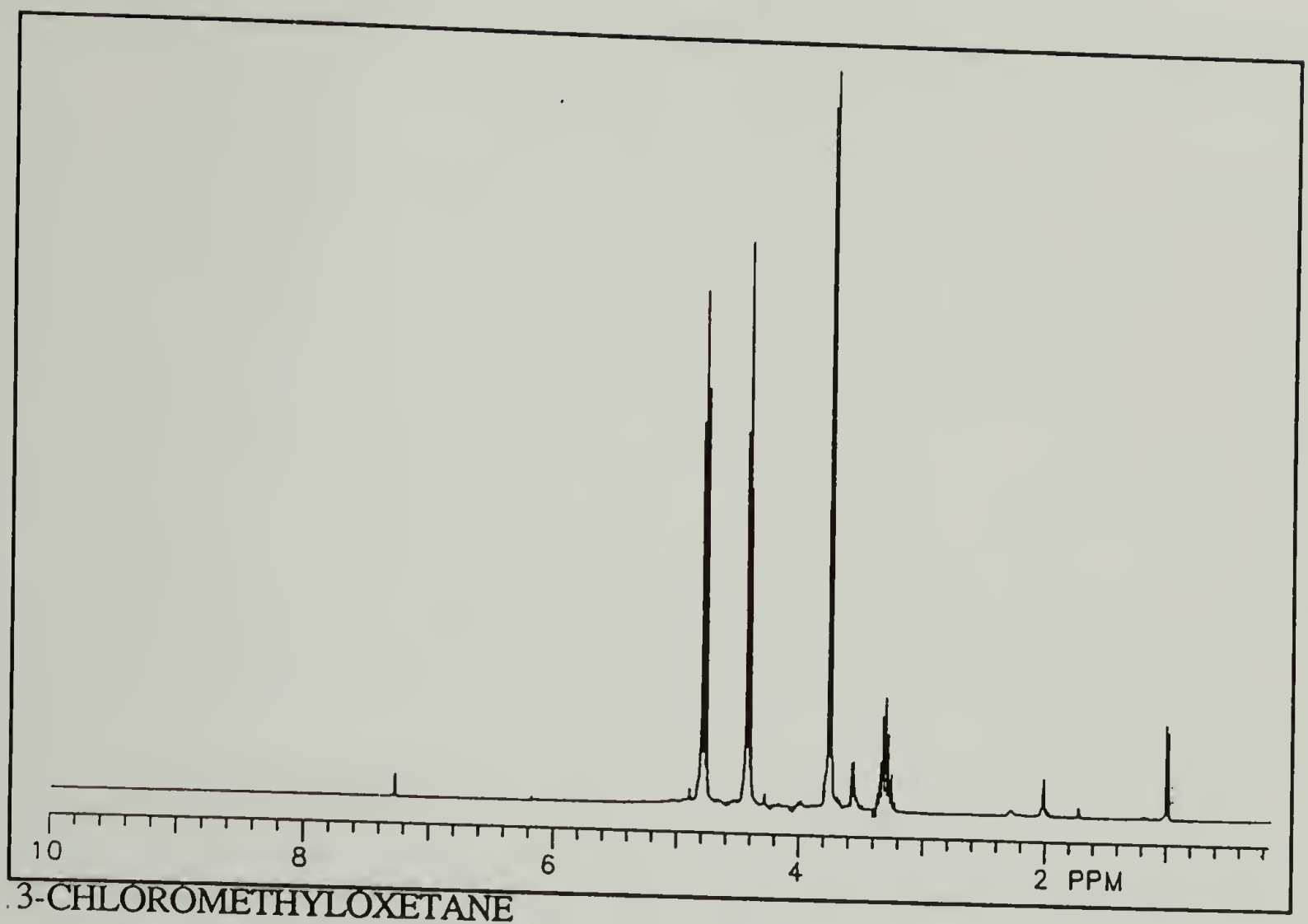


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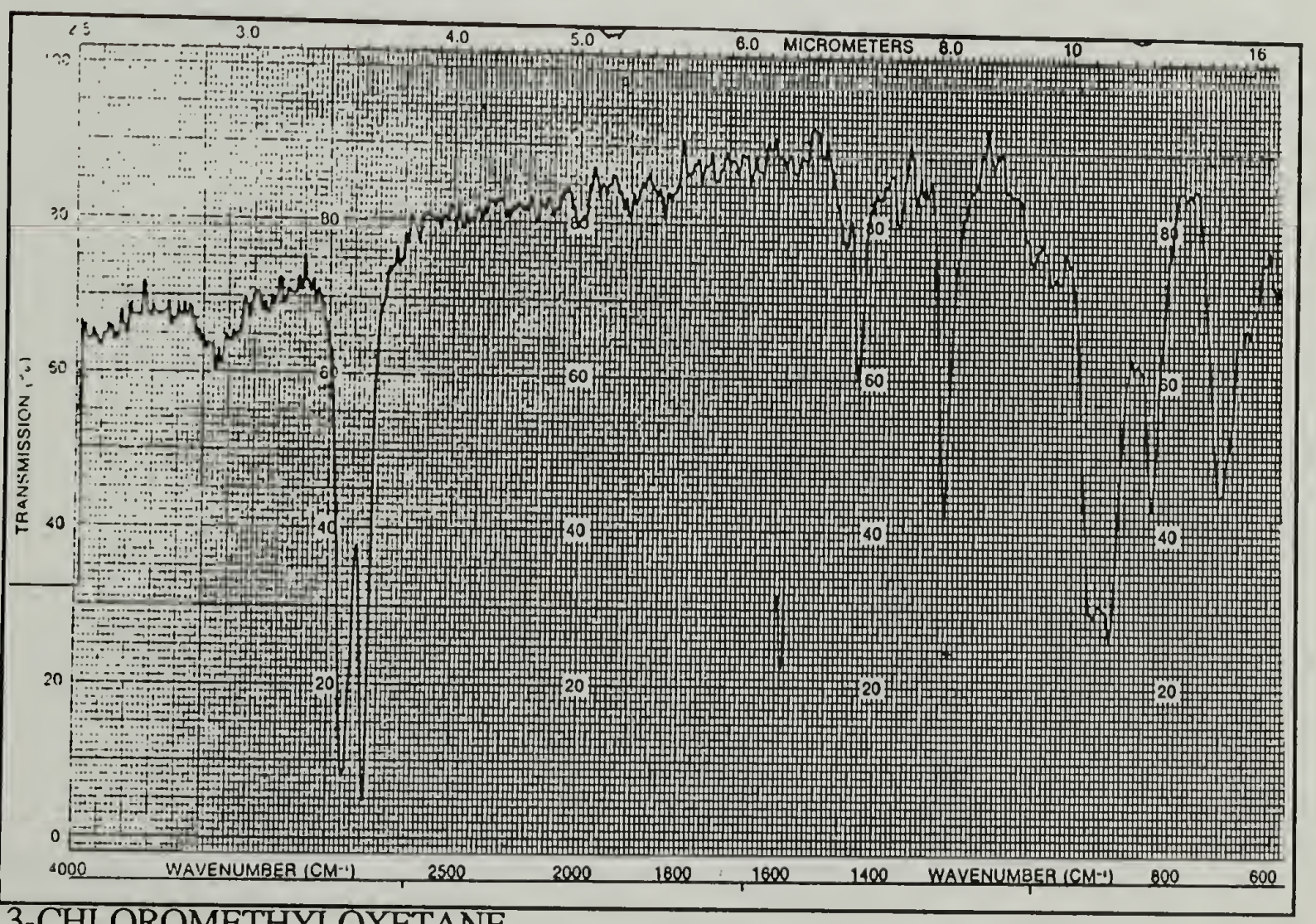


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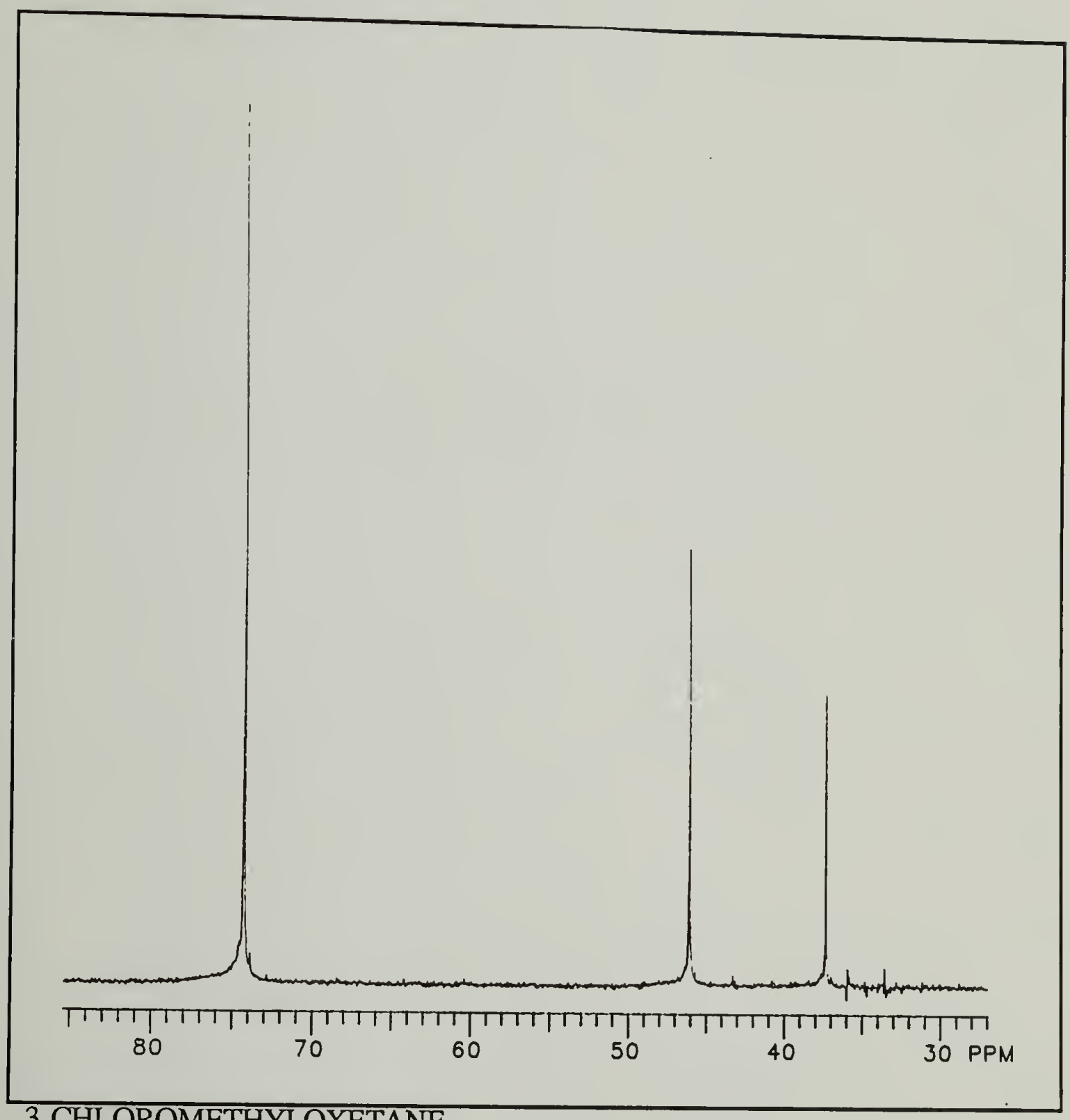


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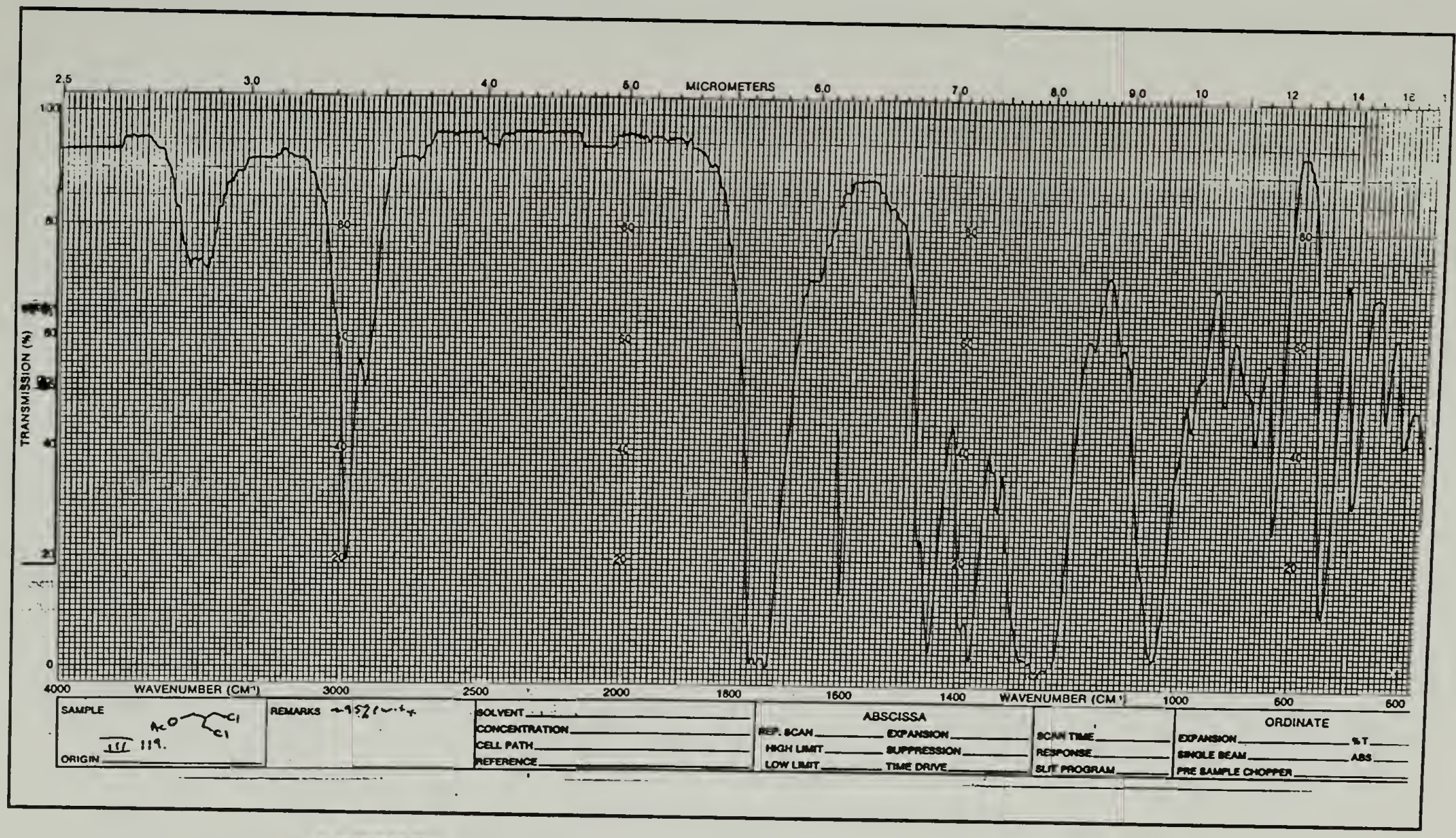
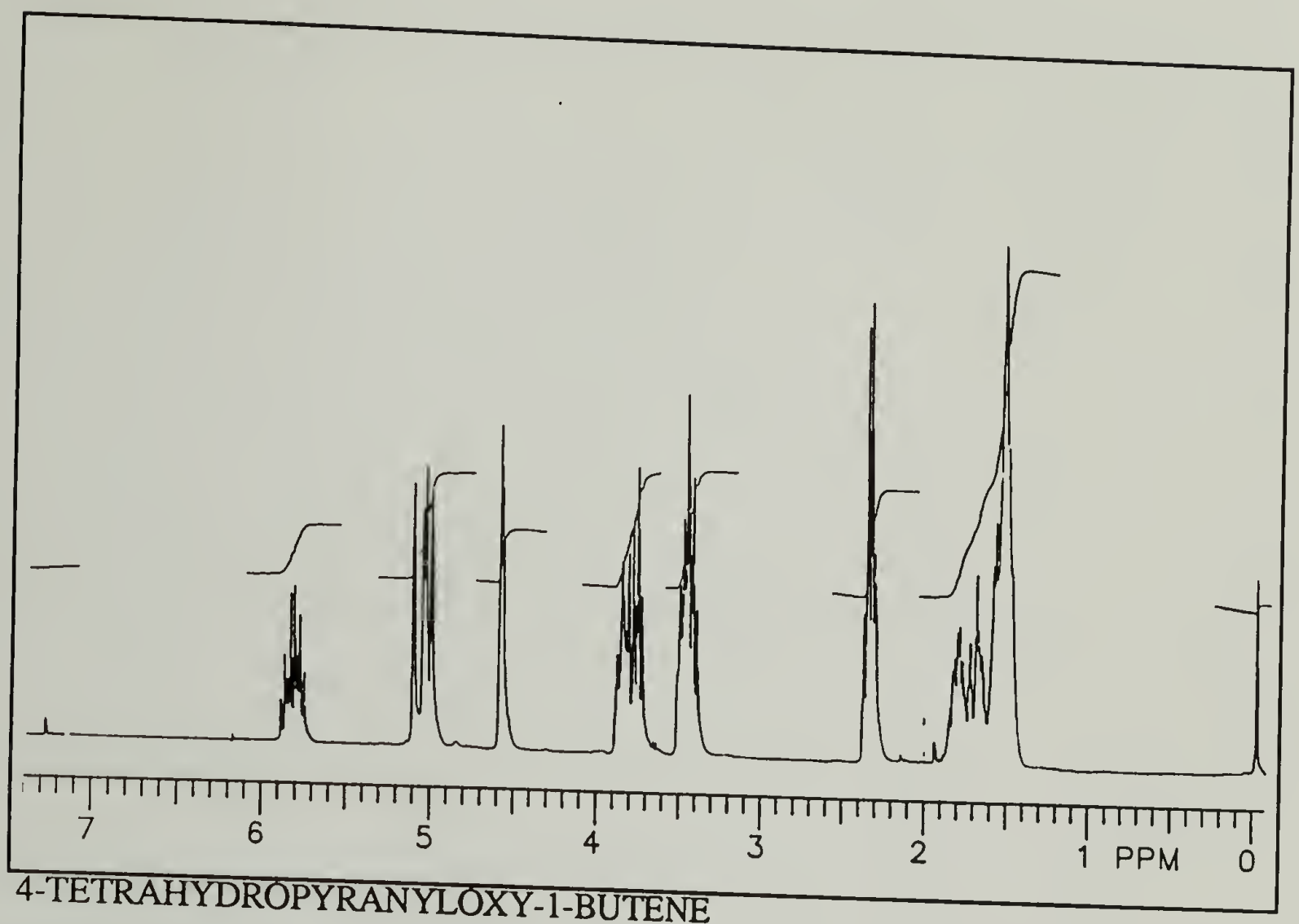



3-CHLORO-2-CHLOROMETHYL-1-PROPYLACETATE

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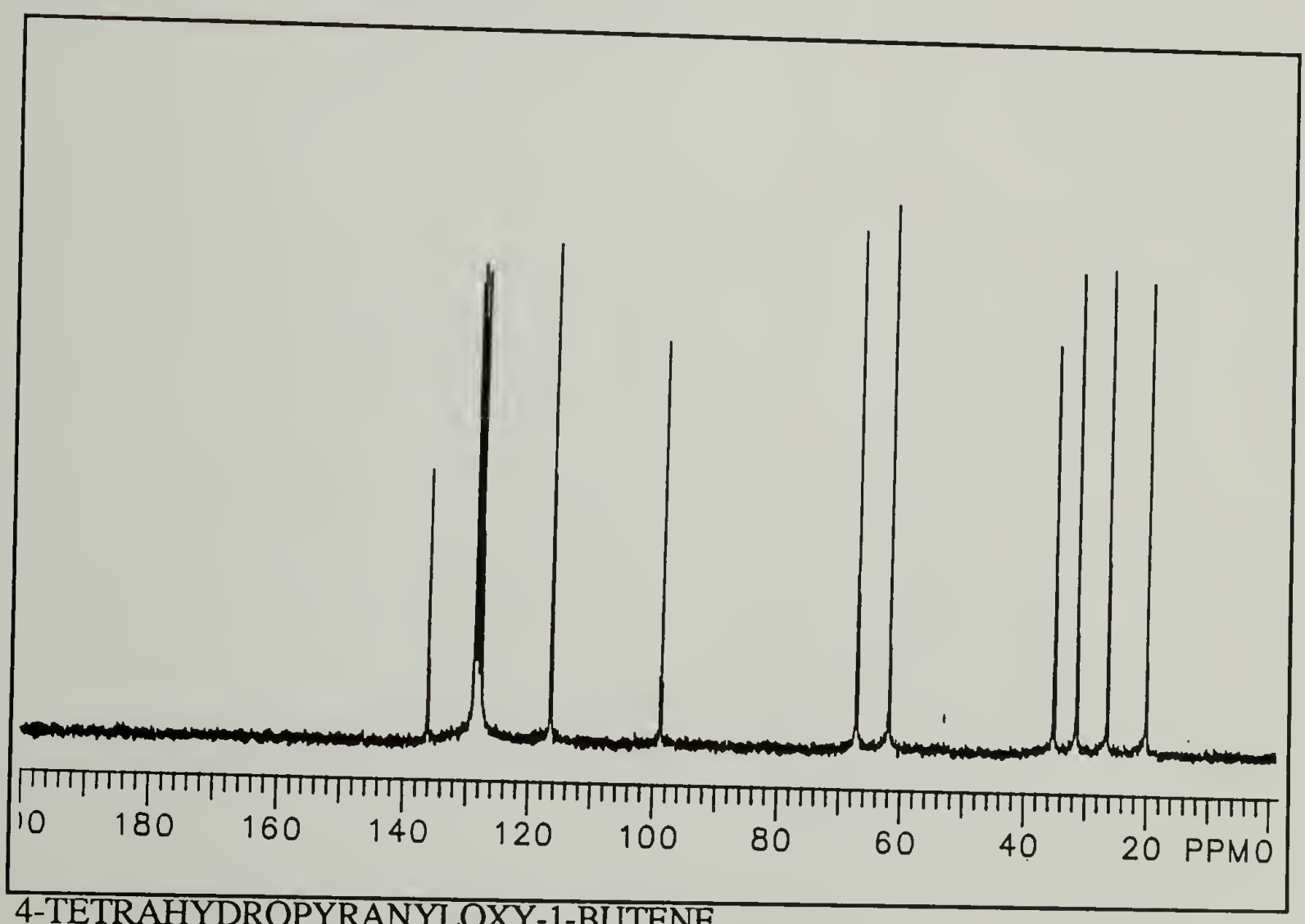
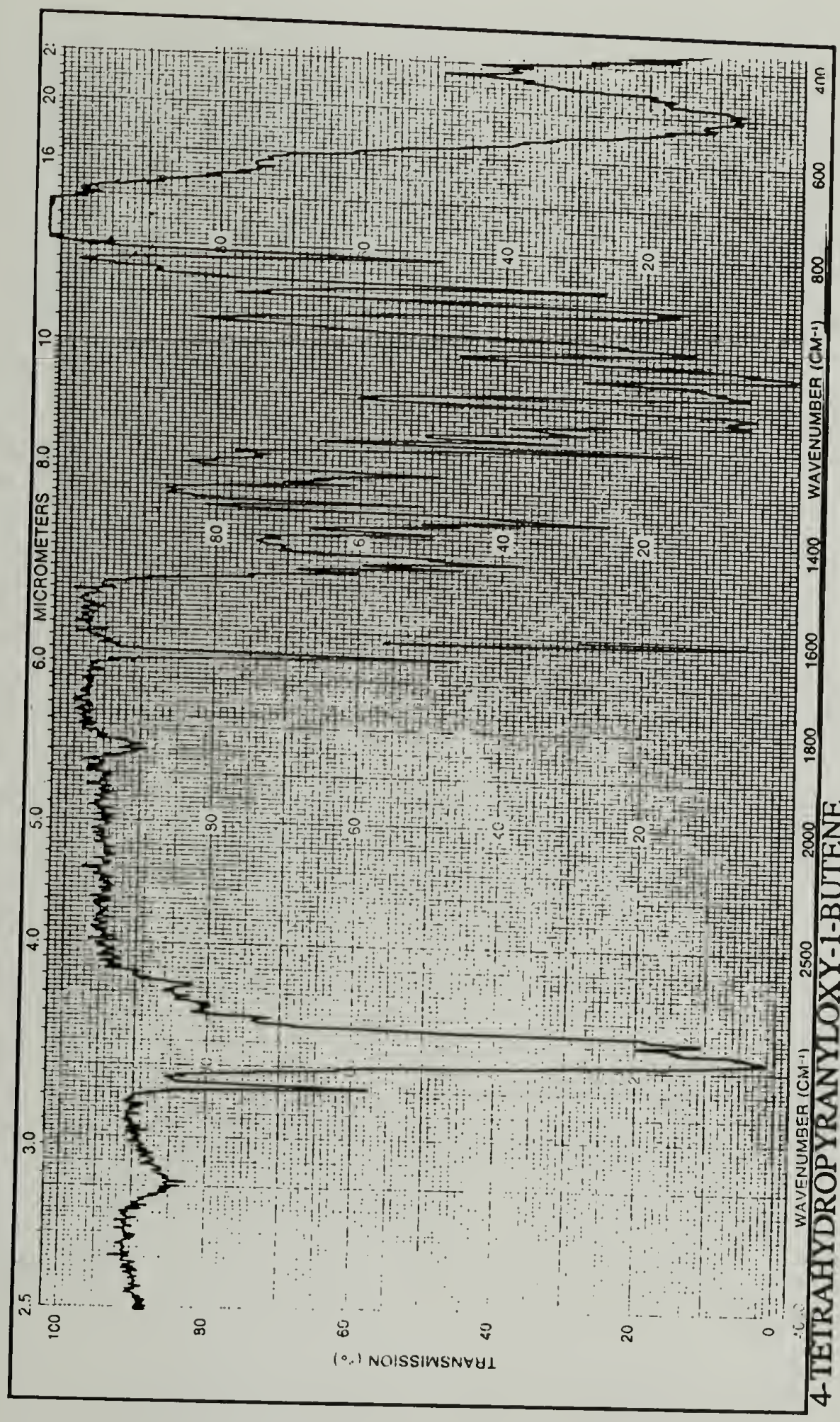
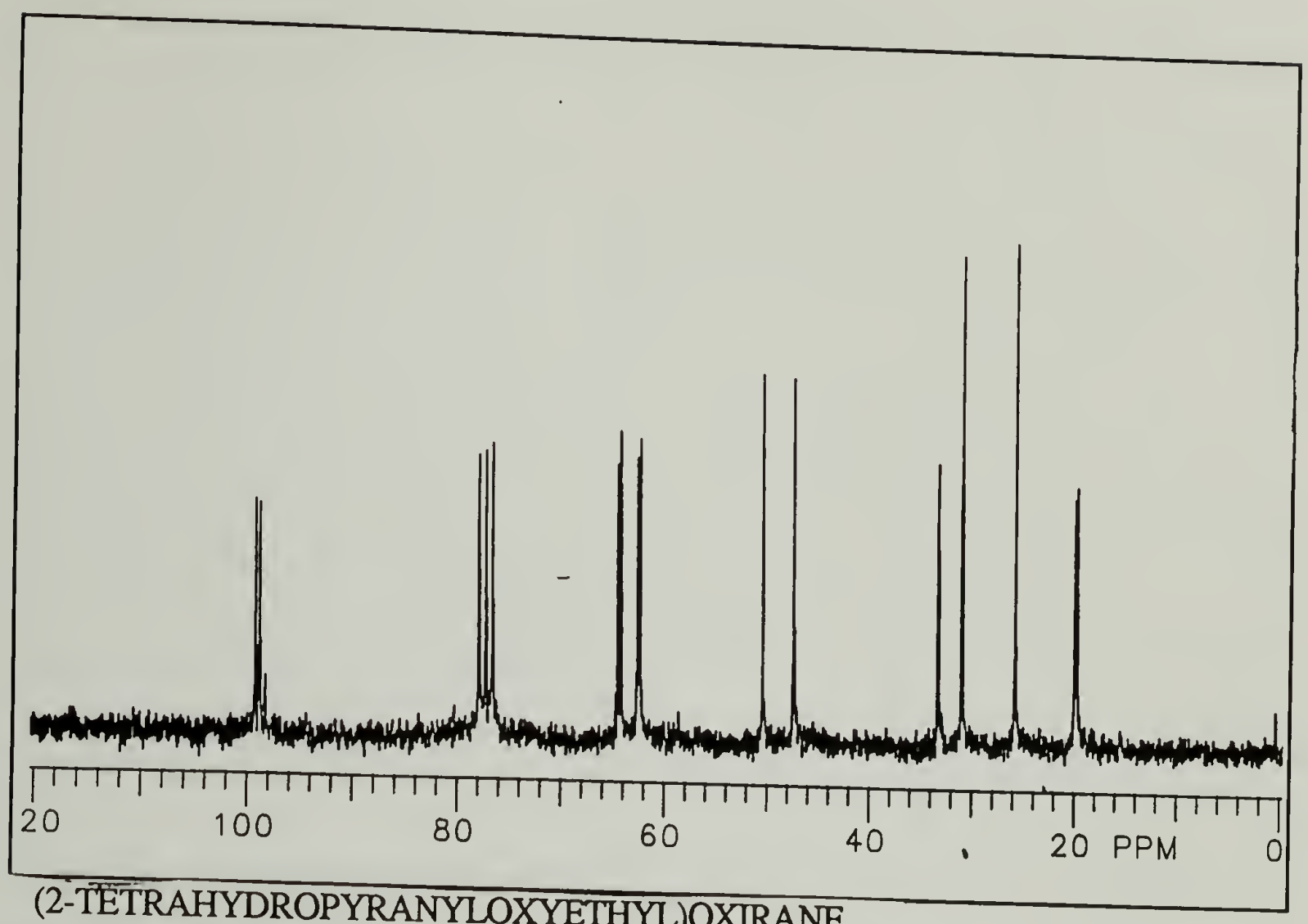


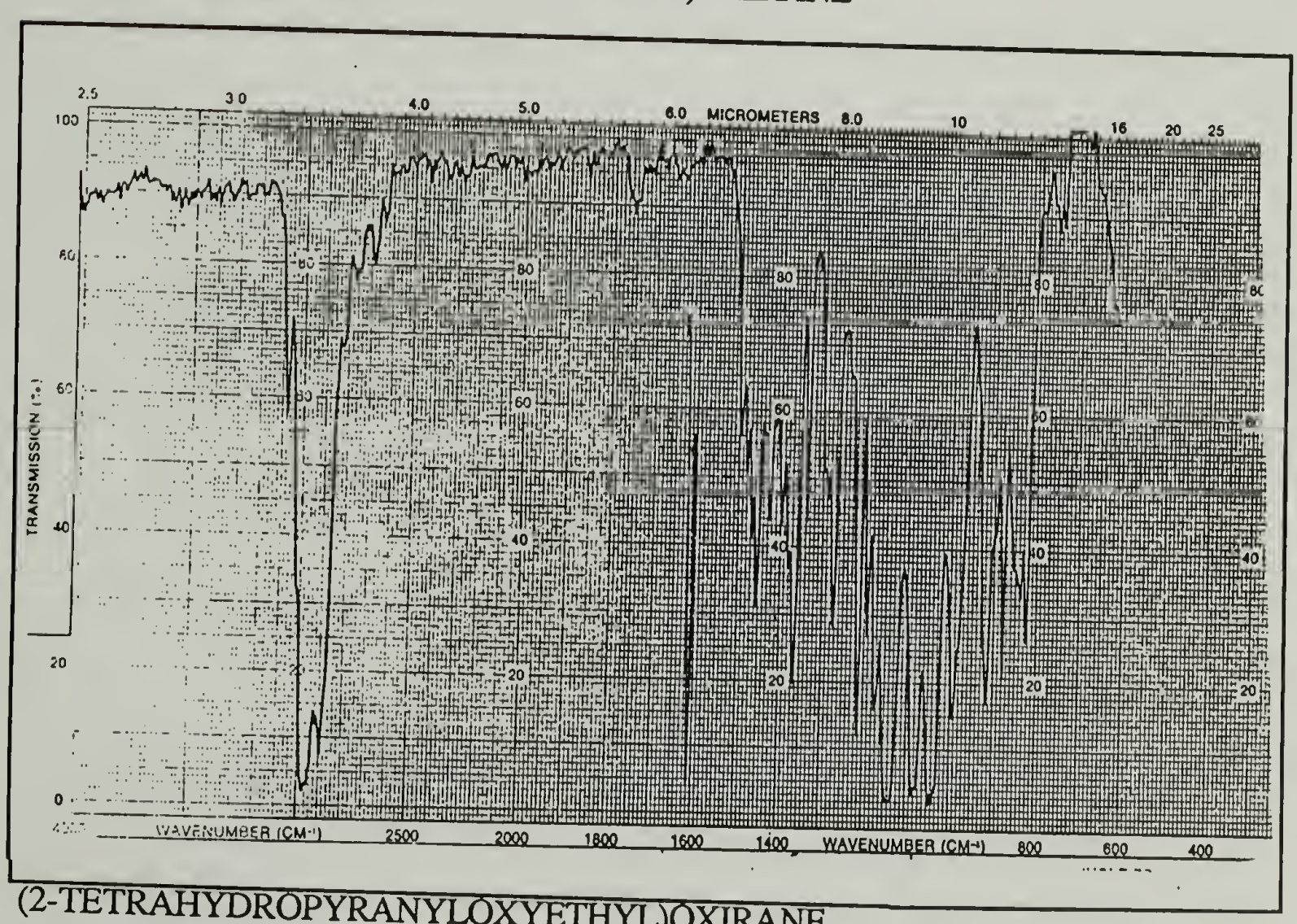

4-TETRAHYDROPYRANYLOXY-1-BUTENE



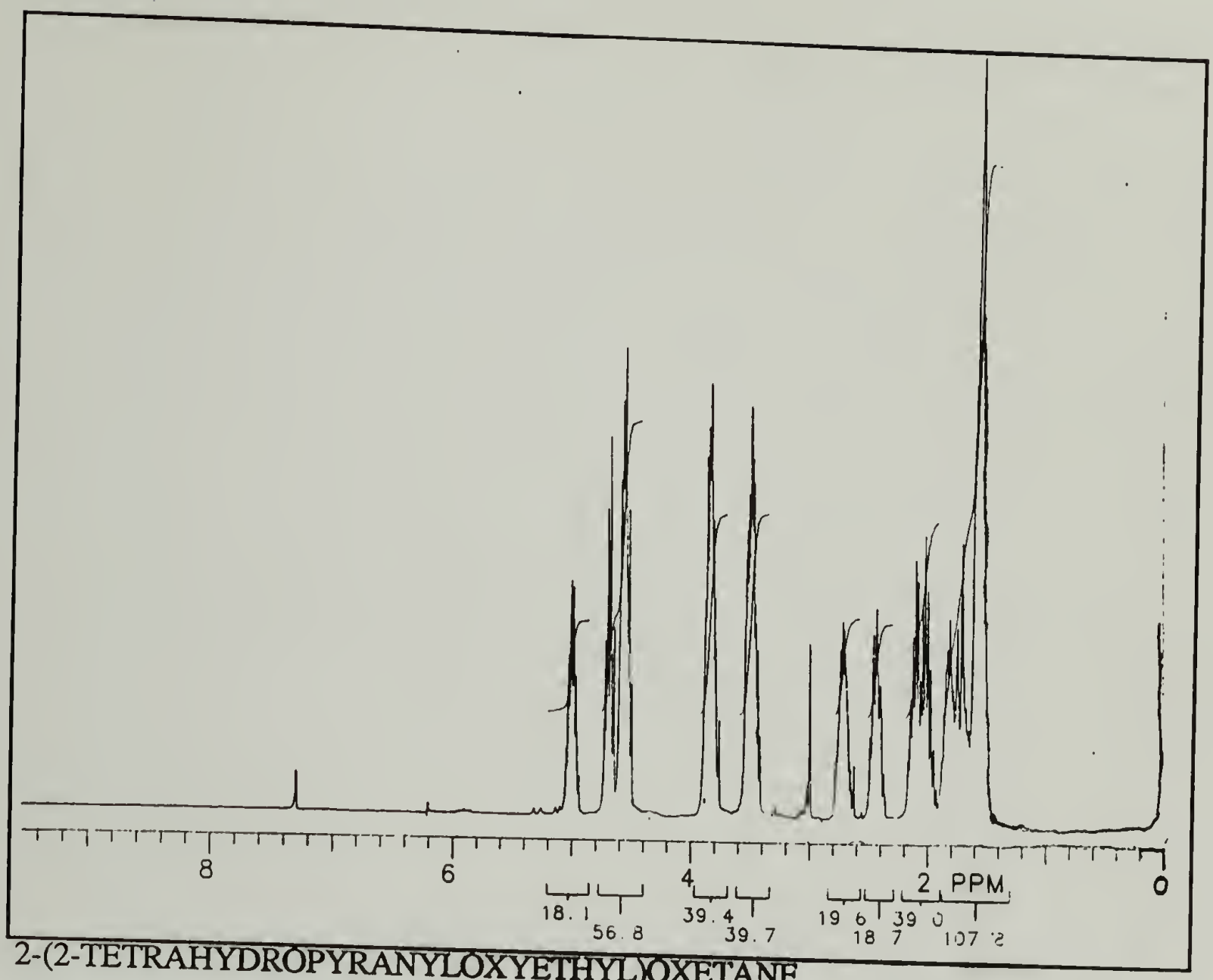

4-TETRAHYDROPYRANYLOXY-1-BUTENE



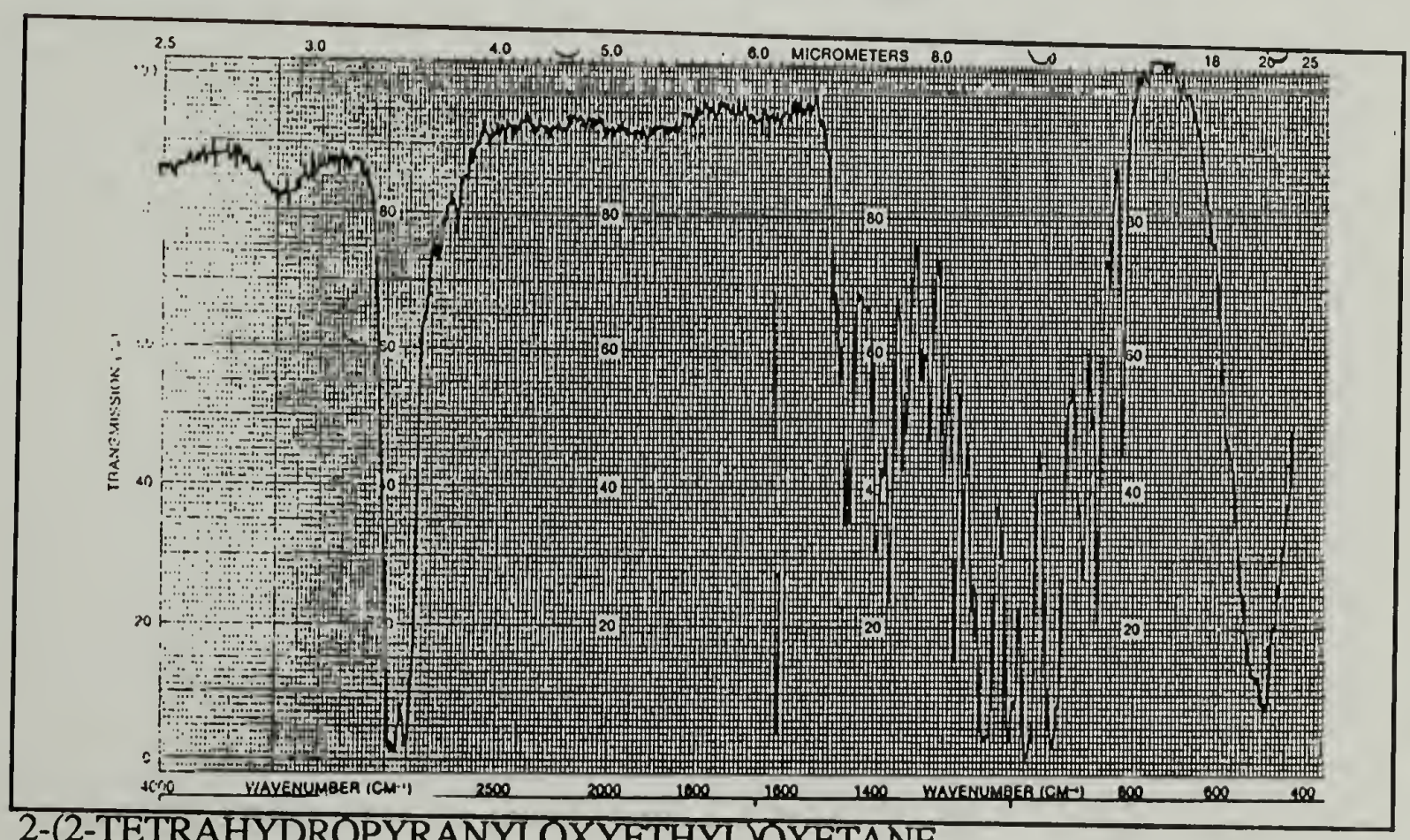

(2-TETRAHYDROPYRANYLOXYETHYL)OXIRANE



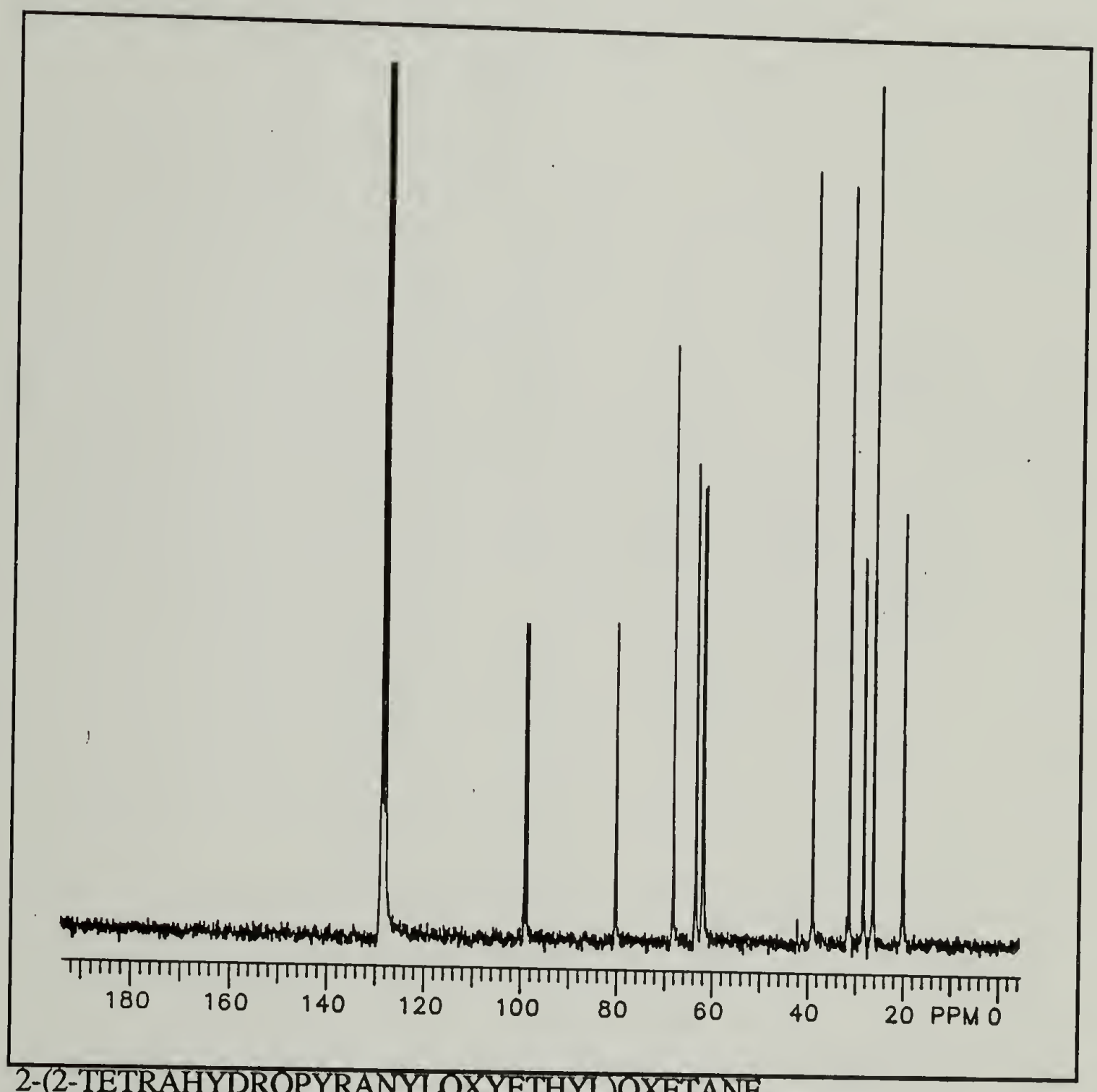

(2-TETRAHYDROPYRANYLOXYETHYL)OXIRANE



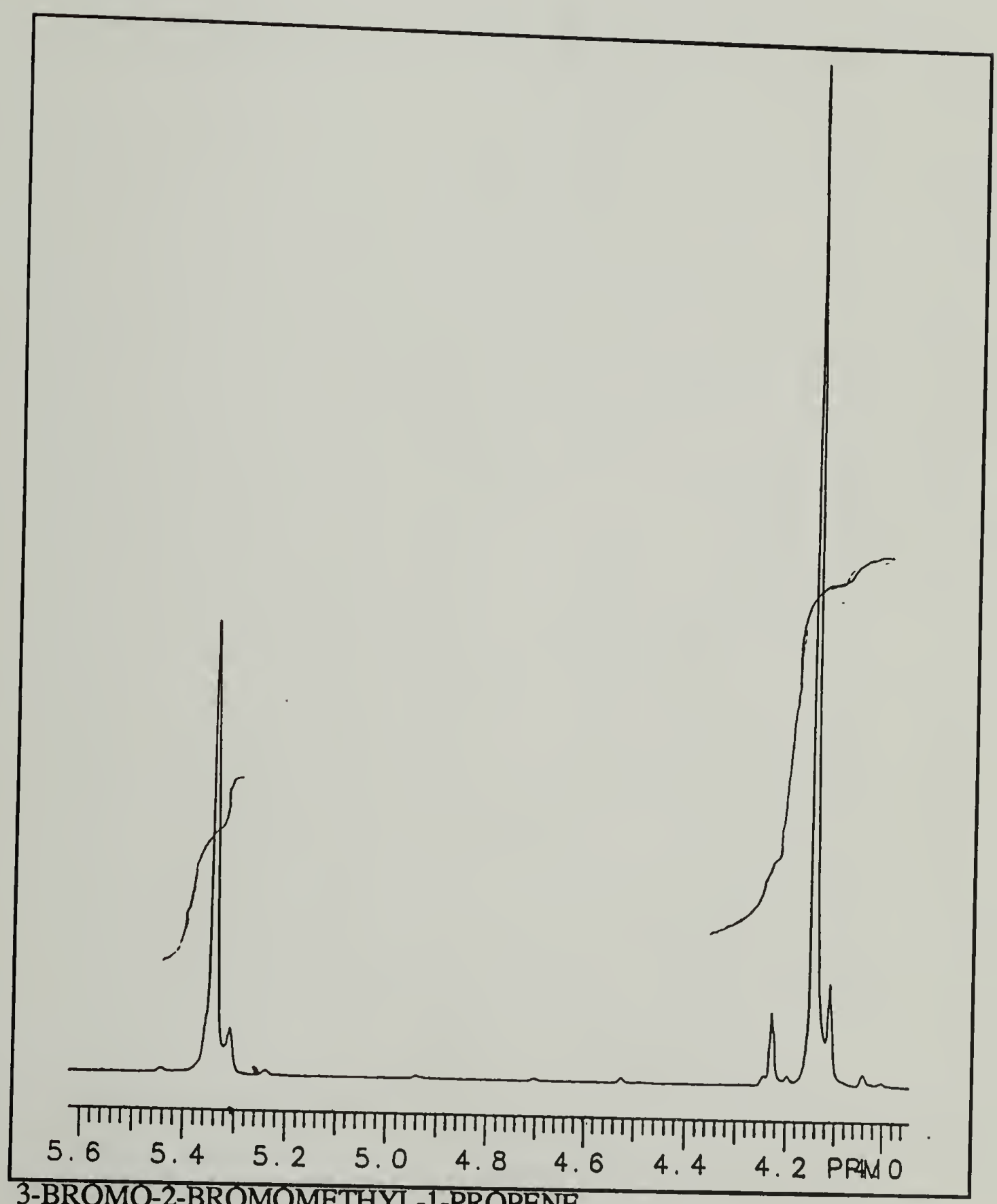

2-(2-TETRAHYDROPYRANYLOXYETHYL)OXETANE



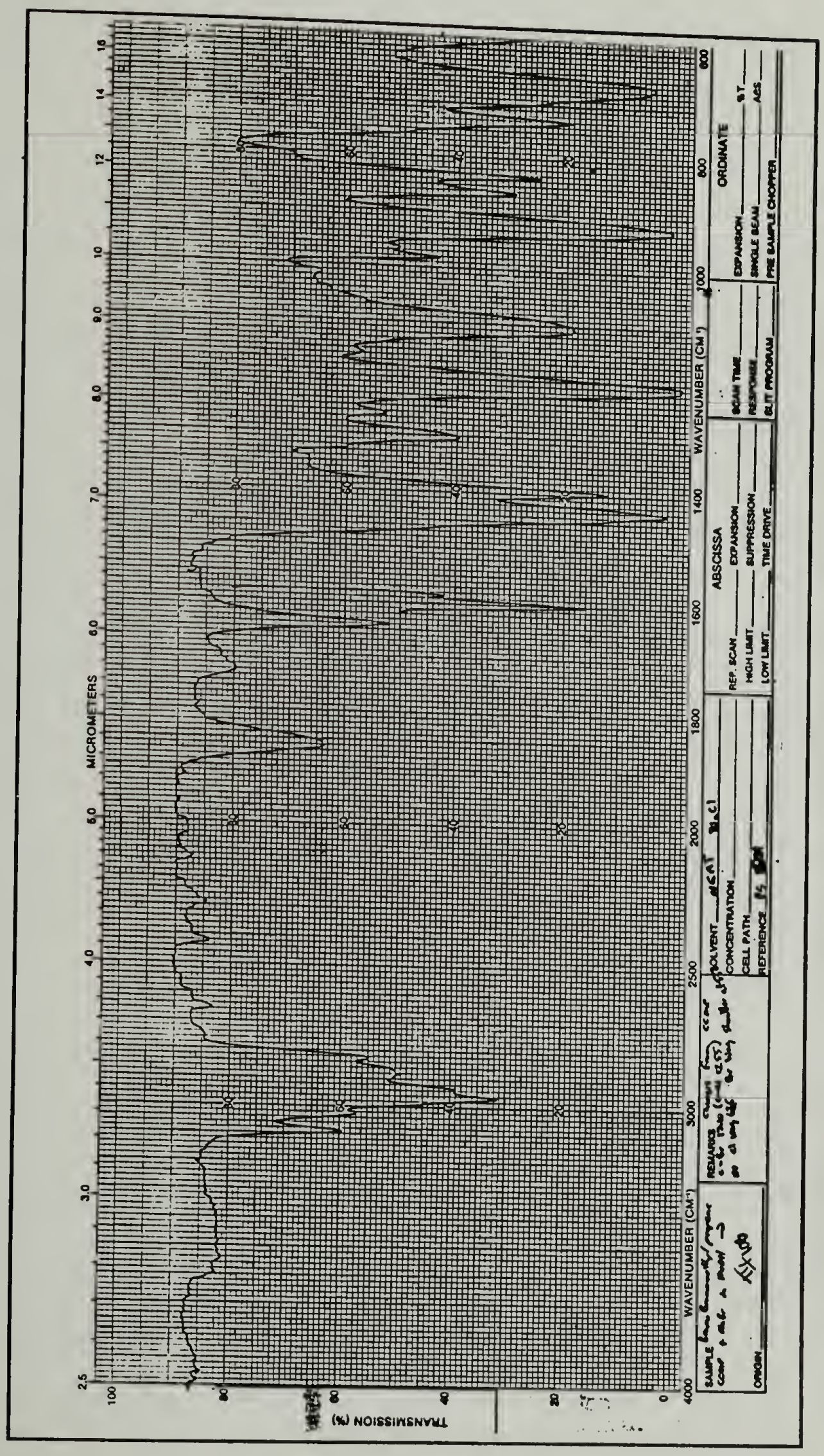

2-(2-TETRAHYDROPYRANYLOXYETHYL)OXETANE



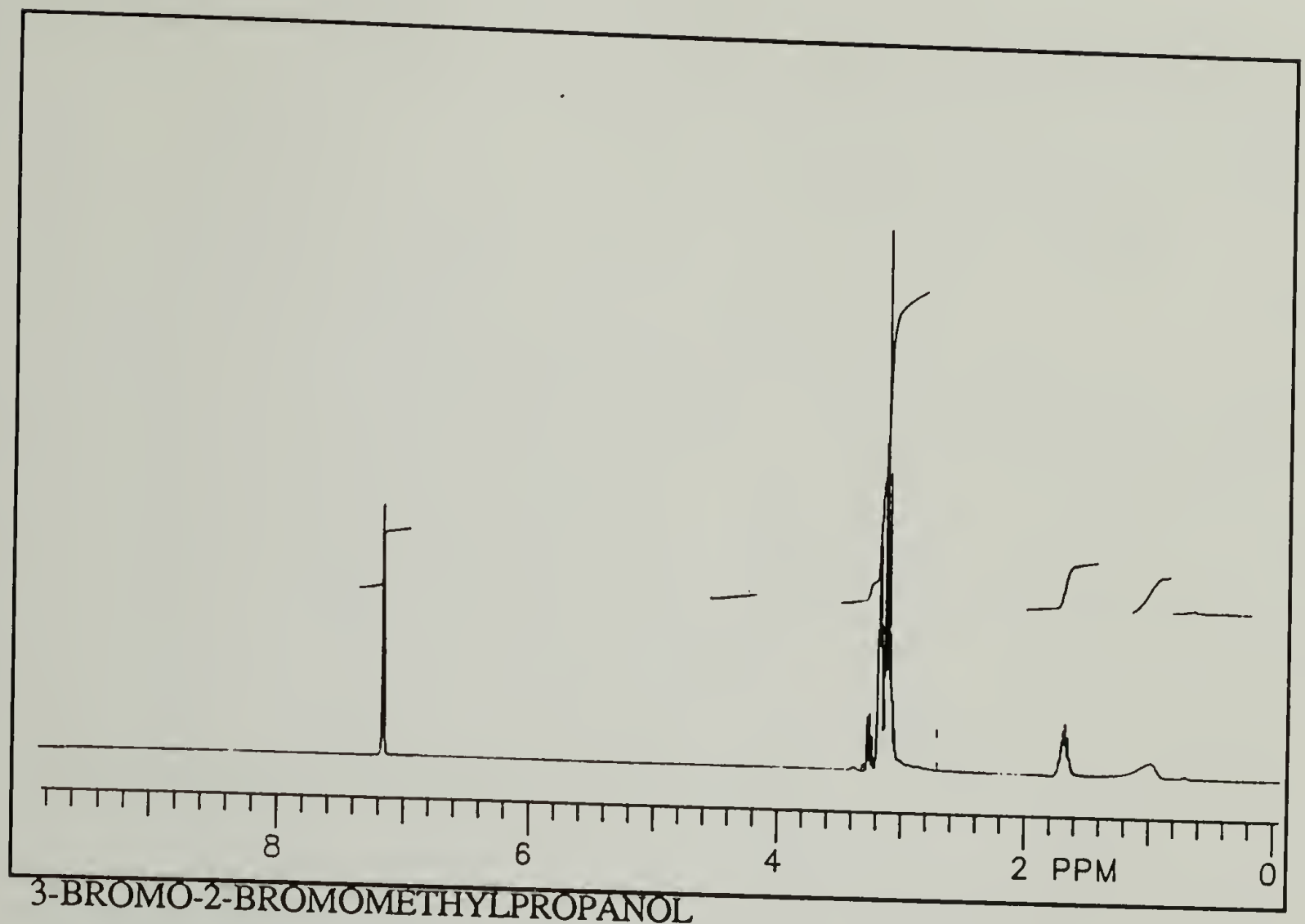

2-(2-TETRAHYDROPYRANYLOXYETHYL)OXETANE



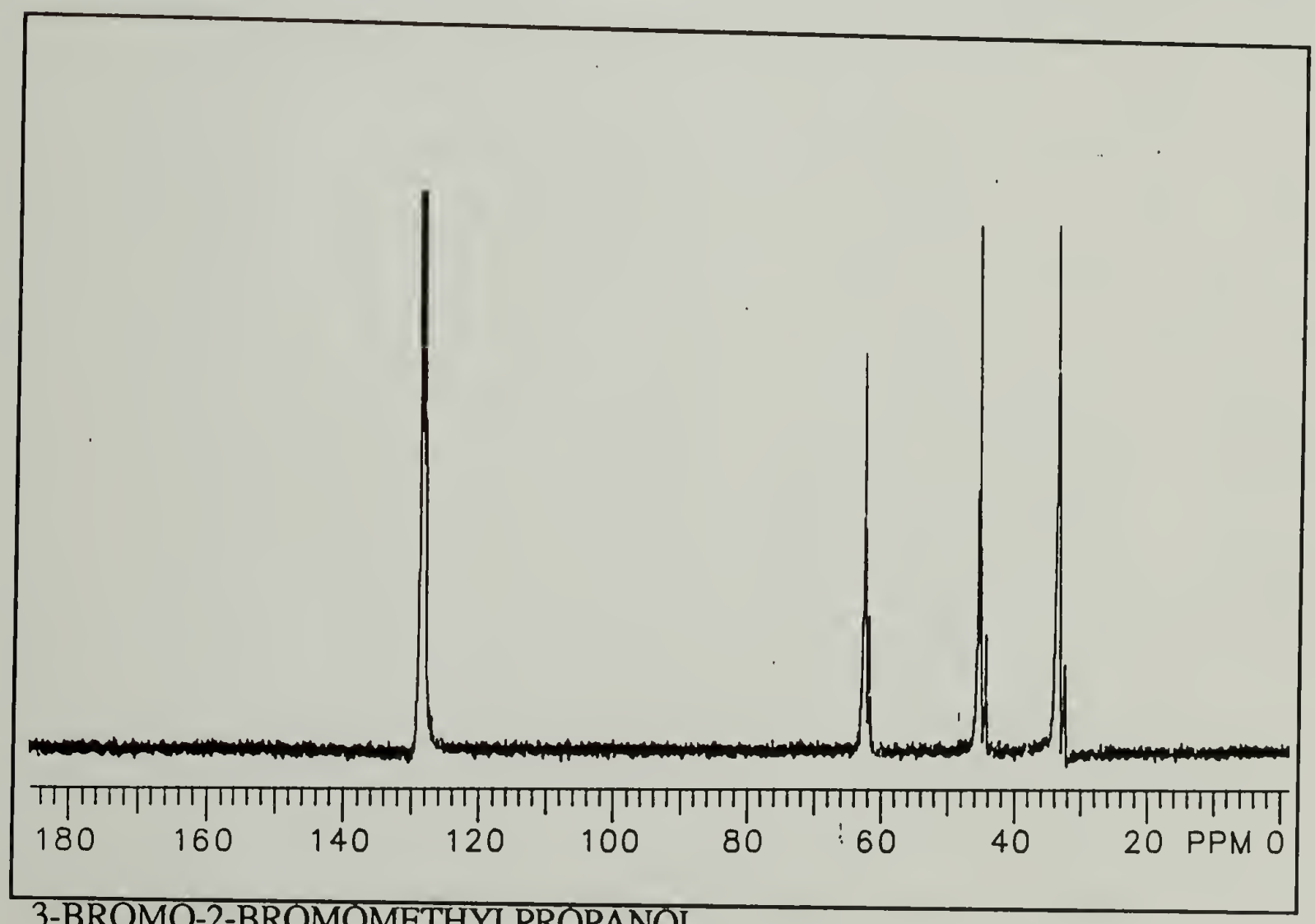

3-BROMO-2-BROMOMETHYL-1-PROPENE



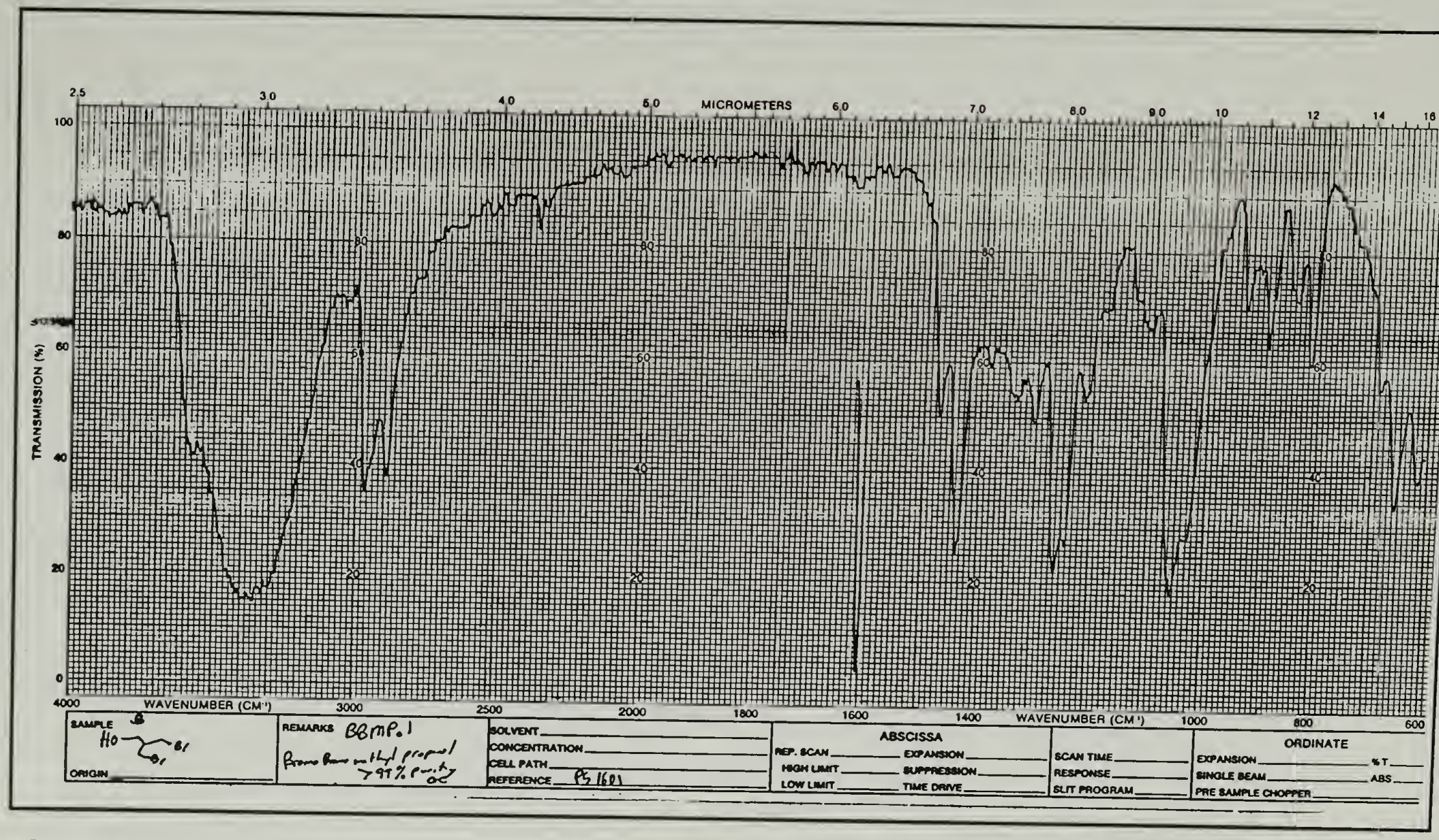

3-BROMO-2-BROMOMETHYL-1-PROPENE



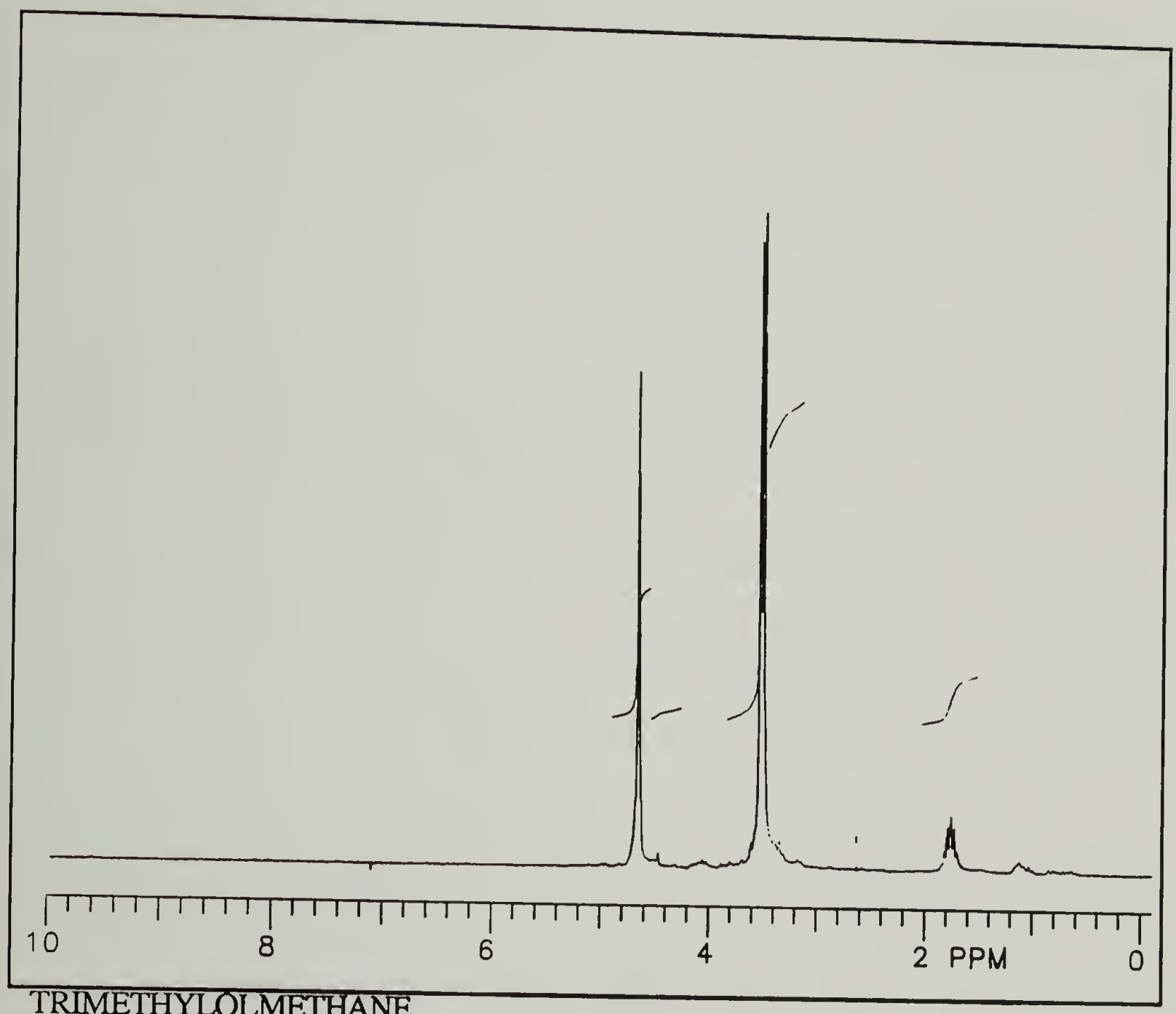

3-BROMO-2-BROMOMETHYLPROPANOL



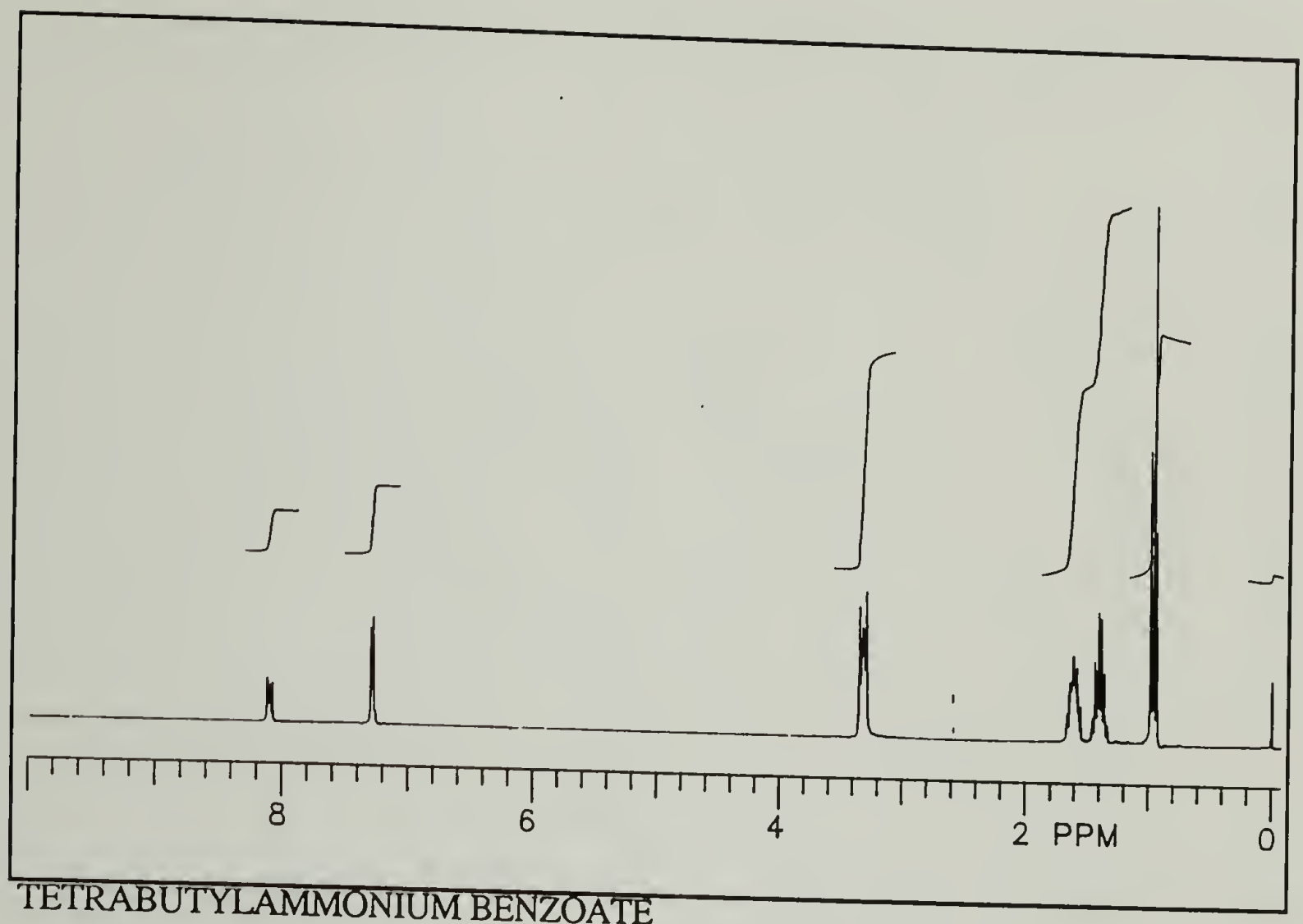

3-BROMO-2-BROMOMETHYLPROPANOL



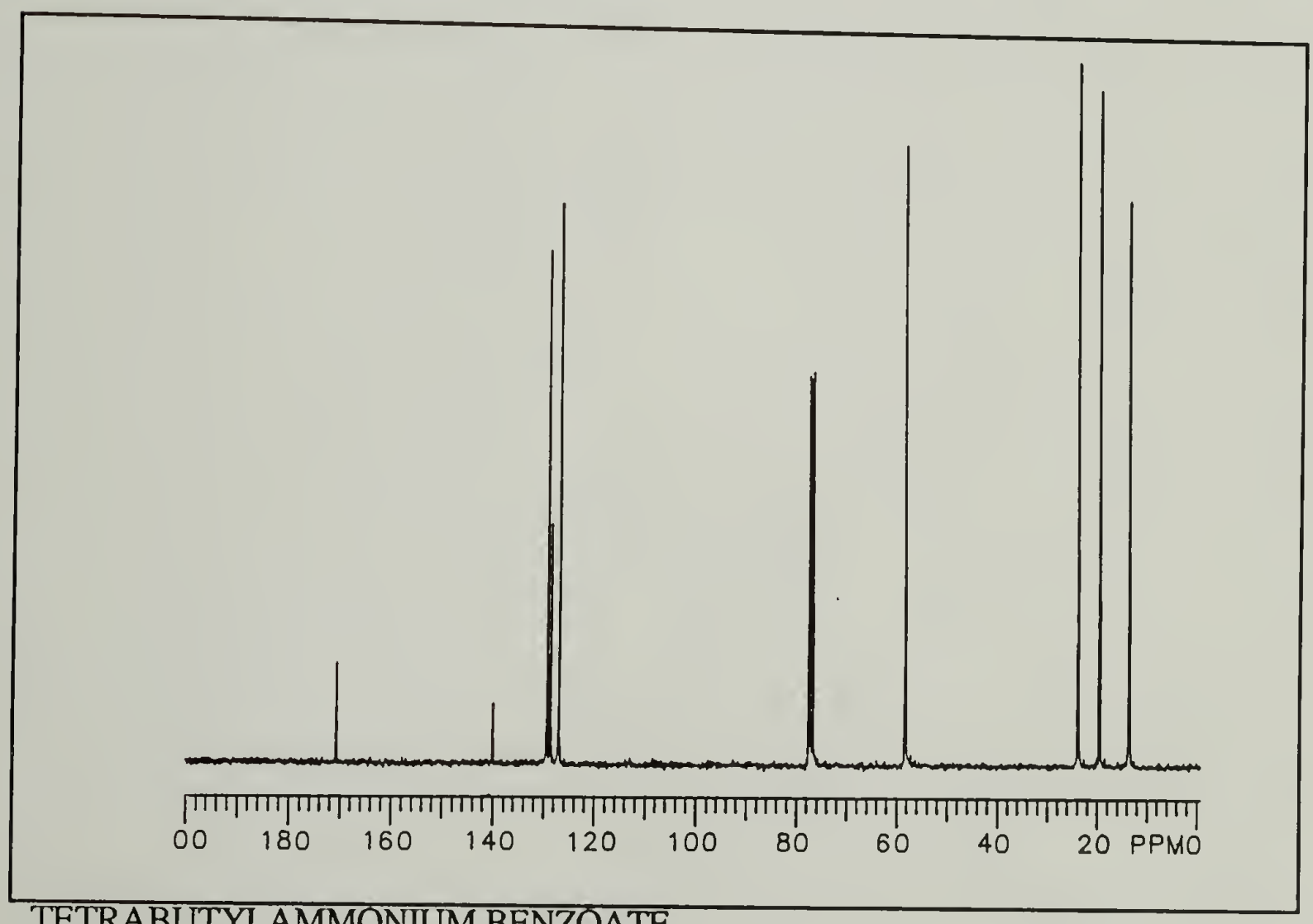

3-BROMO-2-BROMOMETHYL-1-PROPANOL




TRIMETHYLOLMETHANE



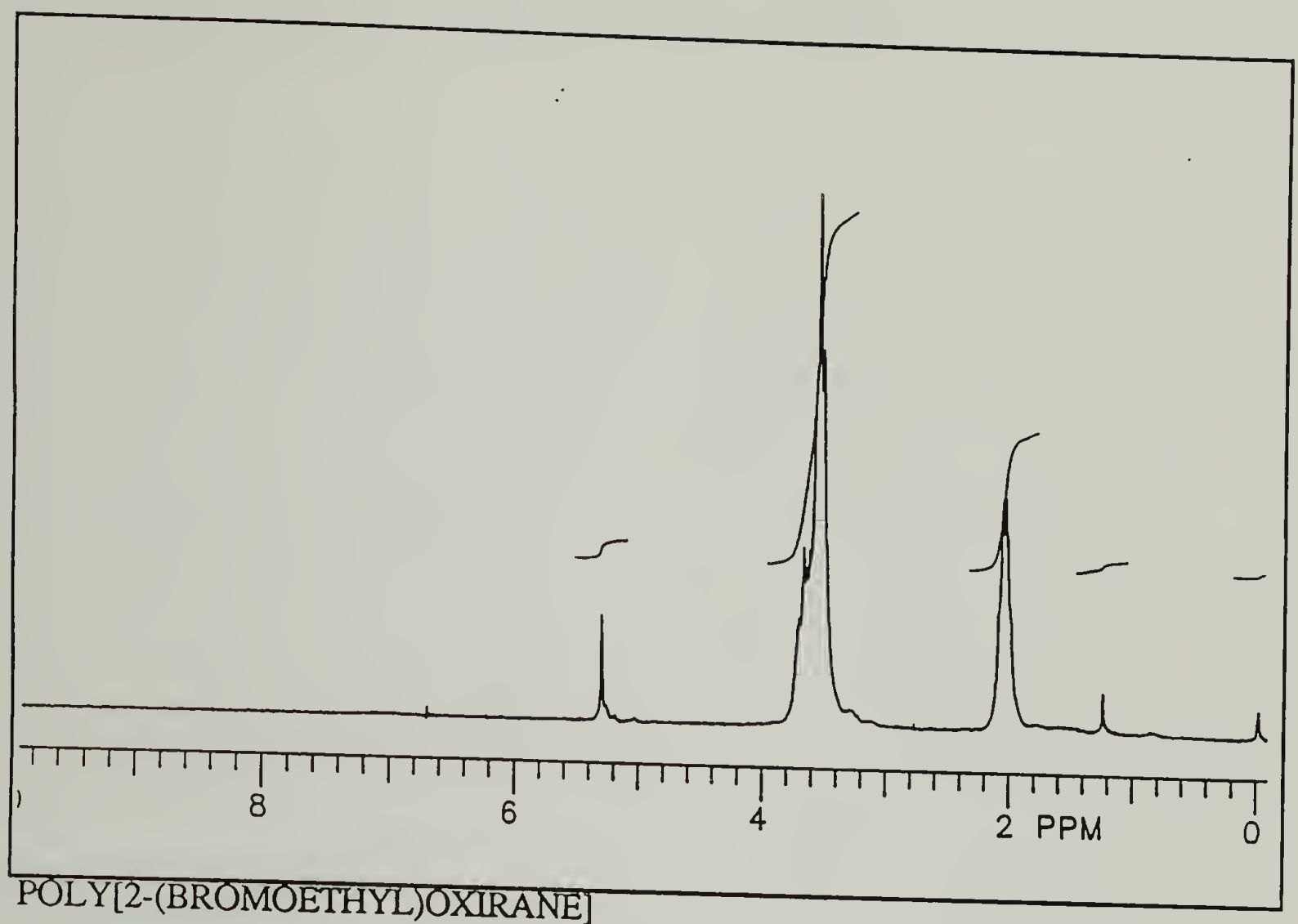

TETRABUTYLAMMONIUM BENZOATE



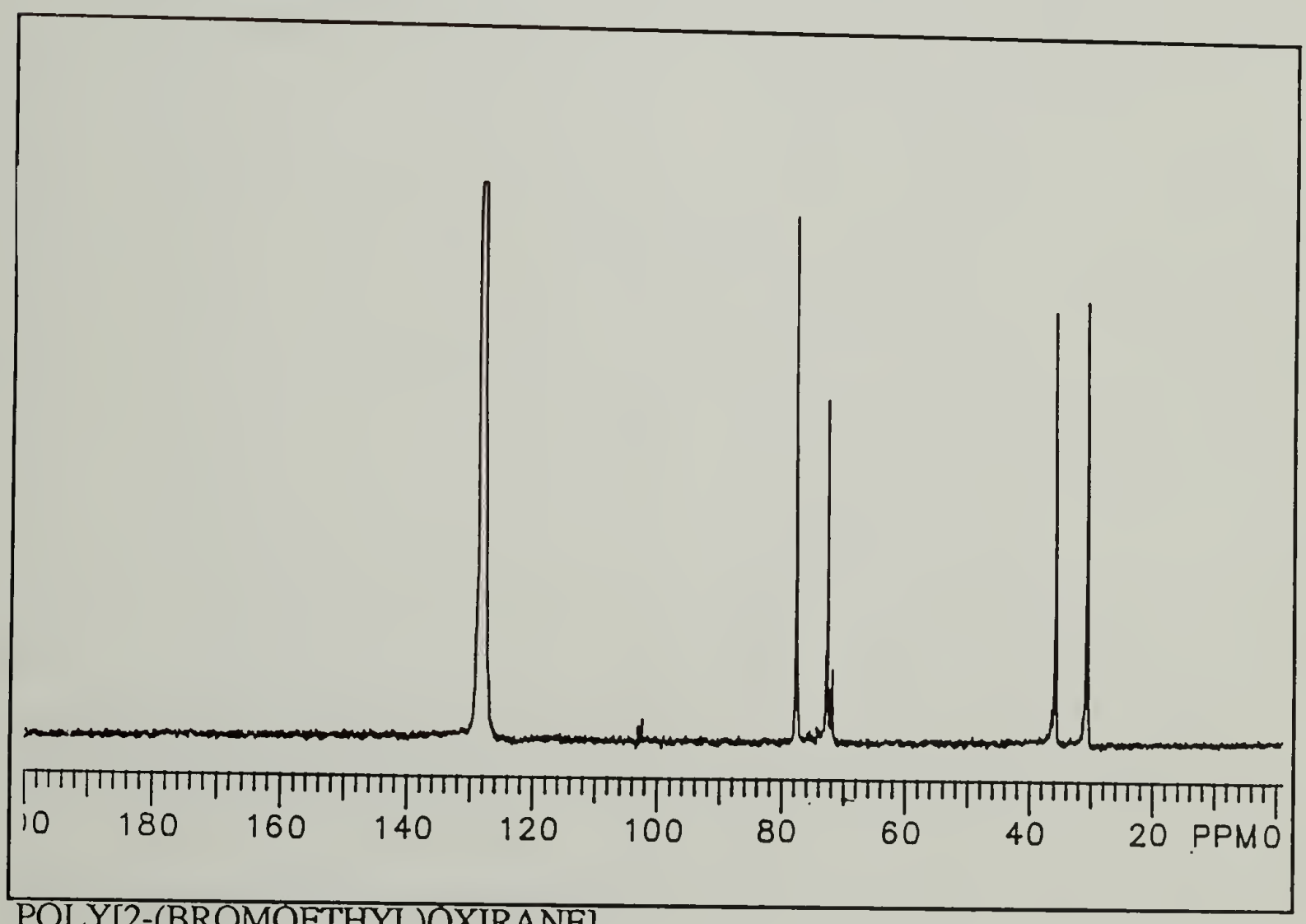

TETRABUTYLAMMONIUM BENZOATE

# APPENDIX B.

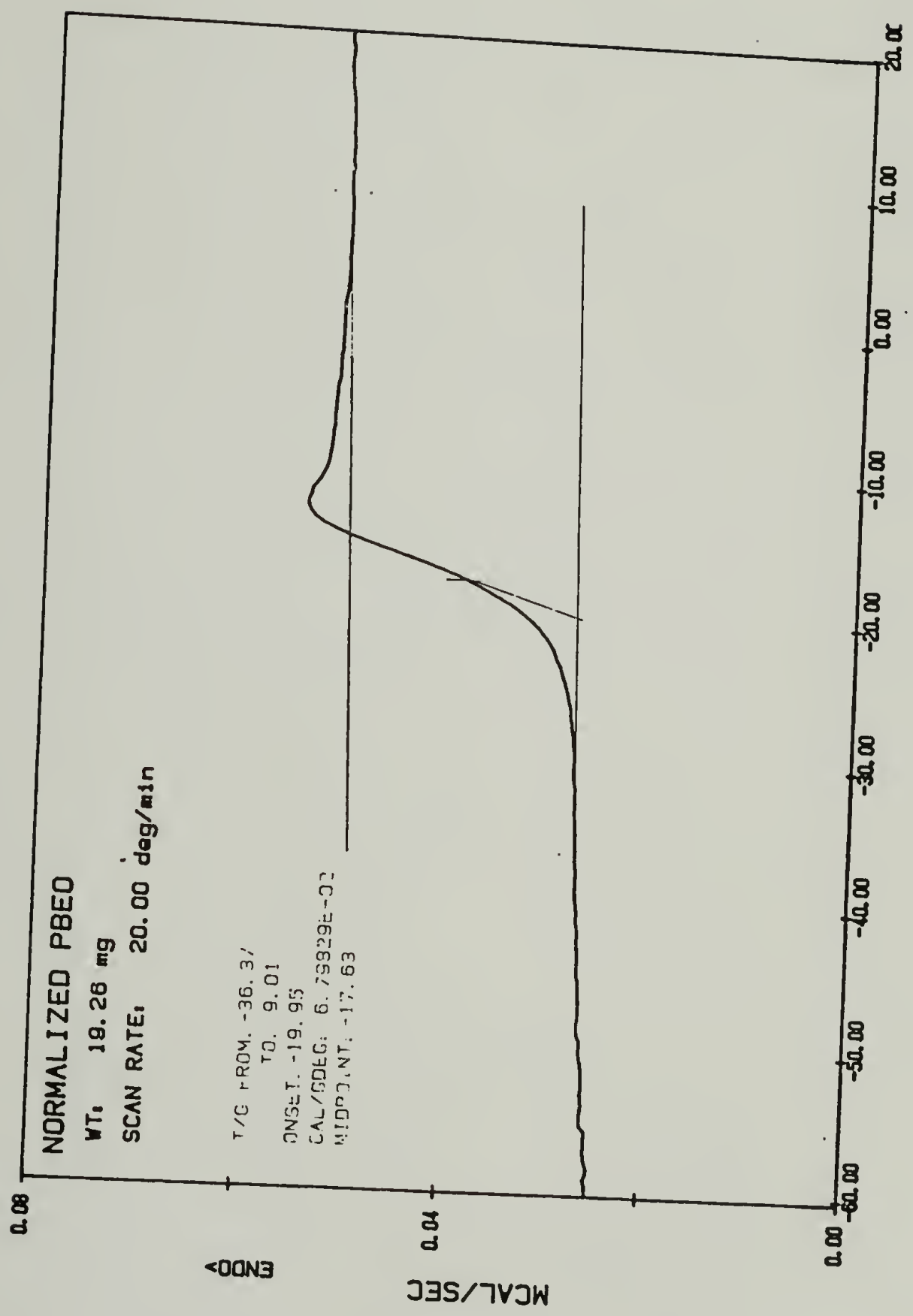
## Reference Spectra for Characterization of Polymers.

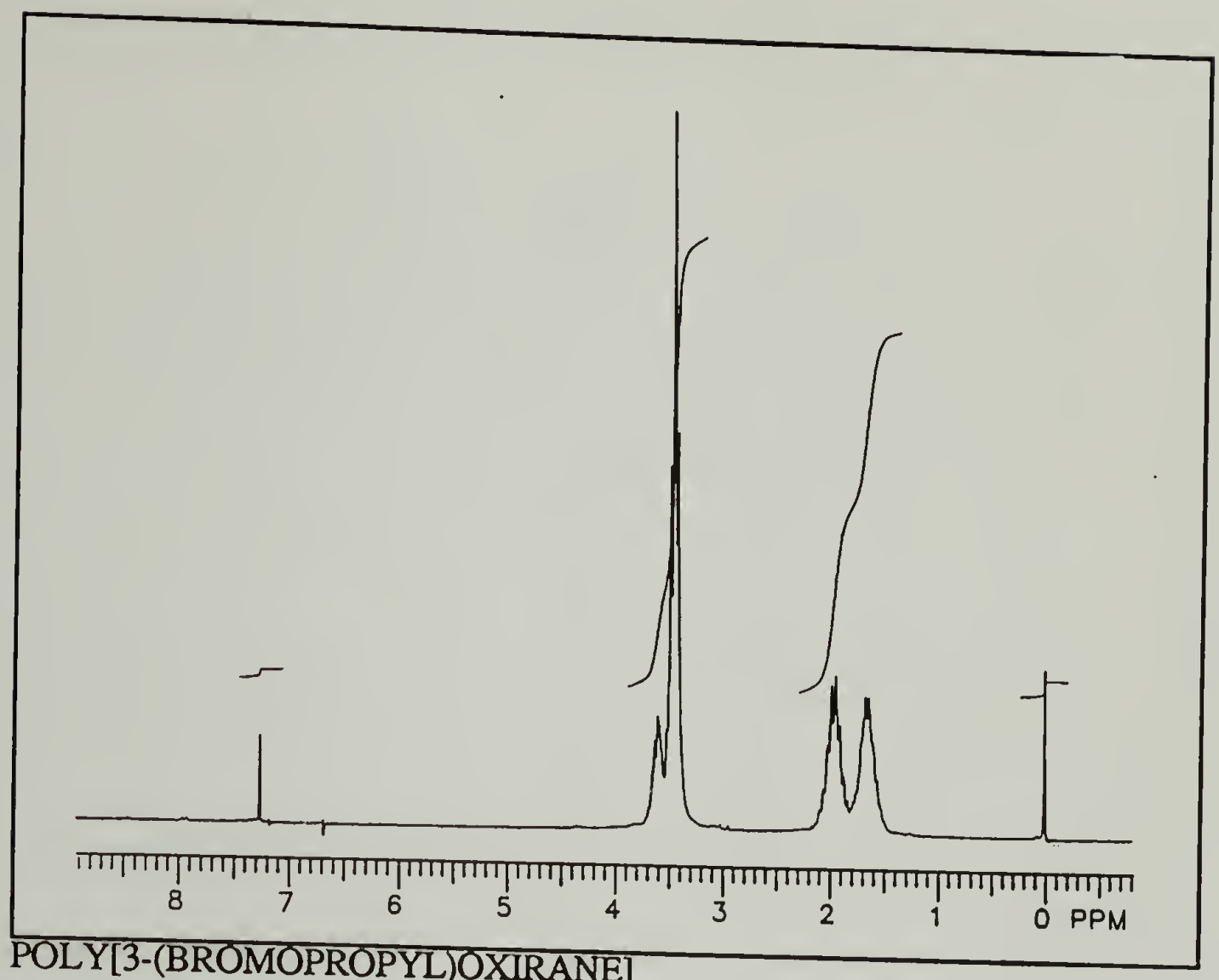



POLY[2-(BROMOETHYL)OXIRANE]

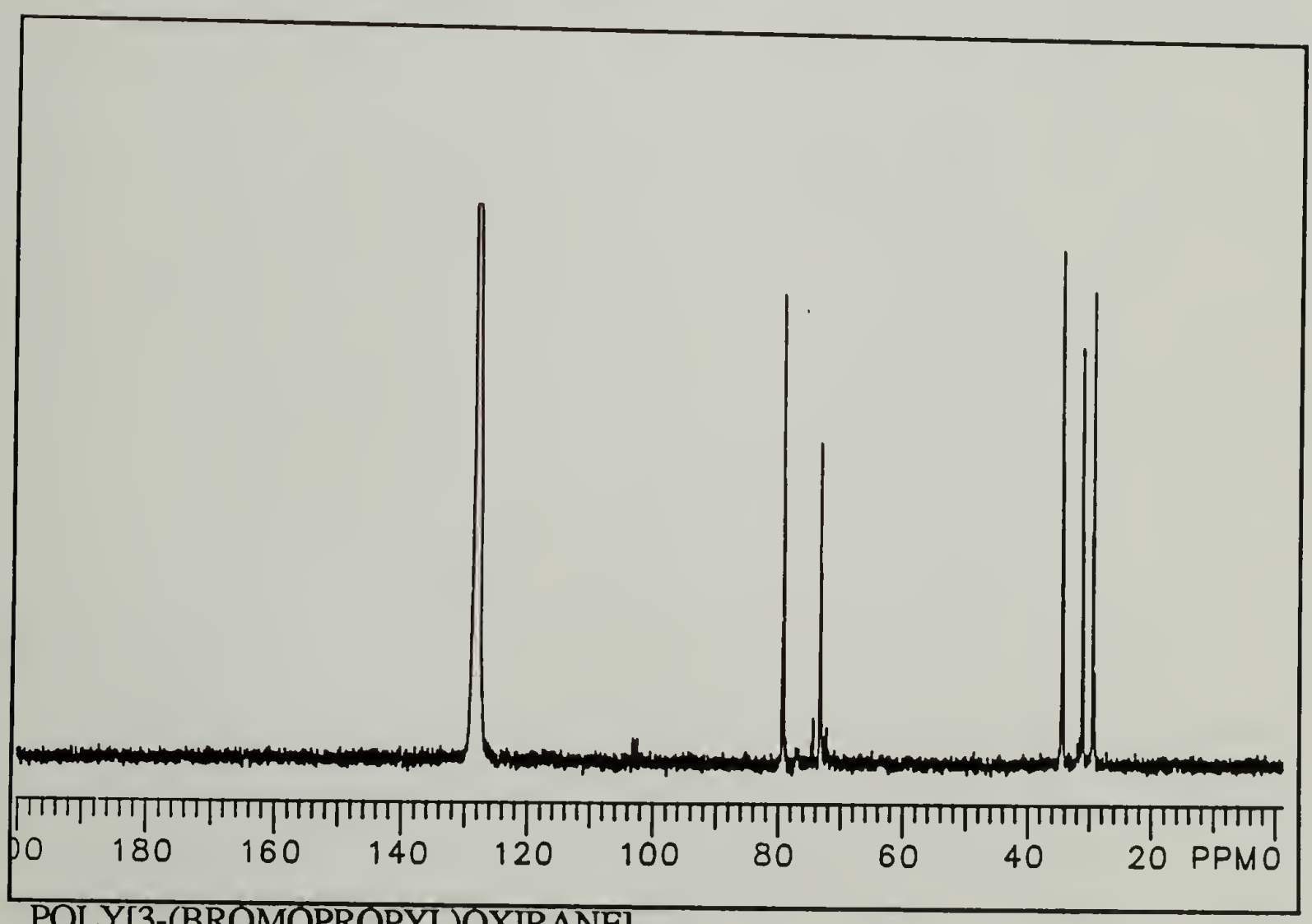



POLY[2-(BROMOETHYL)OXIRANE]

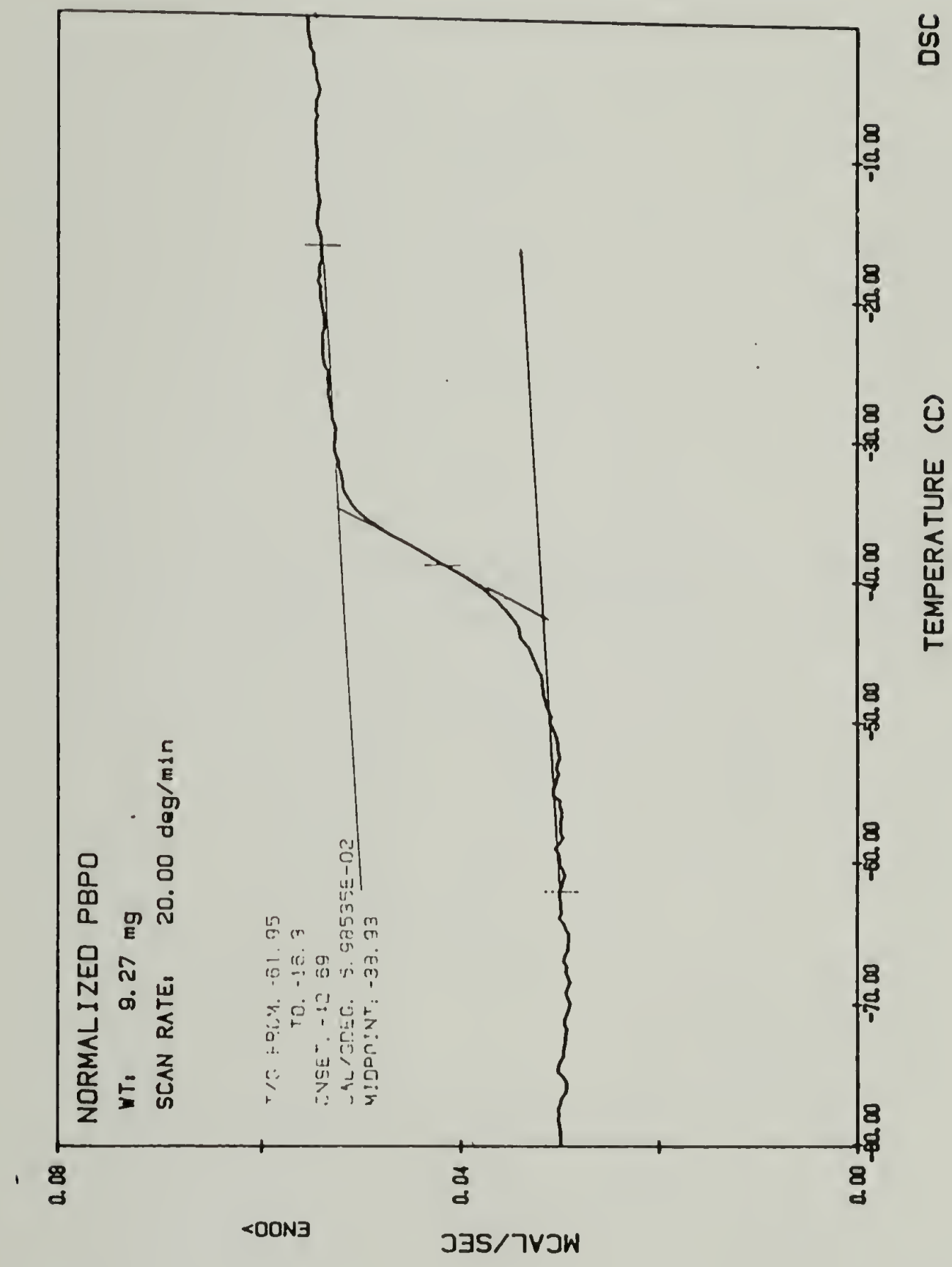

NORMALIZED PBEO
WT: 19.28 mg
SCAN RATE: 20.00 deg/min
T/C FROM: -36.37
TO: 9.01
ONSET: -19.95
CAL/DEG: 6.73329E-03
MIDPOINT: -17.63
MCAL/SEC
ENDO>
0.08
0.04
0.00
20.00
10.00
0.00
-10.00
-20.00
-30.00
-40.00
-50.00
-60.00

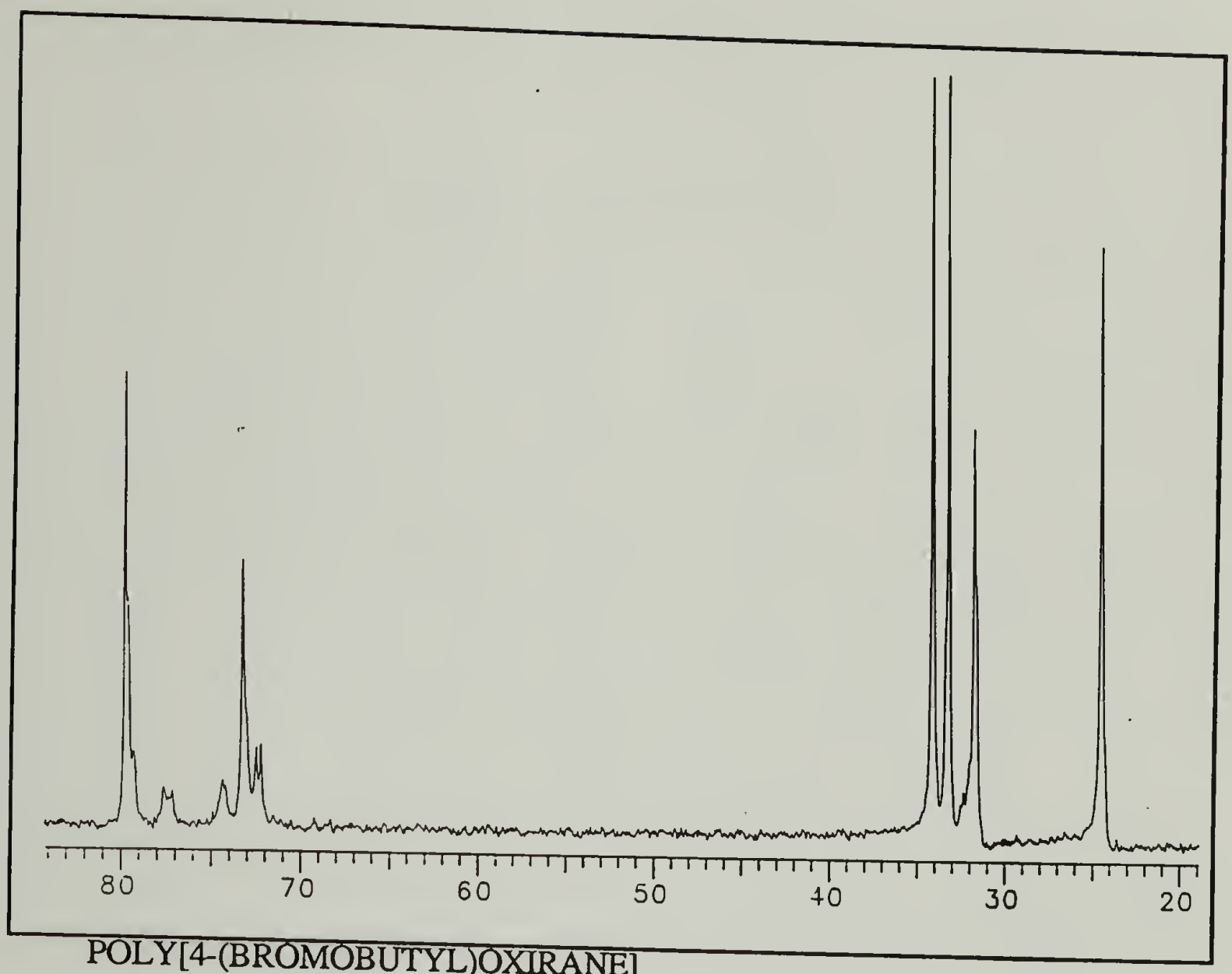



POLY[3-(BROMOPROPYL)OXIRANE]

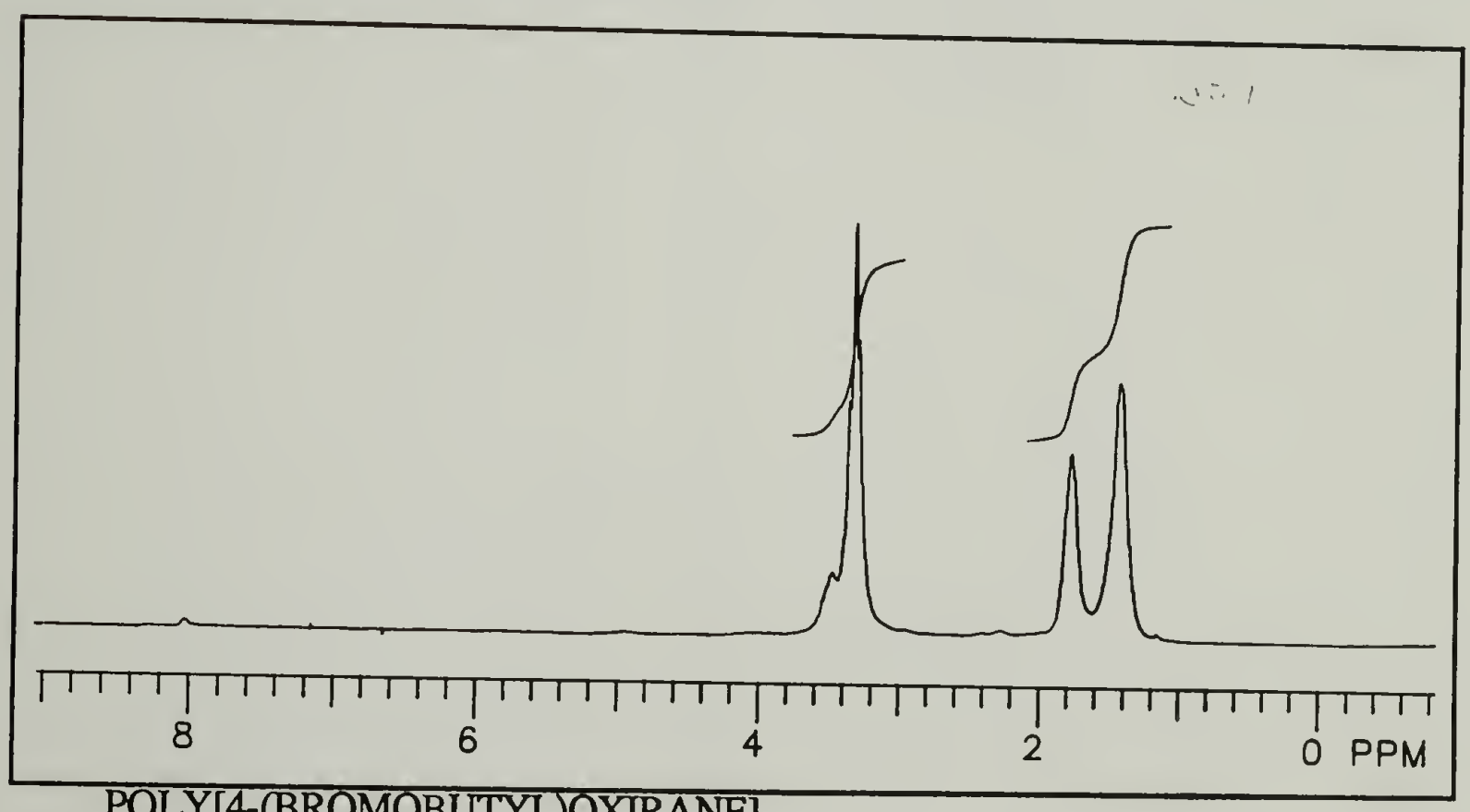



POLY[3-(BROMOPROPYL)OXIRANE]

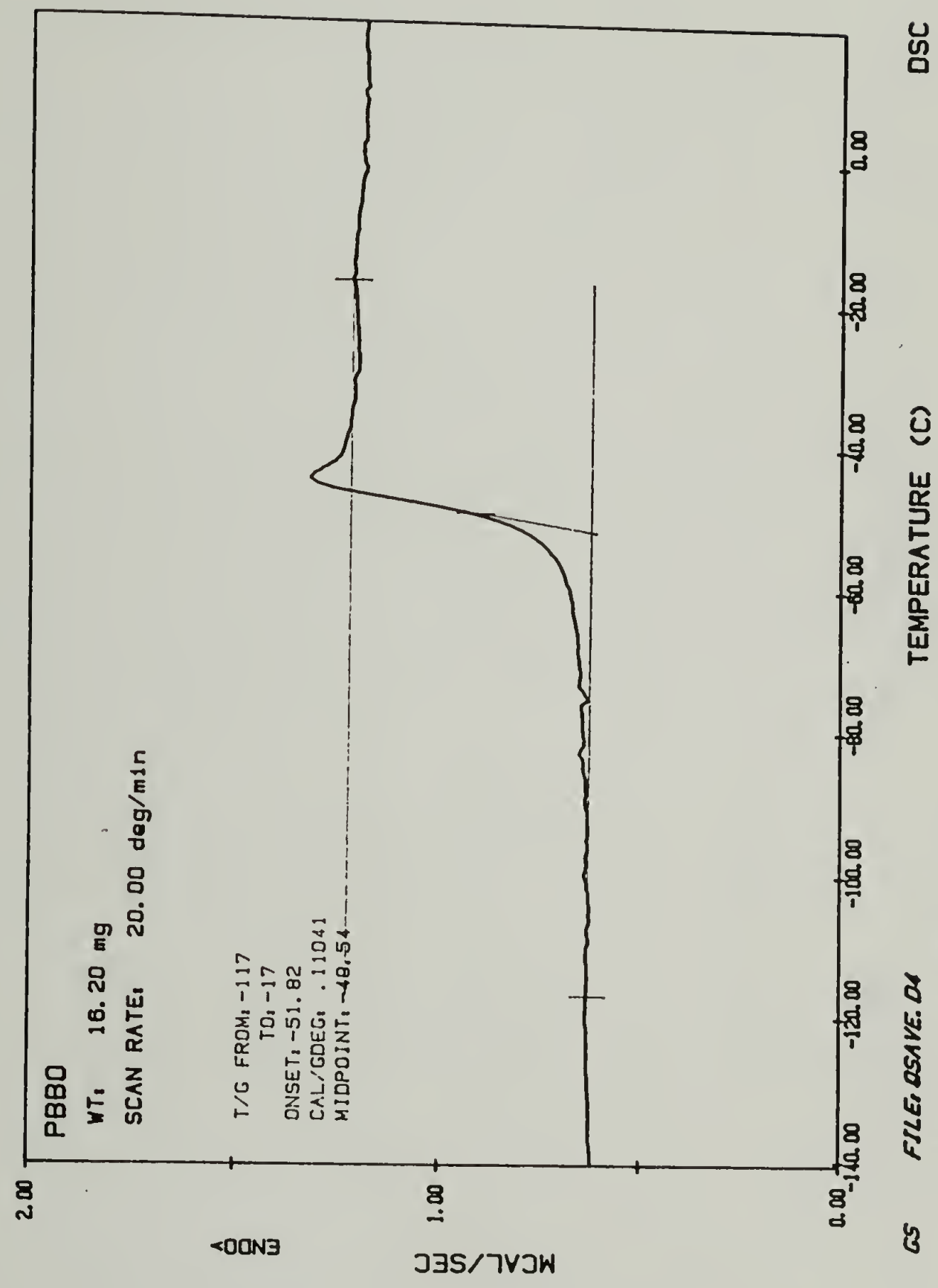

NORMALIZED PBPO
WT: 9.27 mg
SCAN RATE: 20.00 deg/min
TO FROM -61.95
TO -18.3
ONSET -12.89
CAL/DEG 5.985356-02
MIDPOINT -33.93
0.08
0.04
0.00
ENDO>
MCAL/SEC
-10.00
-20.00
-30.00
-40.00
-50.00
-60.00
-70.00
-80.00
DSC
TEMPERATURE (C)

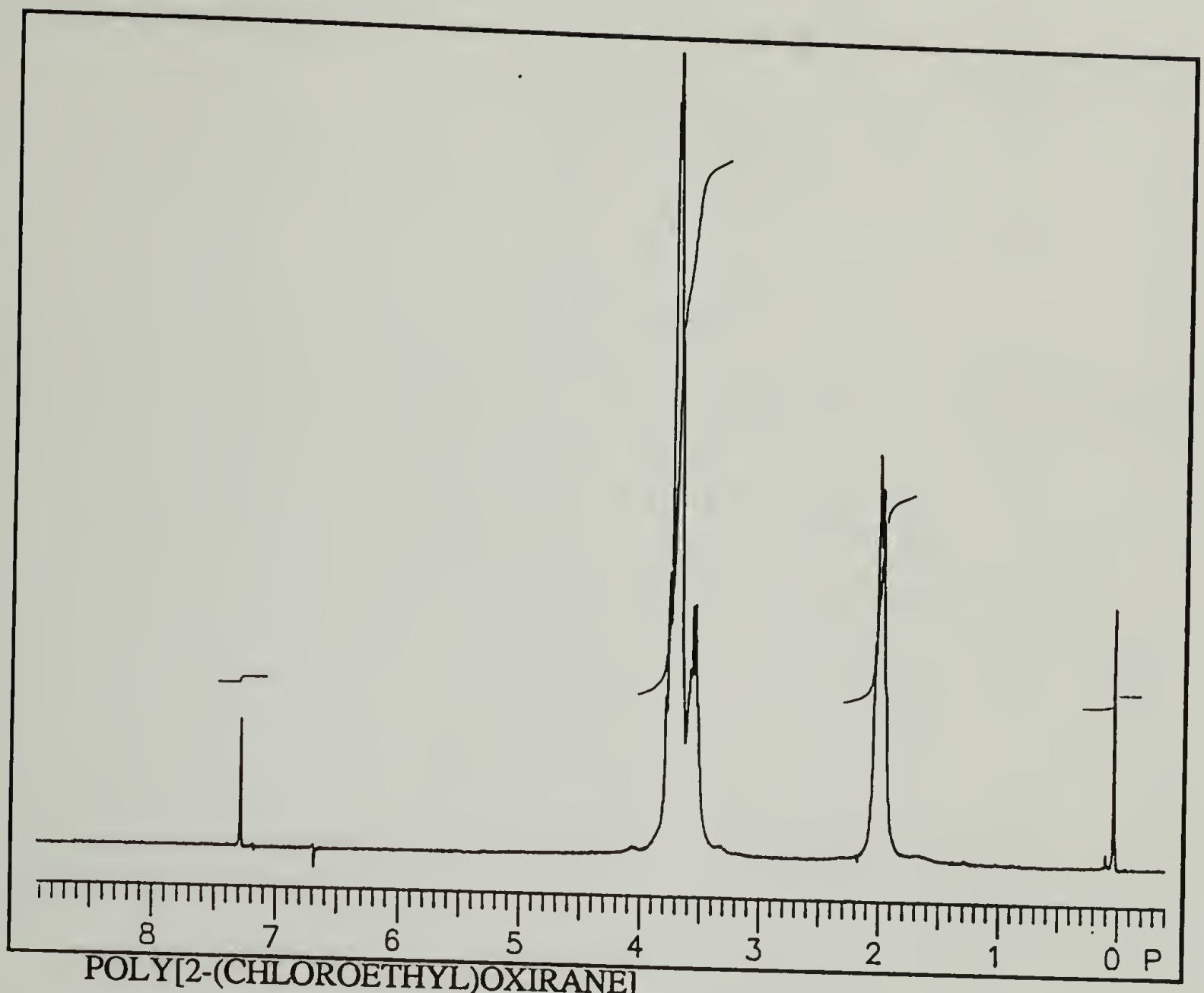



POLY[4-(BROMOBUTYL)OXIRANE]

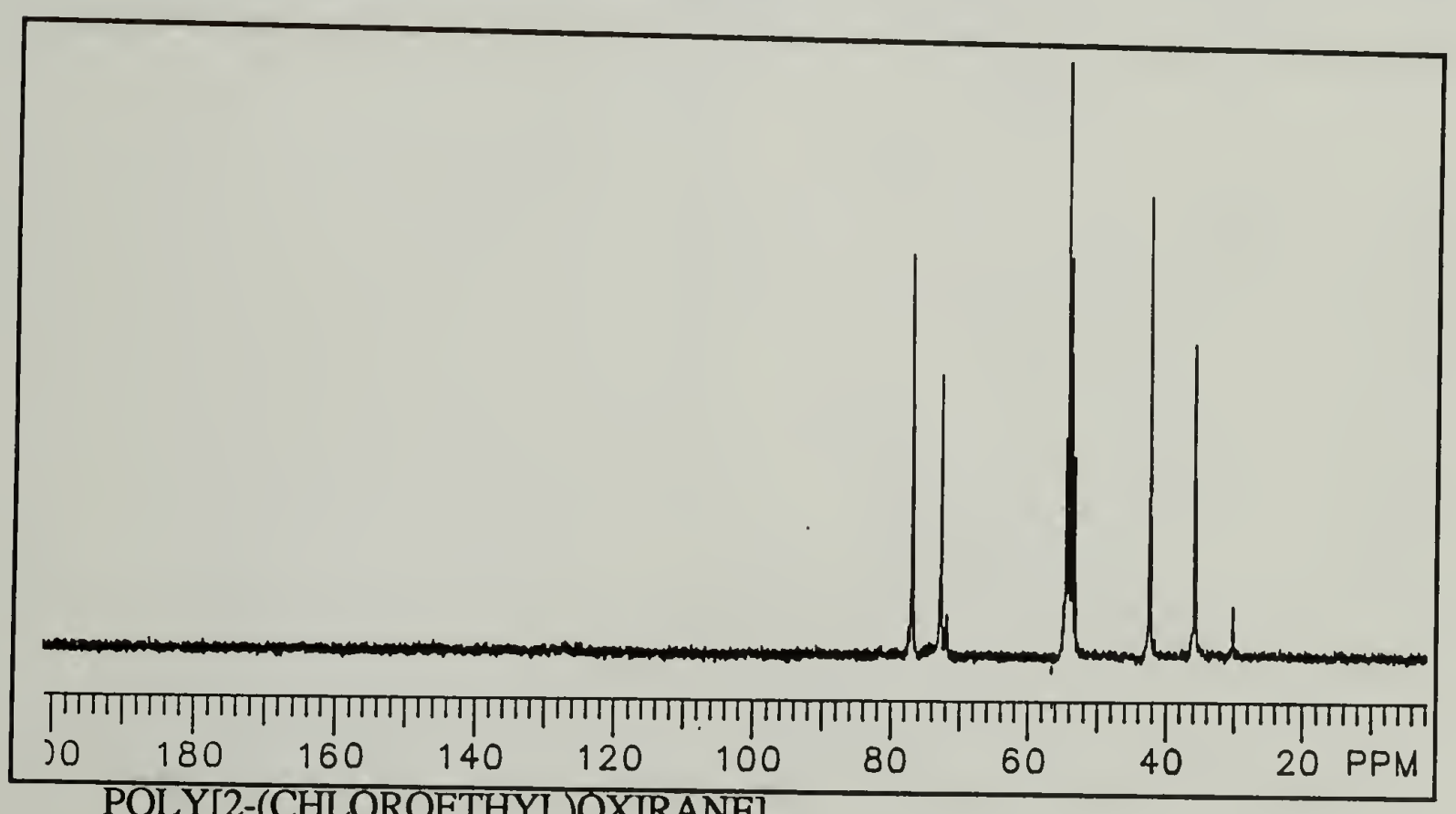



POLY[4-(BROMOBUTYL)OXIRANE]

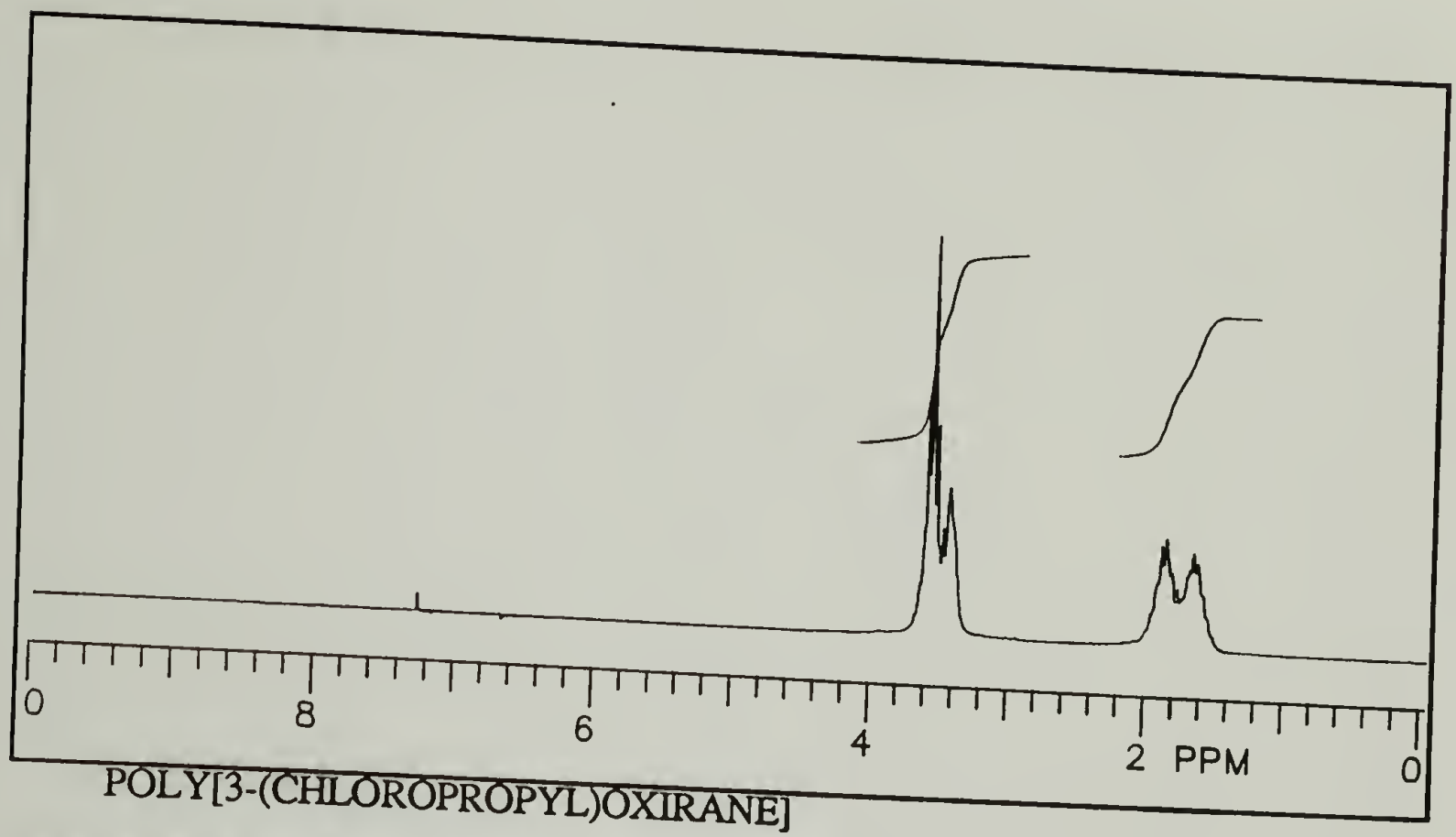

PBBO
WT: 16.20 mg
SCAN RATE: 20.00 deg/min
T/G FROM: -117
TO: -17
ONSET: -51.82
CAL/GDEG: .11041
MIDPOINT: -48.54
ENDO>
MCAL/SEC
2.00
1.00
0.00
0.00
-20.00
-40.00
-60.00
-80.00
-100.00
-120.00
-140.00
DSC
TEMPERATURE (C)
GS FILE: DSAVE.04
DATE: 88/03/09 TIME: 21:18



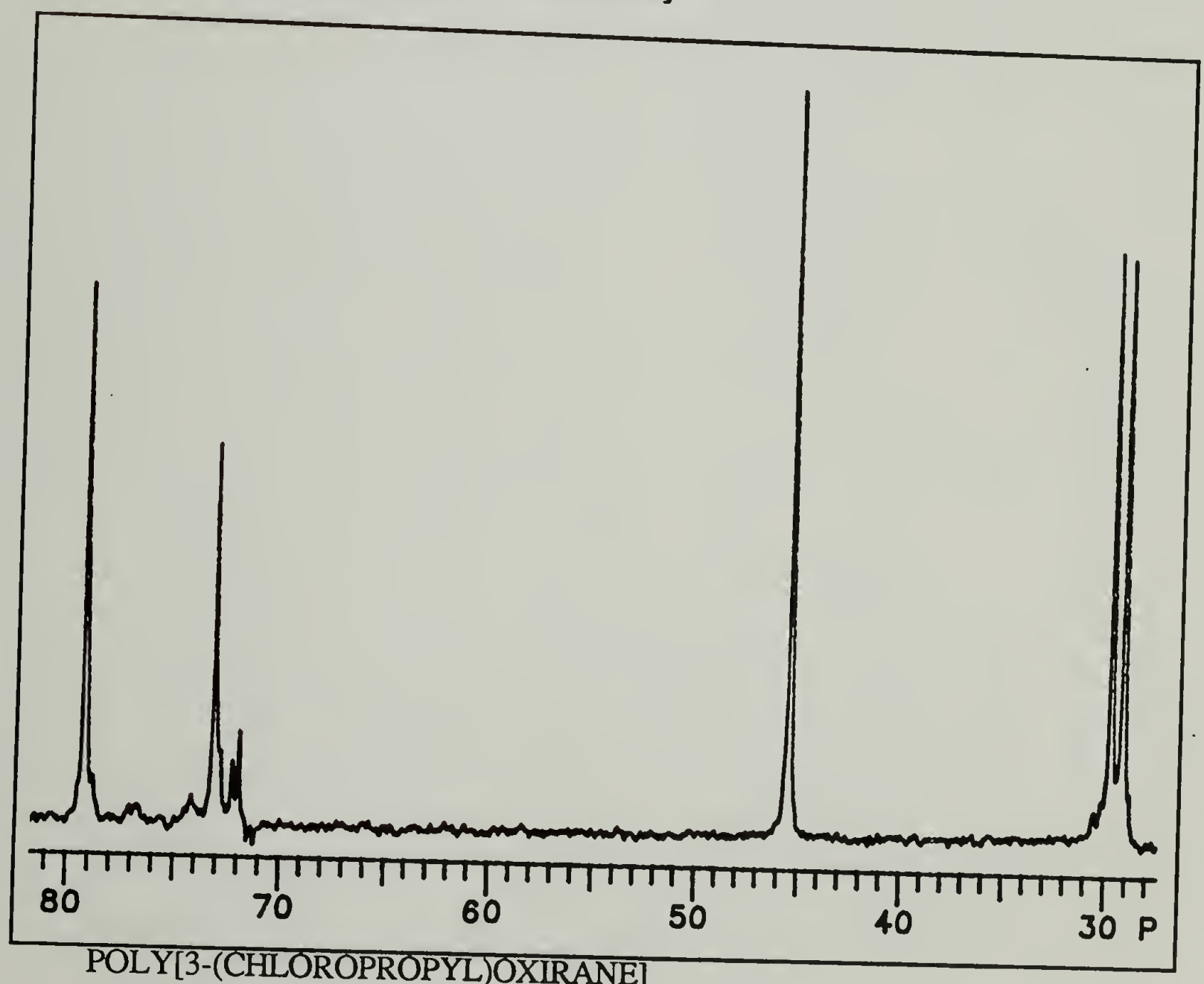

POLY[2-(CHLOROETHYL)OXIRANE]



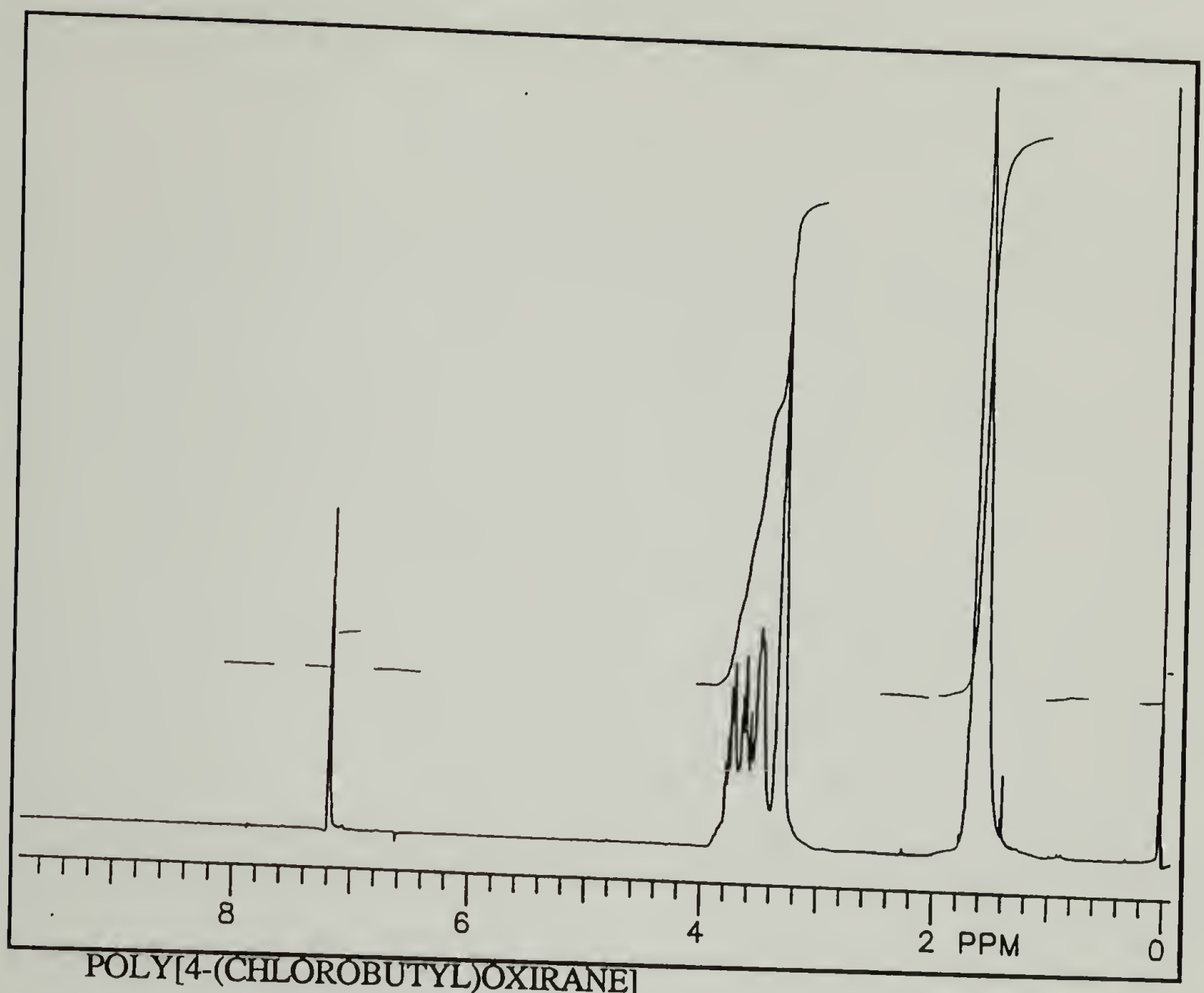

POLY[2-(CHLOROETHYL)OXIRANE]



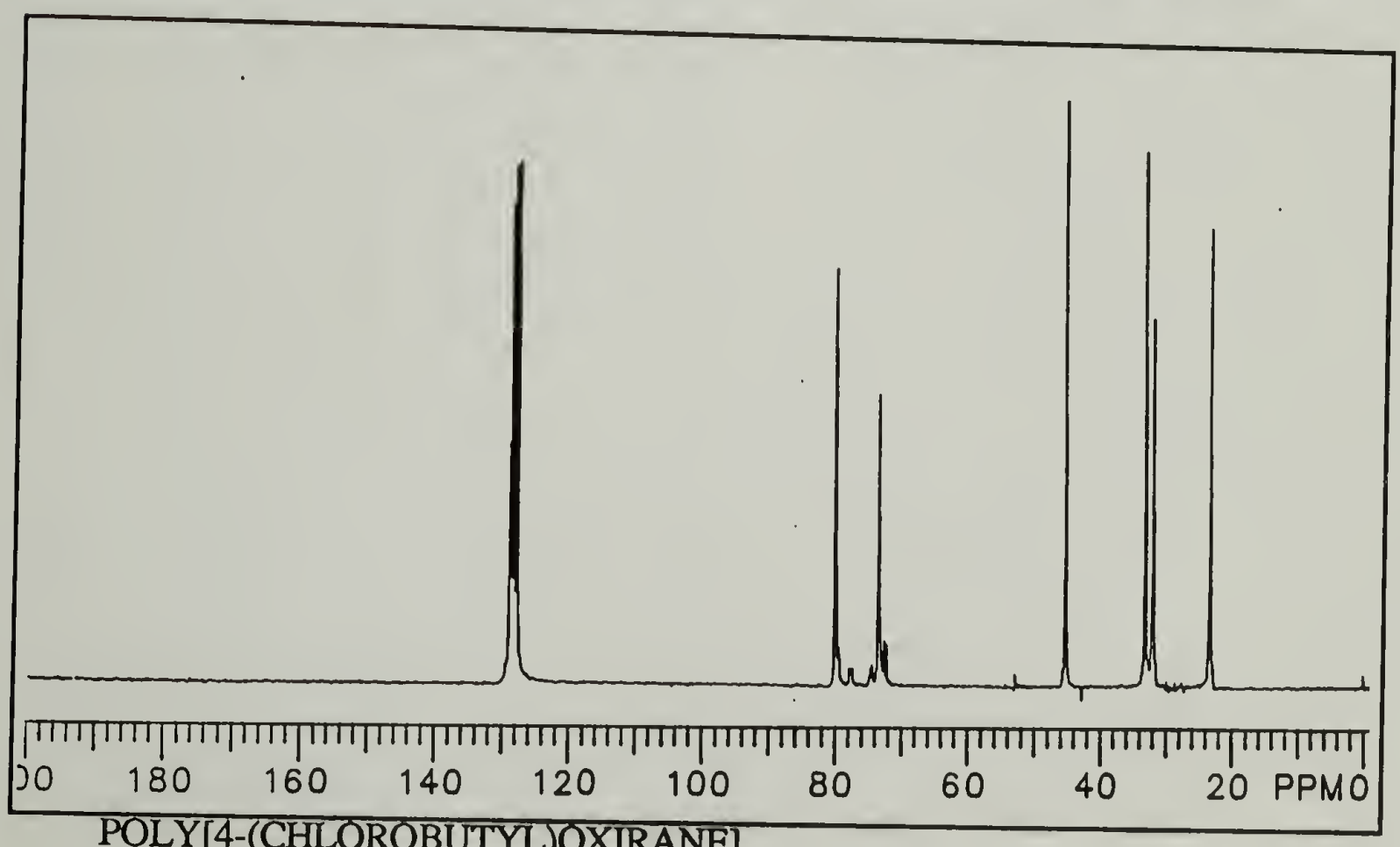

POLY[3-(CHLOROPROPYL)OXIRANE]



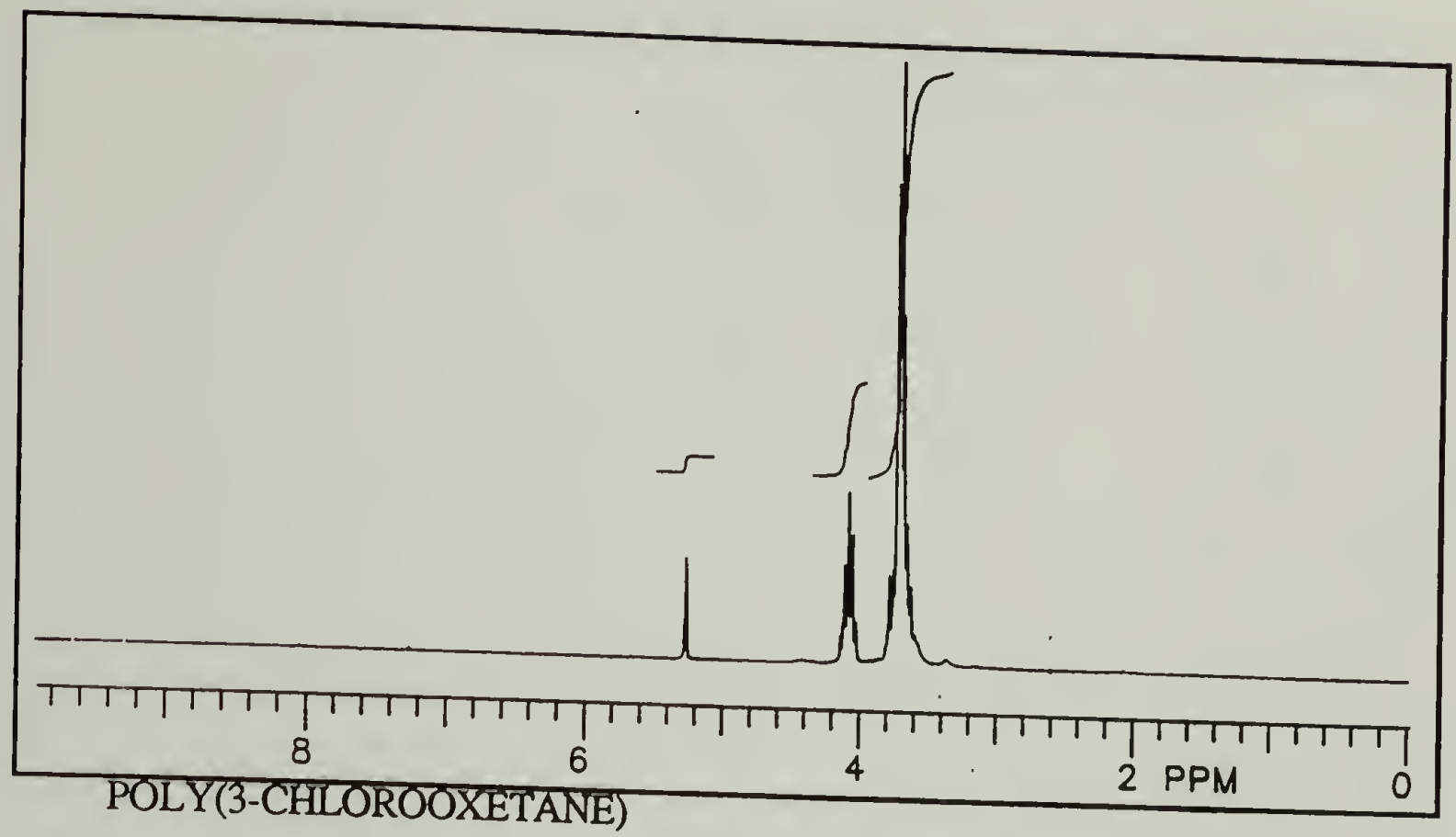

POLY[3-(CHLOROPROPYL)OXIRANE]



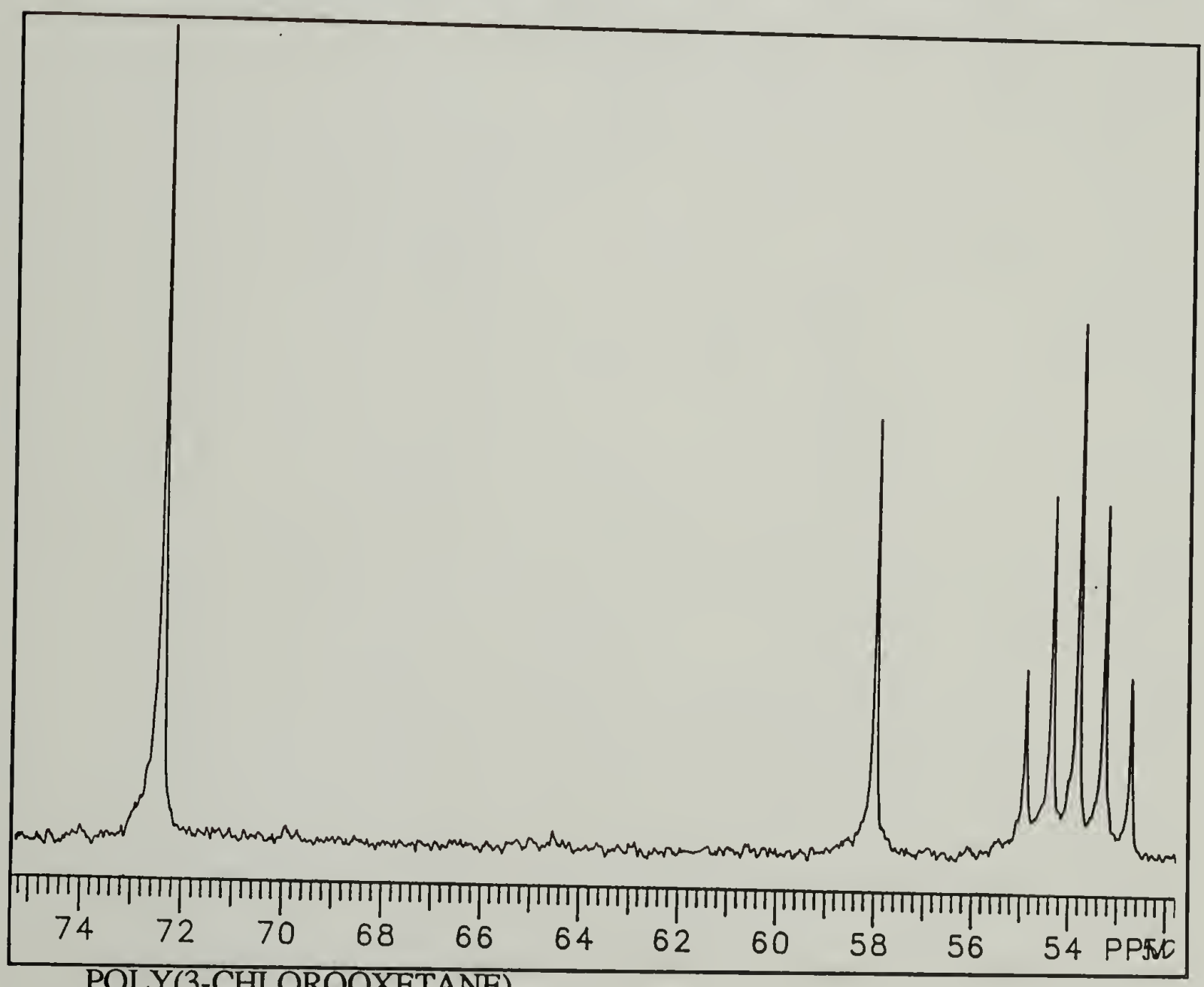

POLY[4-(CHLOROBUTYL)OXIRANE]



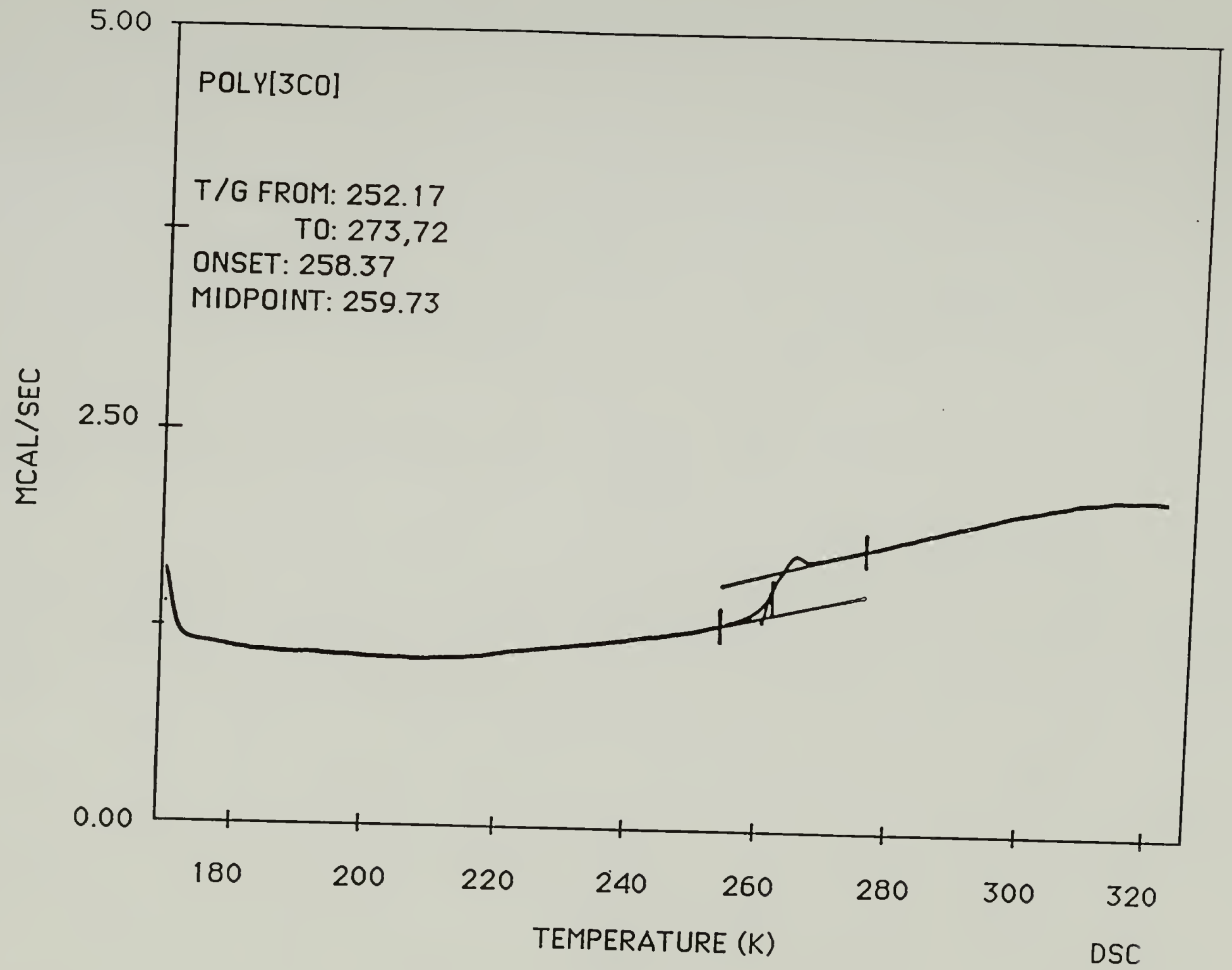

POLY[4-(CHLOROBUTYL)OXIRANE]

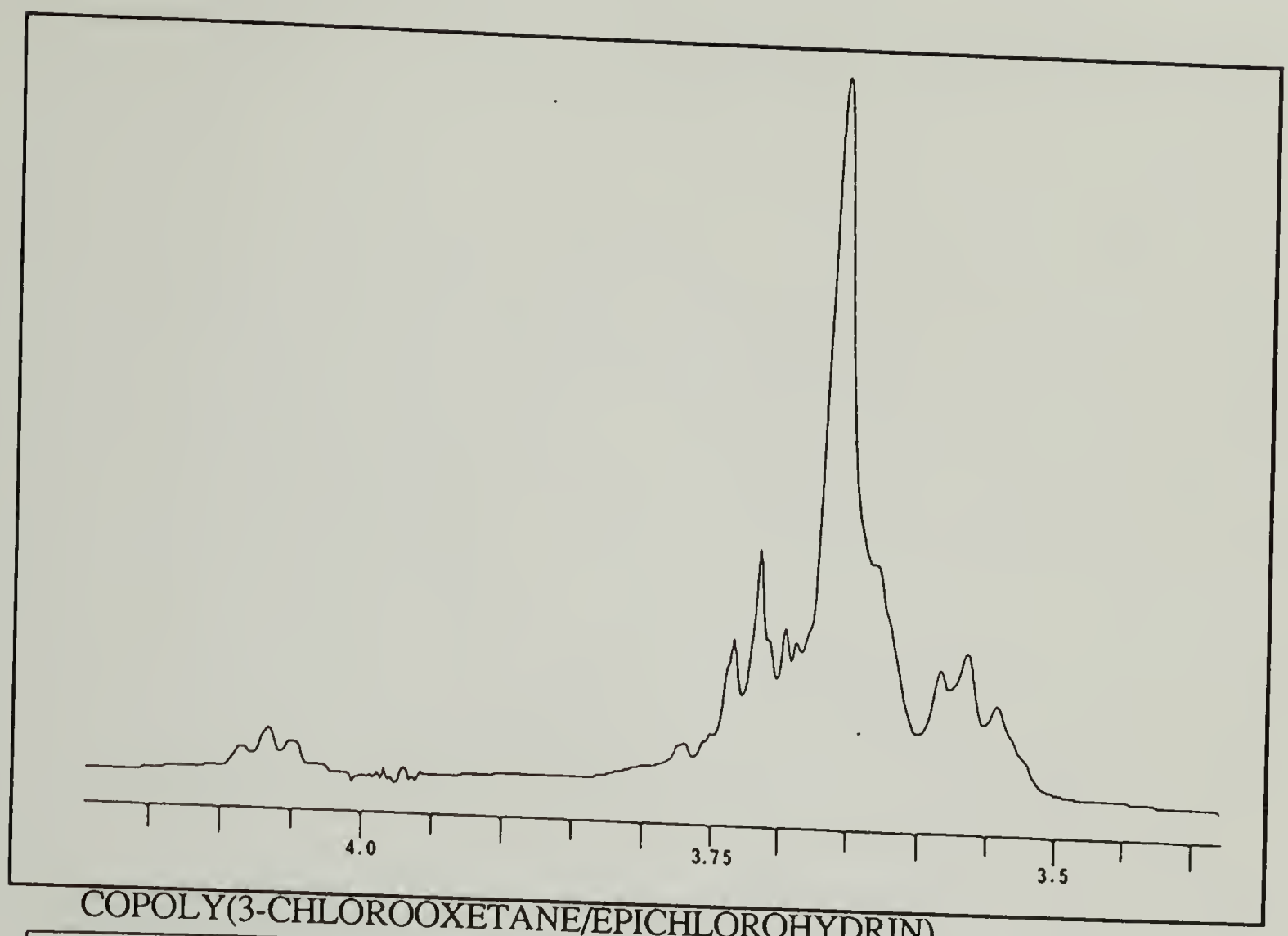



POLY(3-CHLOROOXETANE)

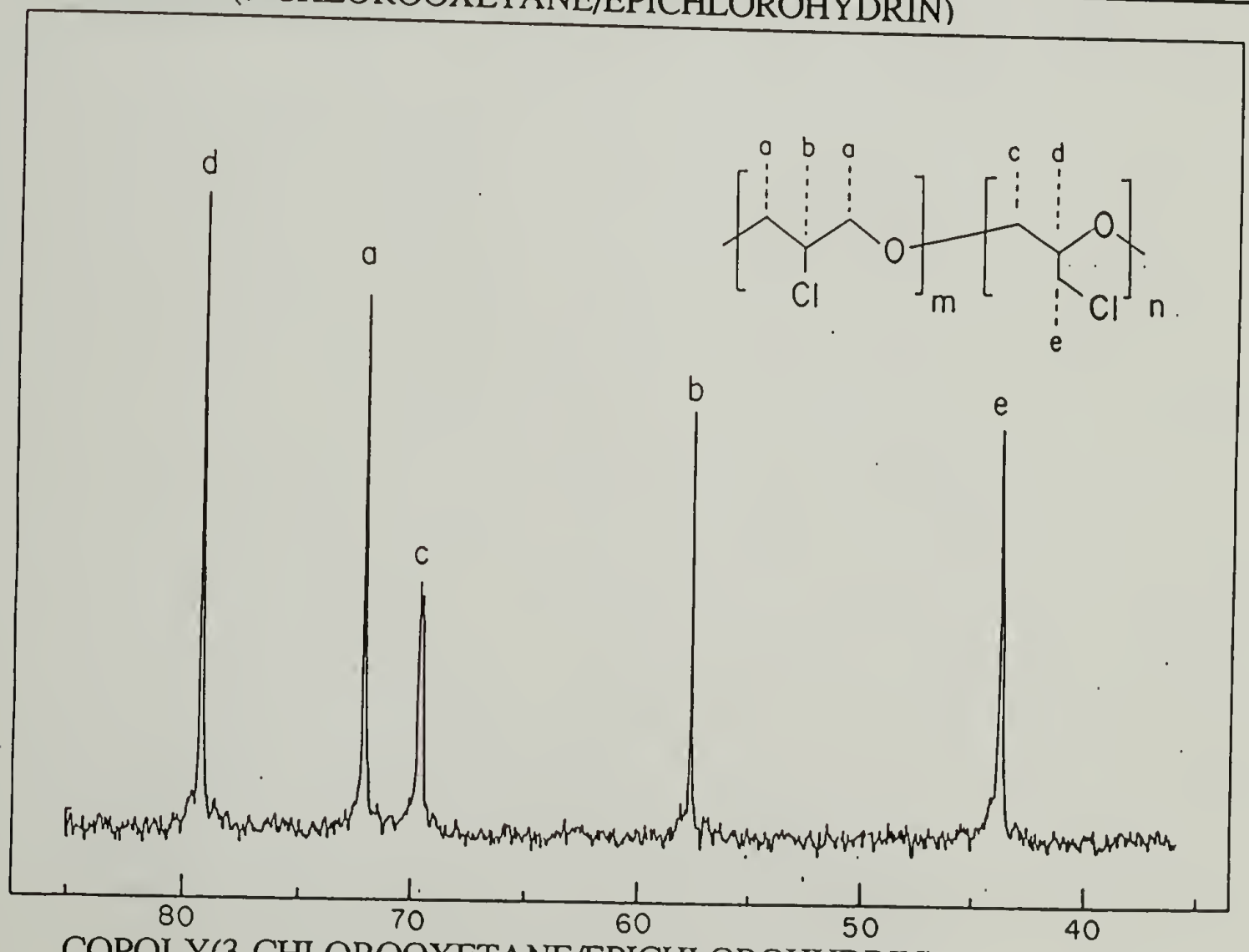



POLY(3-CHLOROOXETANE)

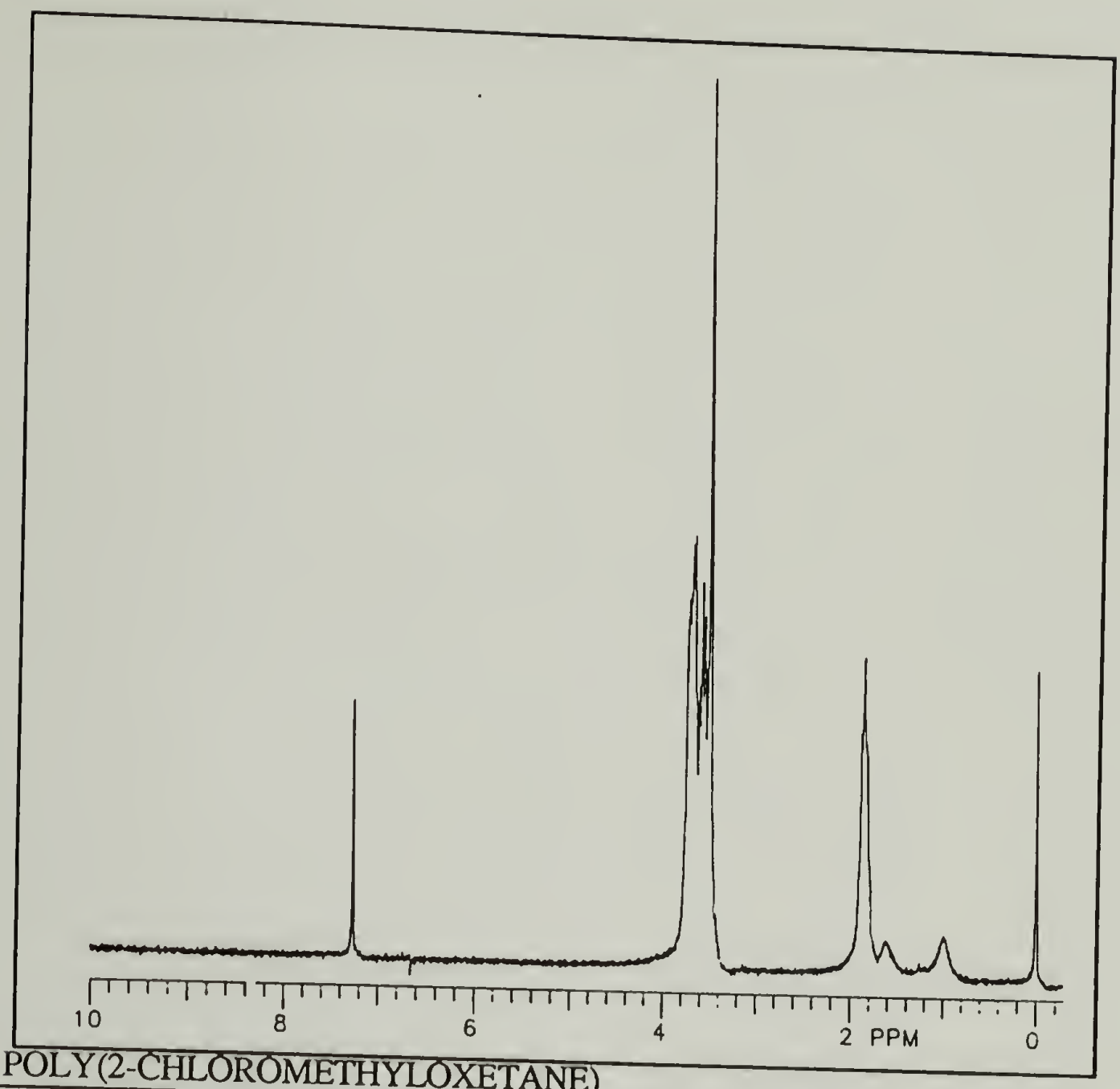

5.00
POLY[3CO]
T/G FROM: 252.17
TO: 273,72
ONSET: 258.37
MIDPOINT: 259.73
2.50
MCAL/SEC
0.00
180
200
220
240
260
280
300
320
TEMPERATURE (K)
DSC



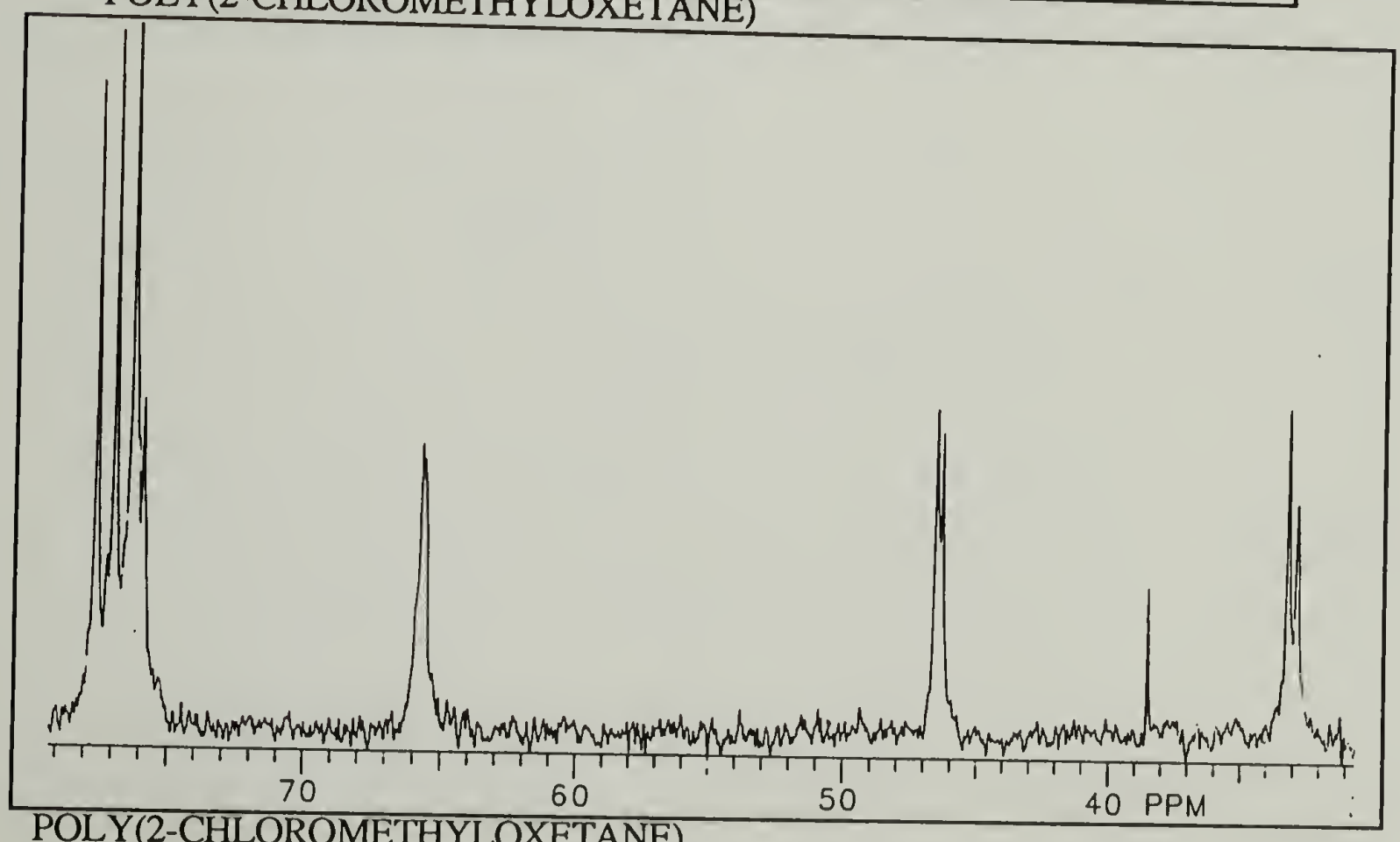

COPOLY(3-CHLOROOXETANE/EPICHLOROHYDRIN)



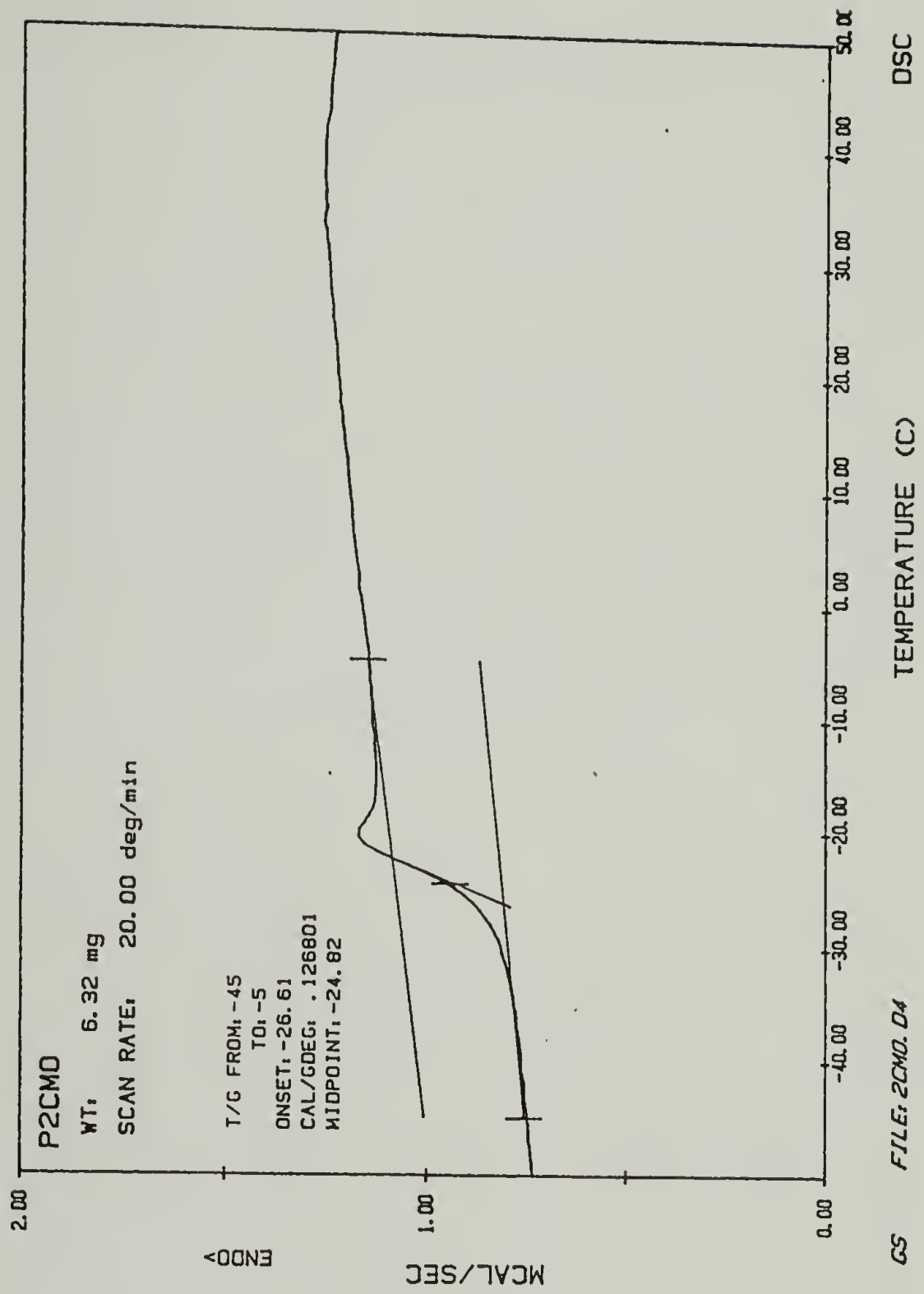

COPOLY(3-CHLOROOXETANE/EPICHLOROHYDRIN)

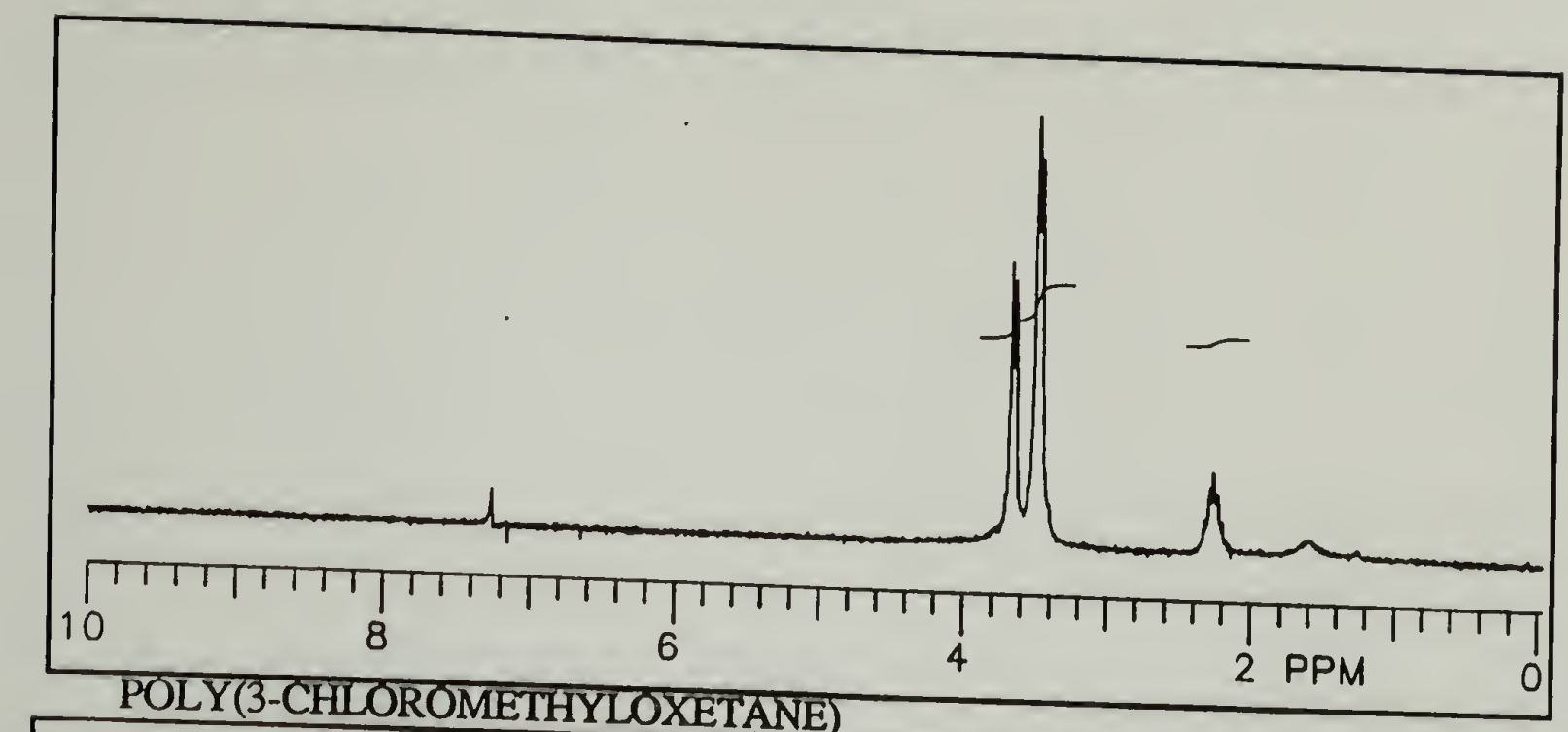



POLY(2-CHLOROMETHYLOXETANE)

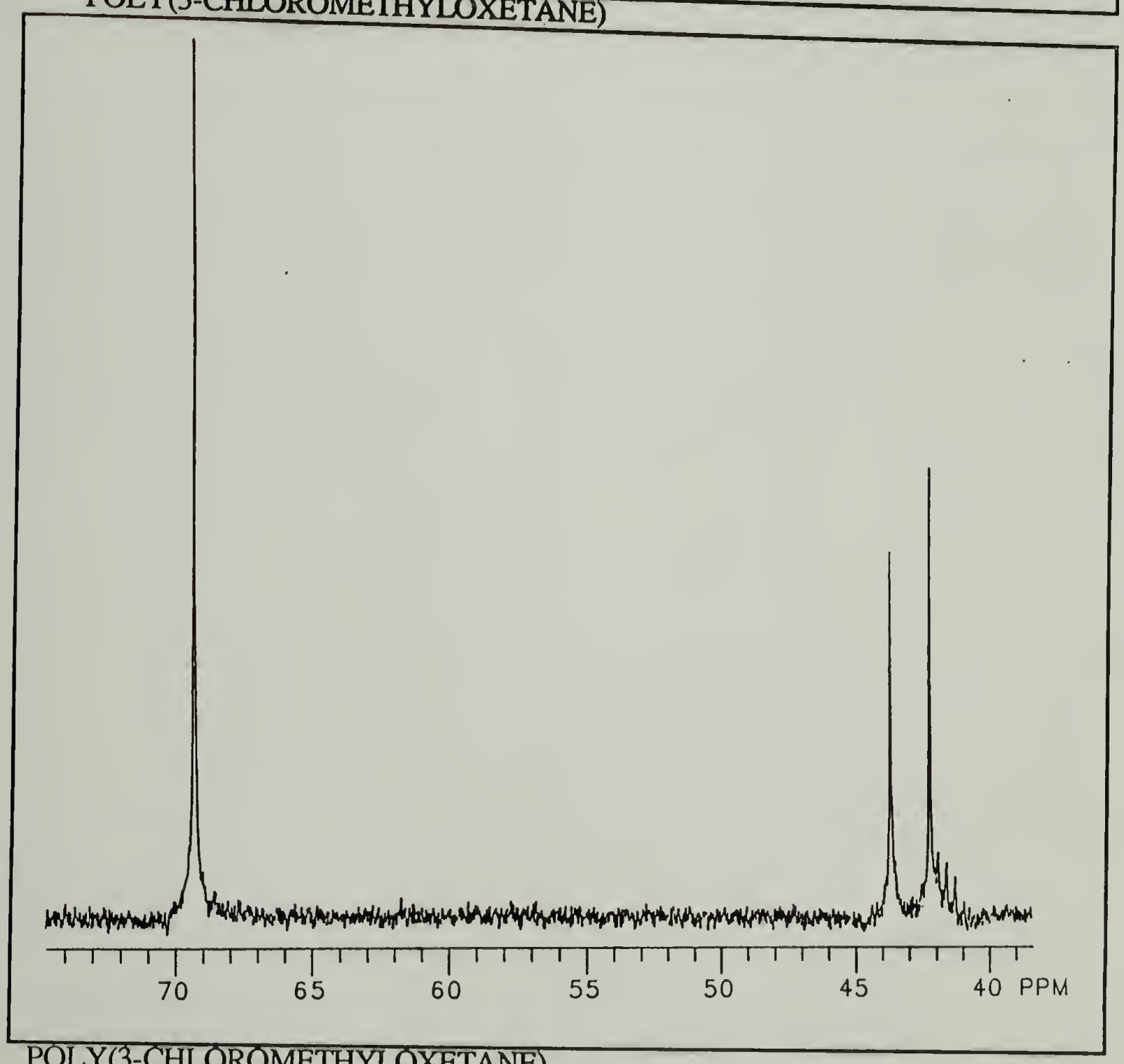



POLY(2-CHLOROMETHYLOXETANE)

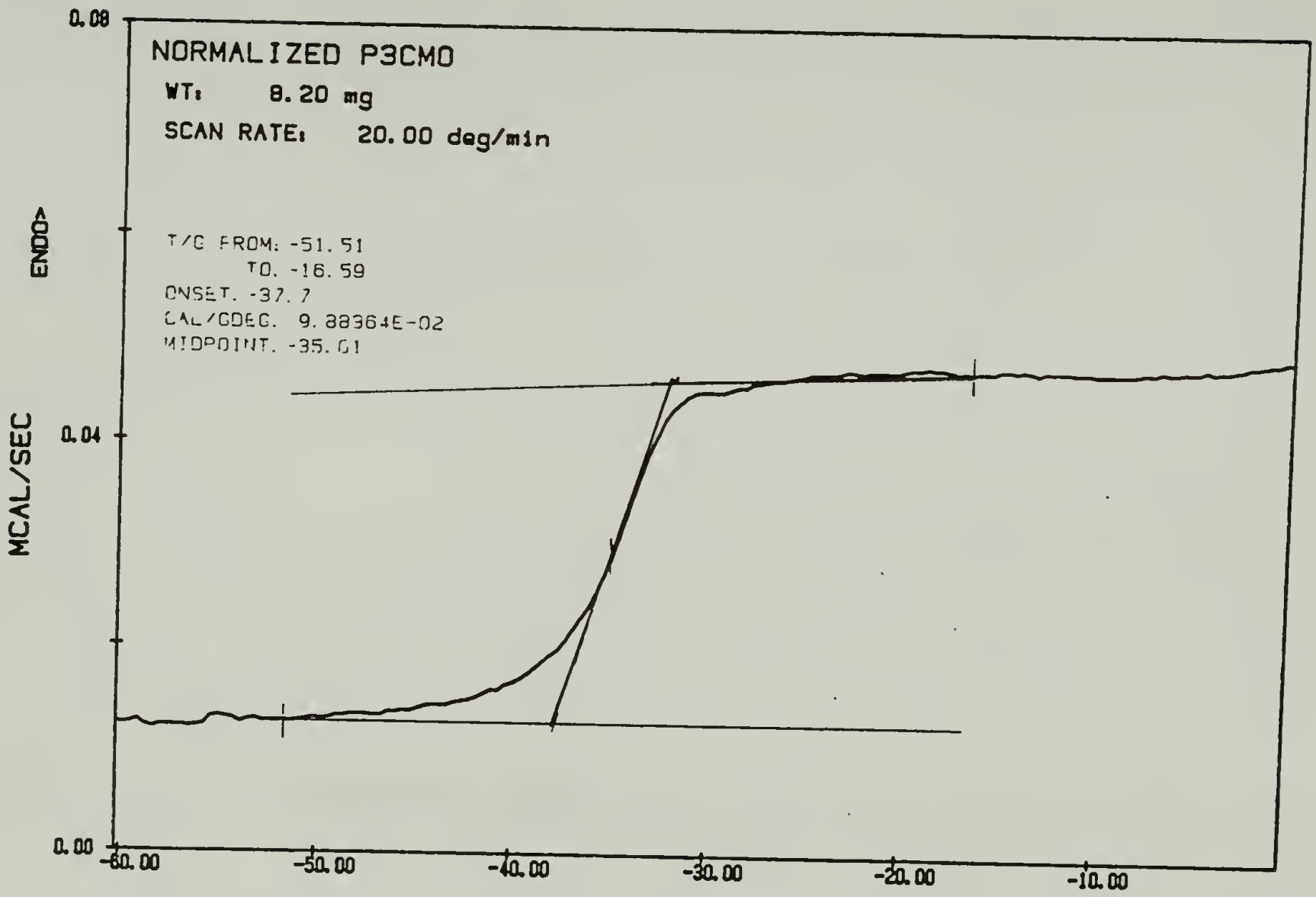

P2CMO
WT: 6.32 mg
SCAN RATE: 20.00 deg/min
T/G FROM: -45
TO: -5
ONSET: -26.61
CAL/GDEG: .126801
MIDPOINT: -24.82
ENDO>
MCAL/SEC
2.00
1.00
0.00
50.00
40.00
30.00
20.00
10.00
0.00
-10.00
-20.00
-30.00
-40.00
DSC
TEMPERATURE (C)
GS FILE: 2CM0.D4
DATE: 88/06/24 TIME: 17:36




POLY(3-CHLOROMETHYLOXETANE)

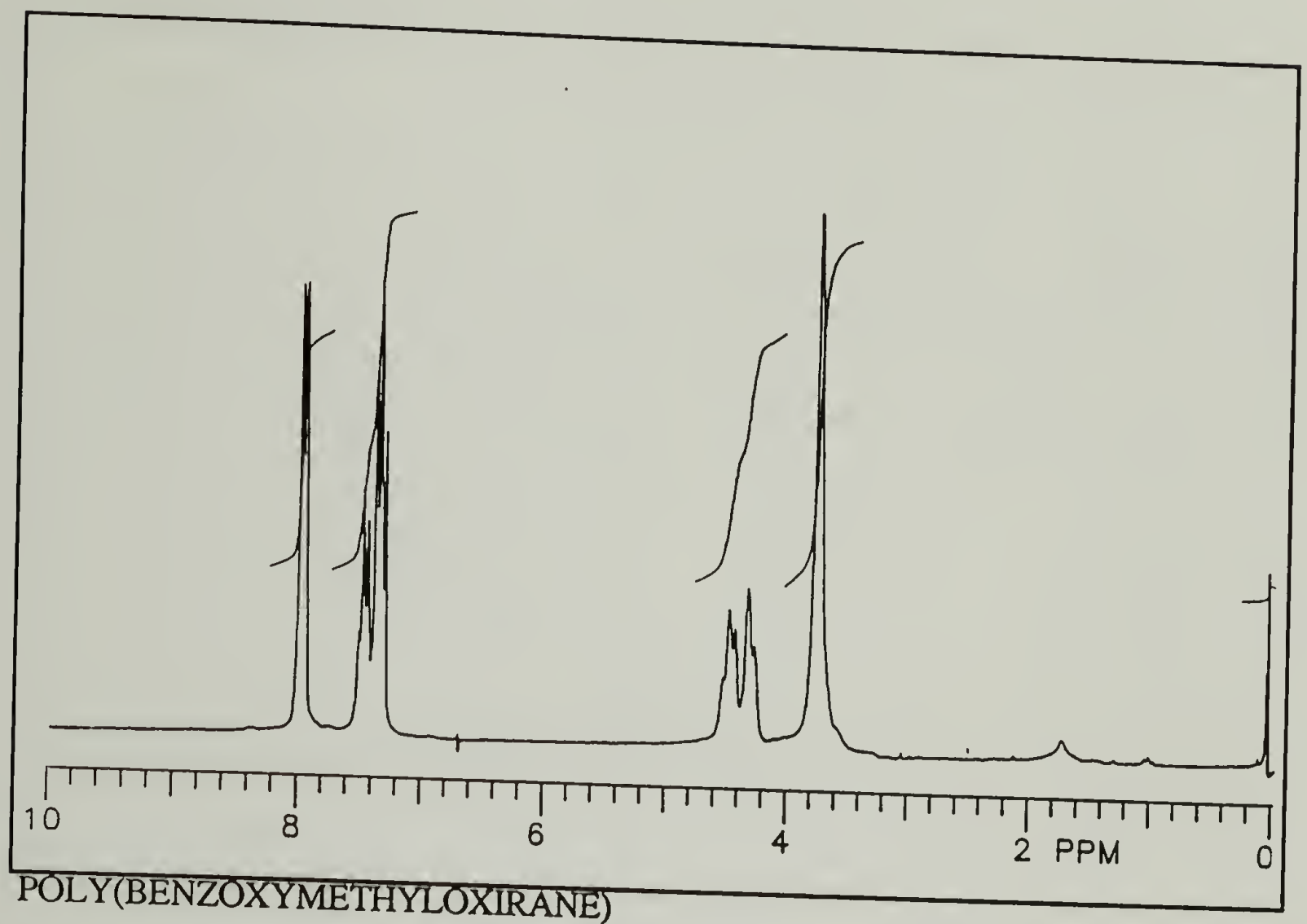



POLY(3-CHLOROMETHYLOXETANE)

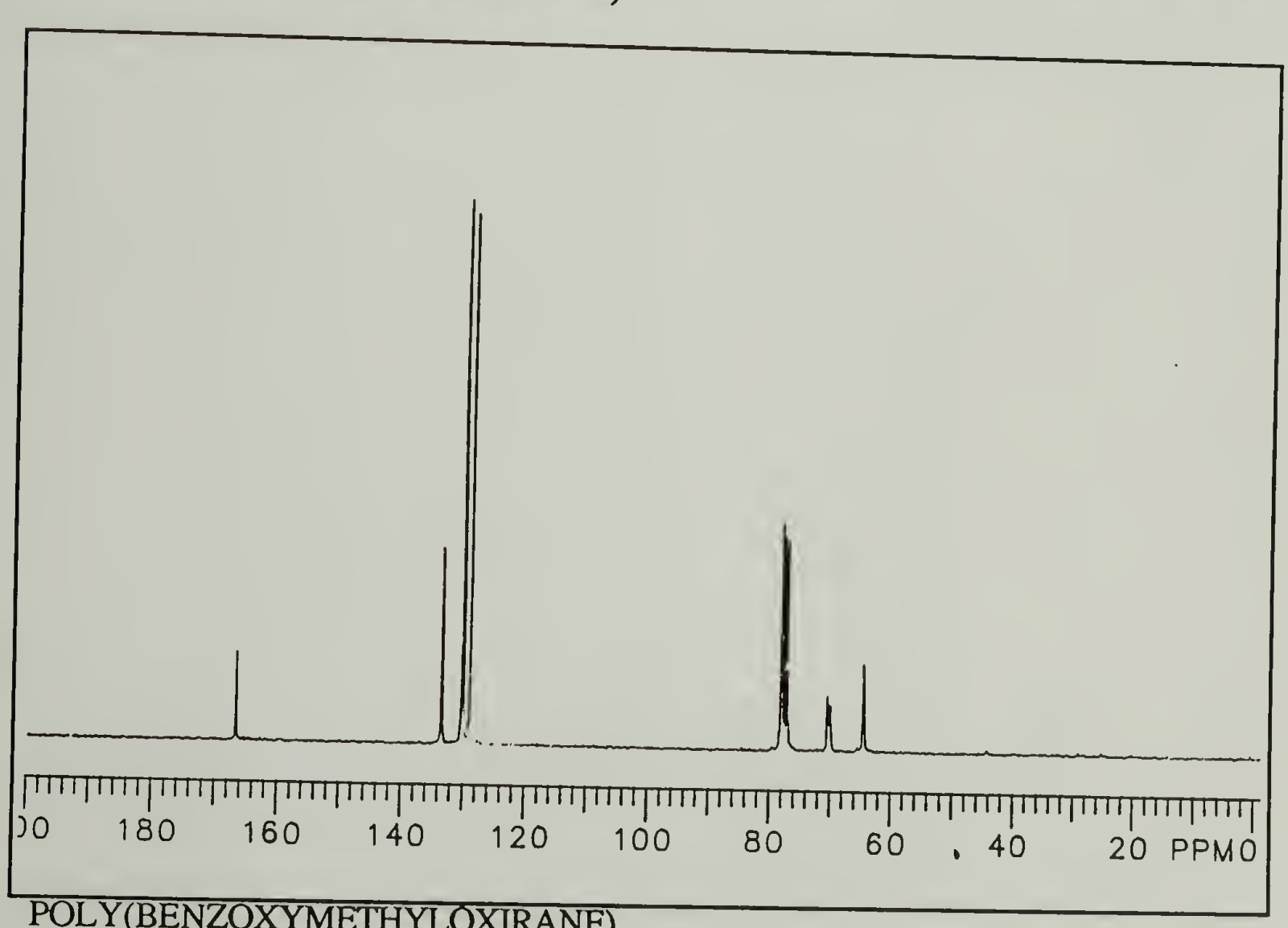



GS FILE: DW3.04

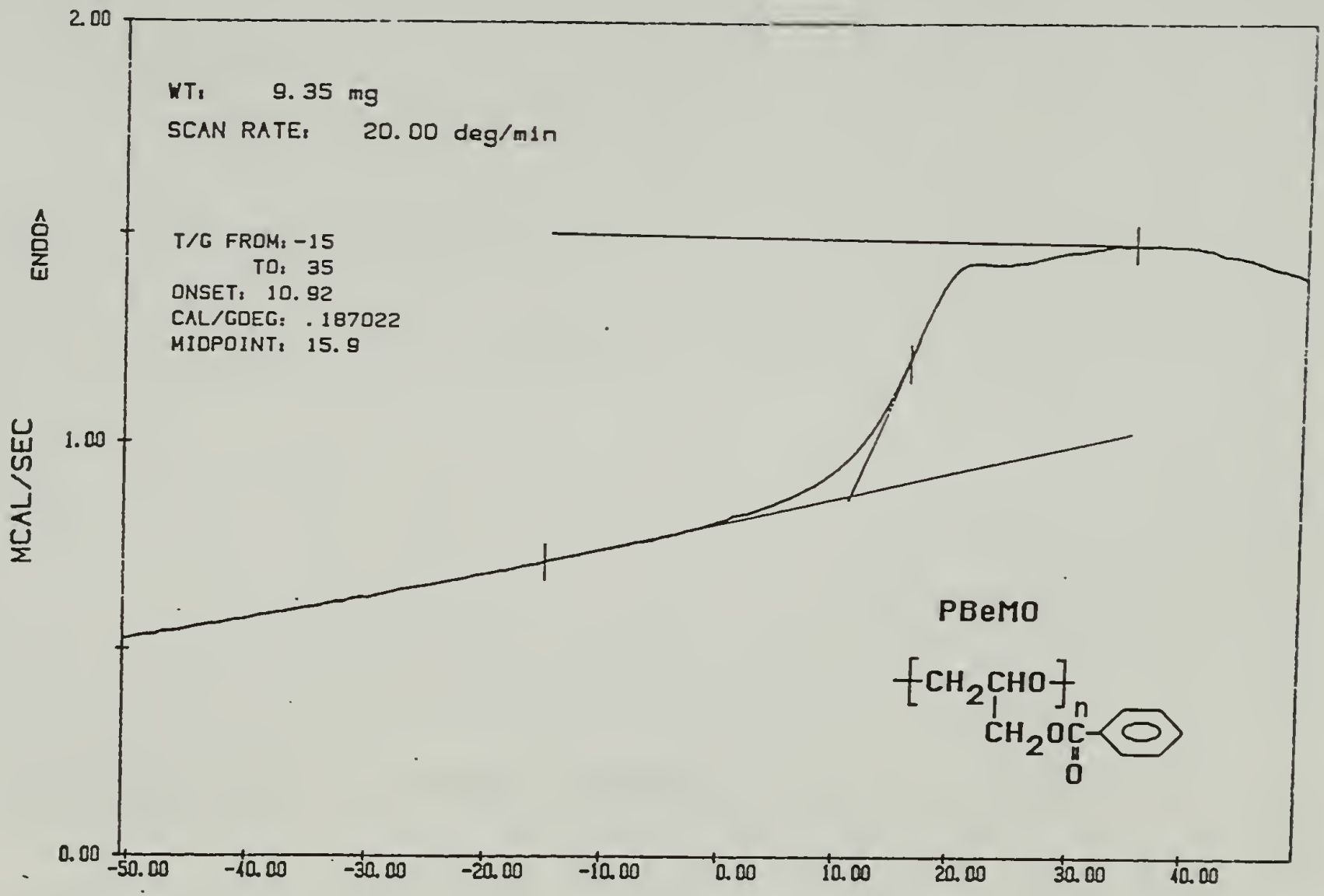
DATE: 88/02/22 TIME: 21:32




POLY(BENZOXYMETHYLOXIRANE)

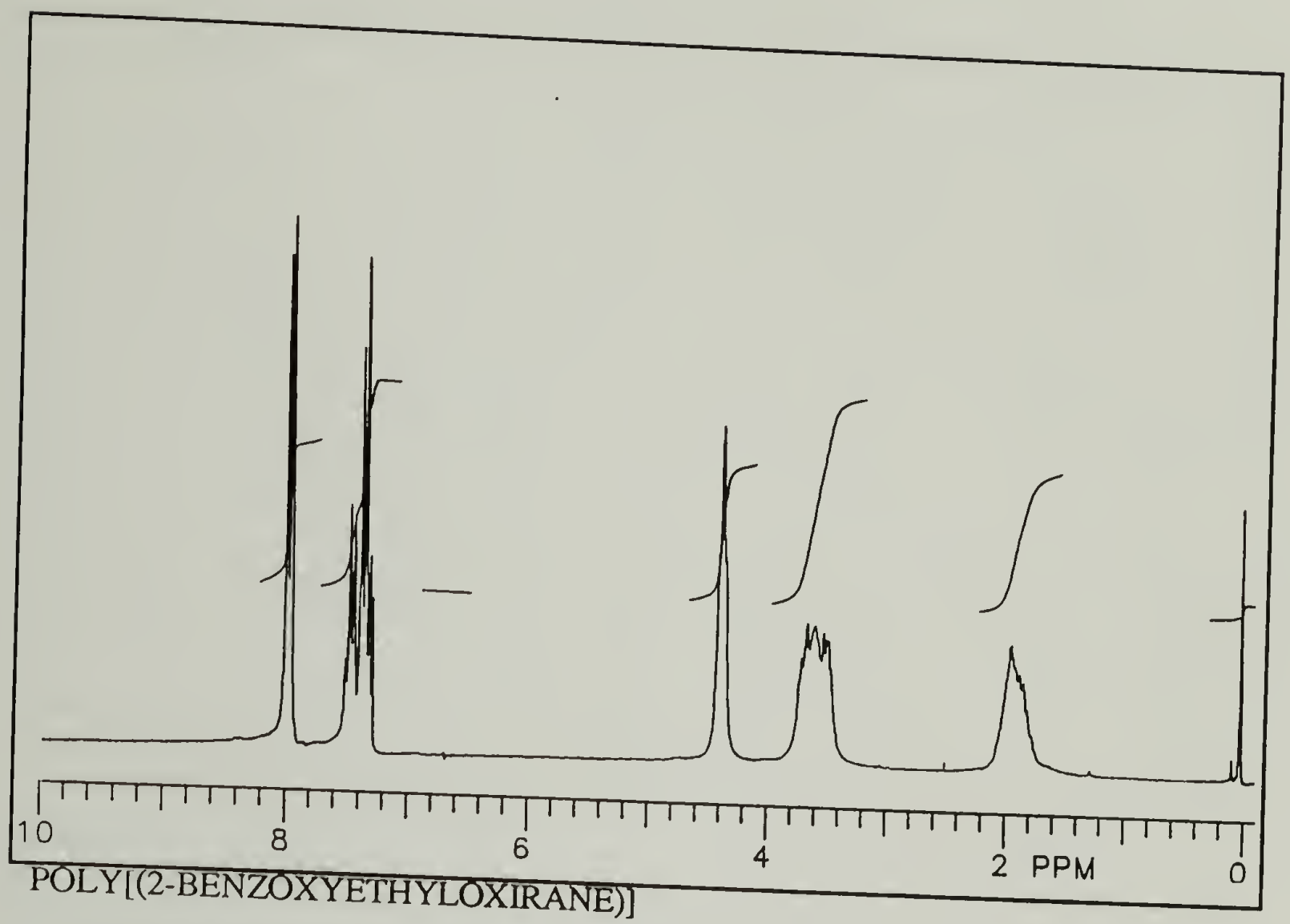



POLY(BENZOXYMETHYLOXIRANE)

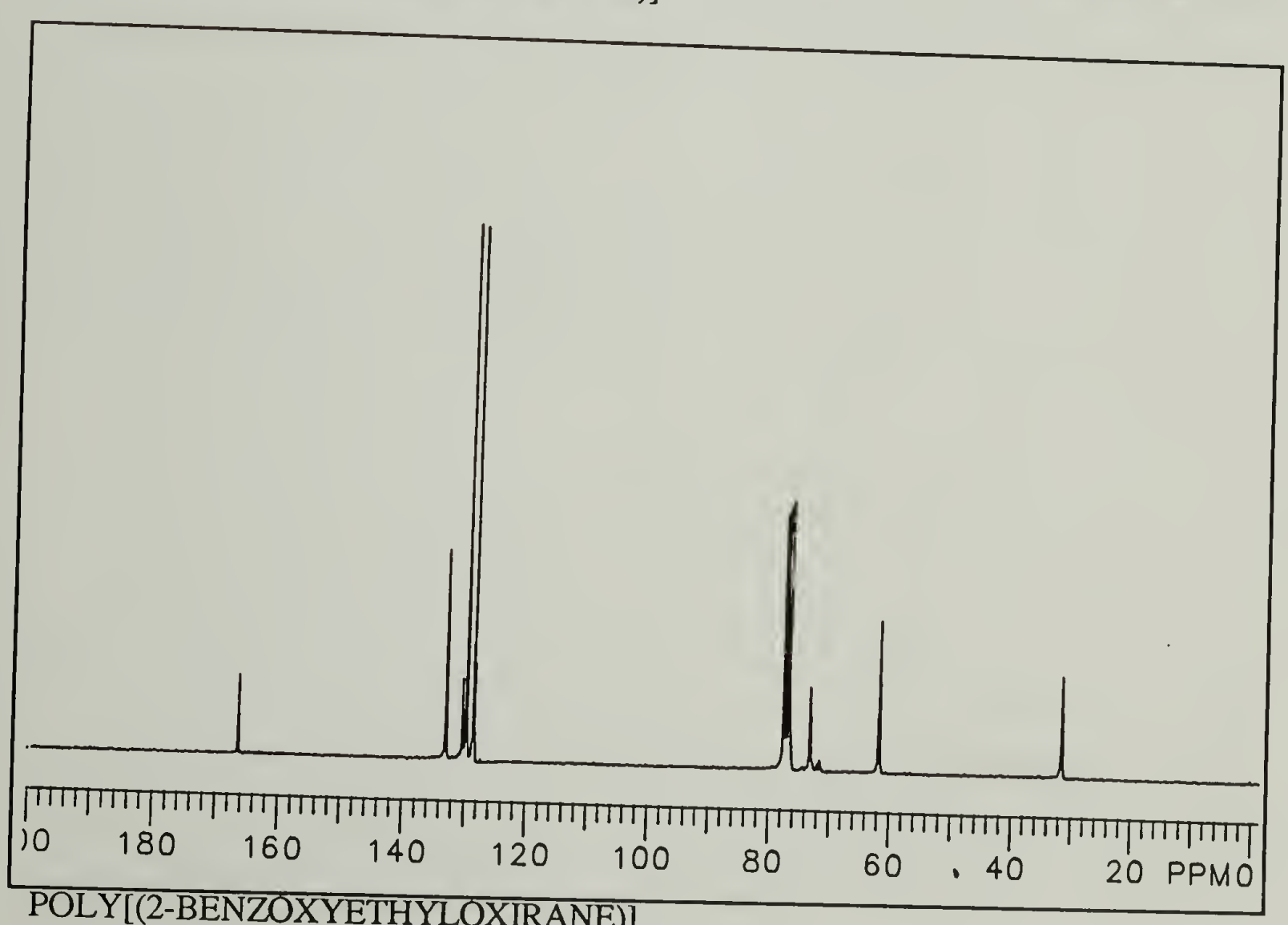



GS FILE: NZMO.D4

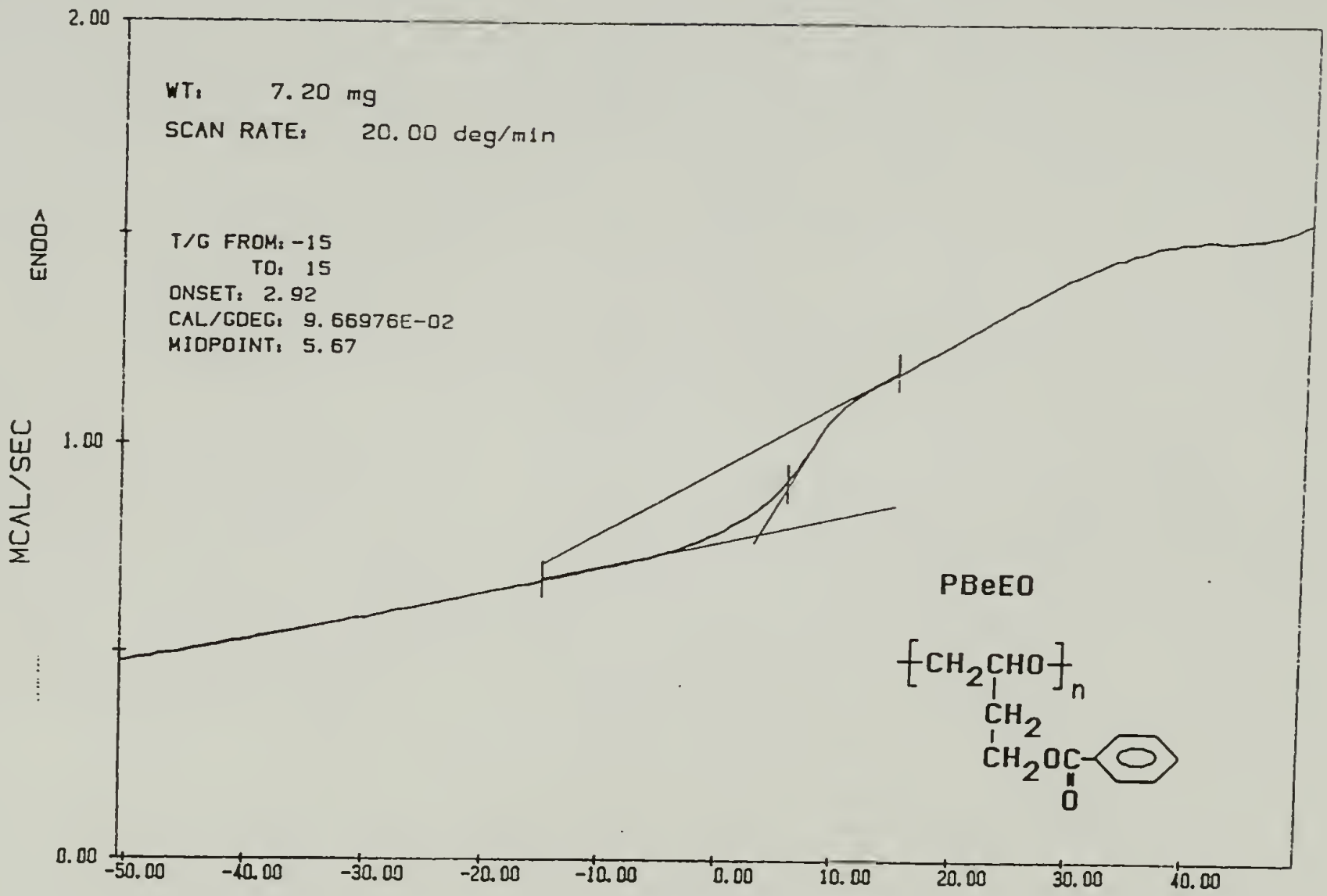
DATE: 88/06/24 TIME: 16:24

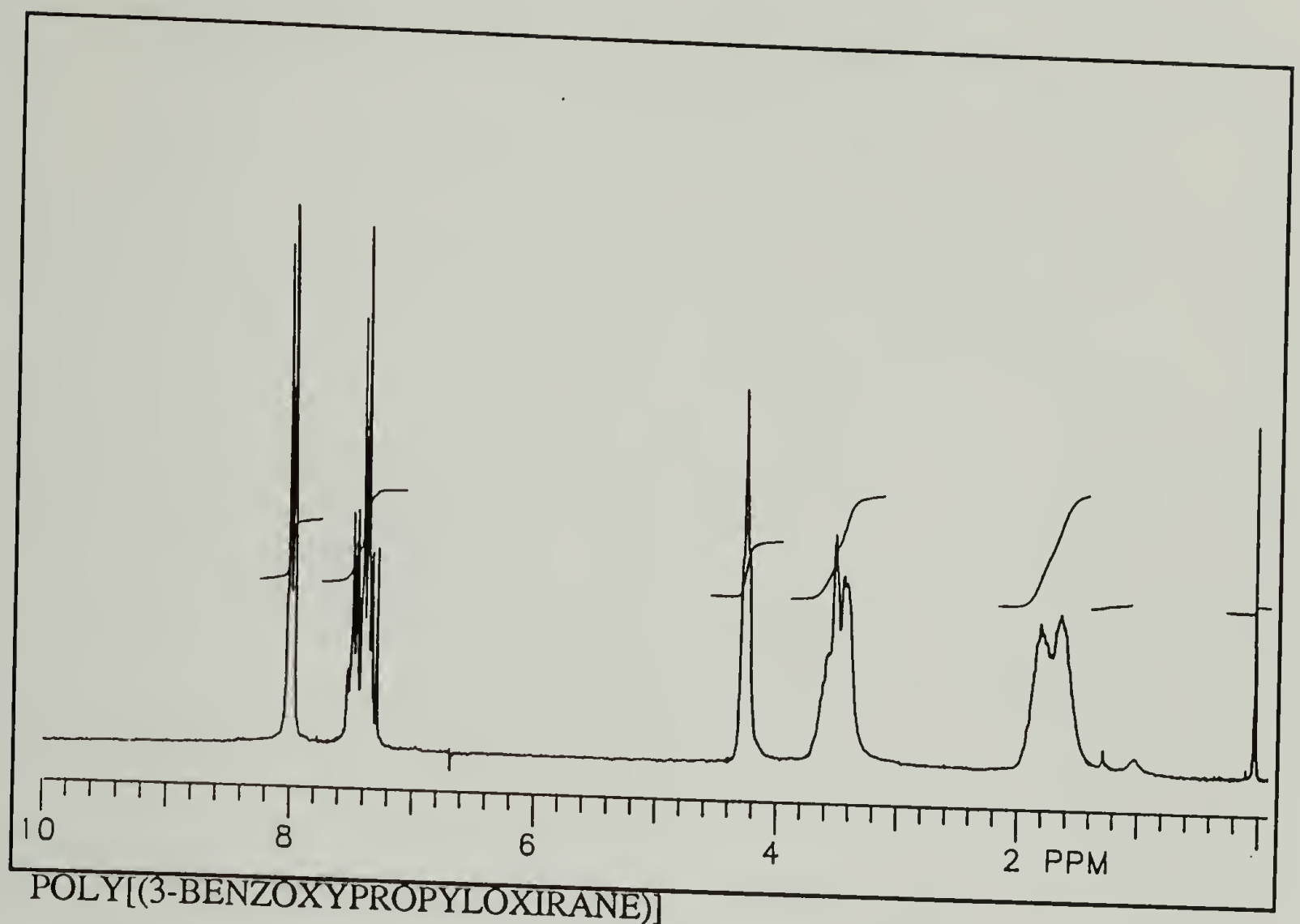



POLY[(2-BENZOXYETHYLOXIRANE)]

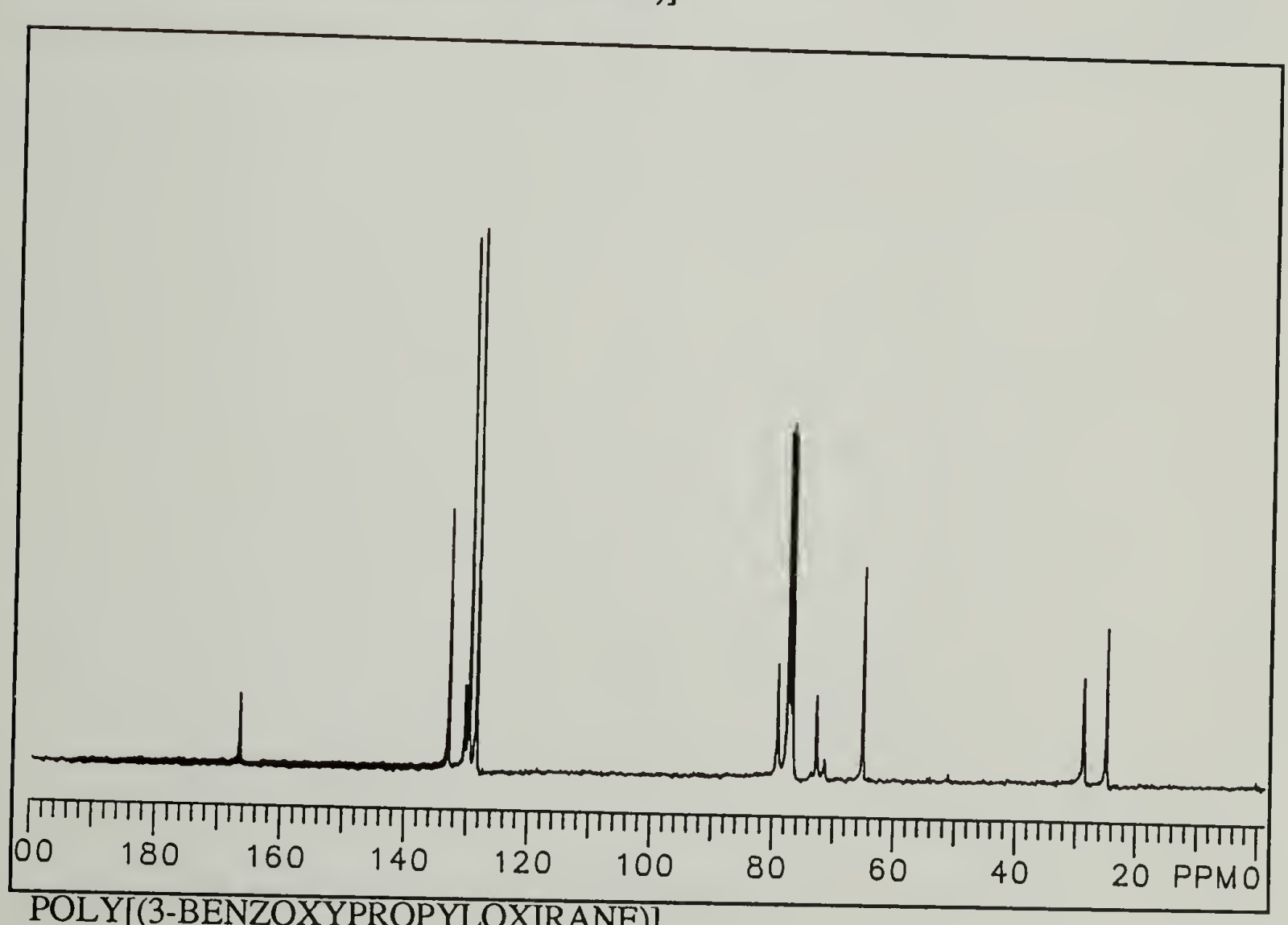



POLY[(2-BENZOXYETHYLOXIRANE)]

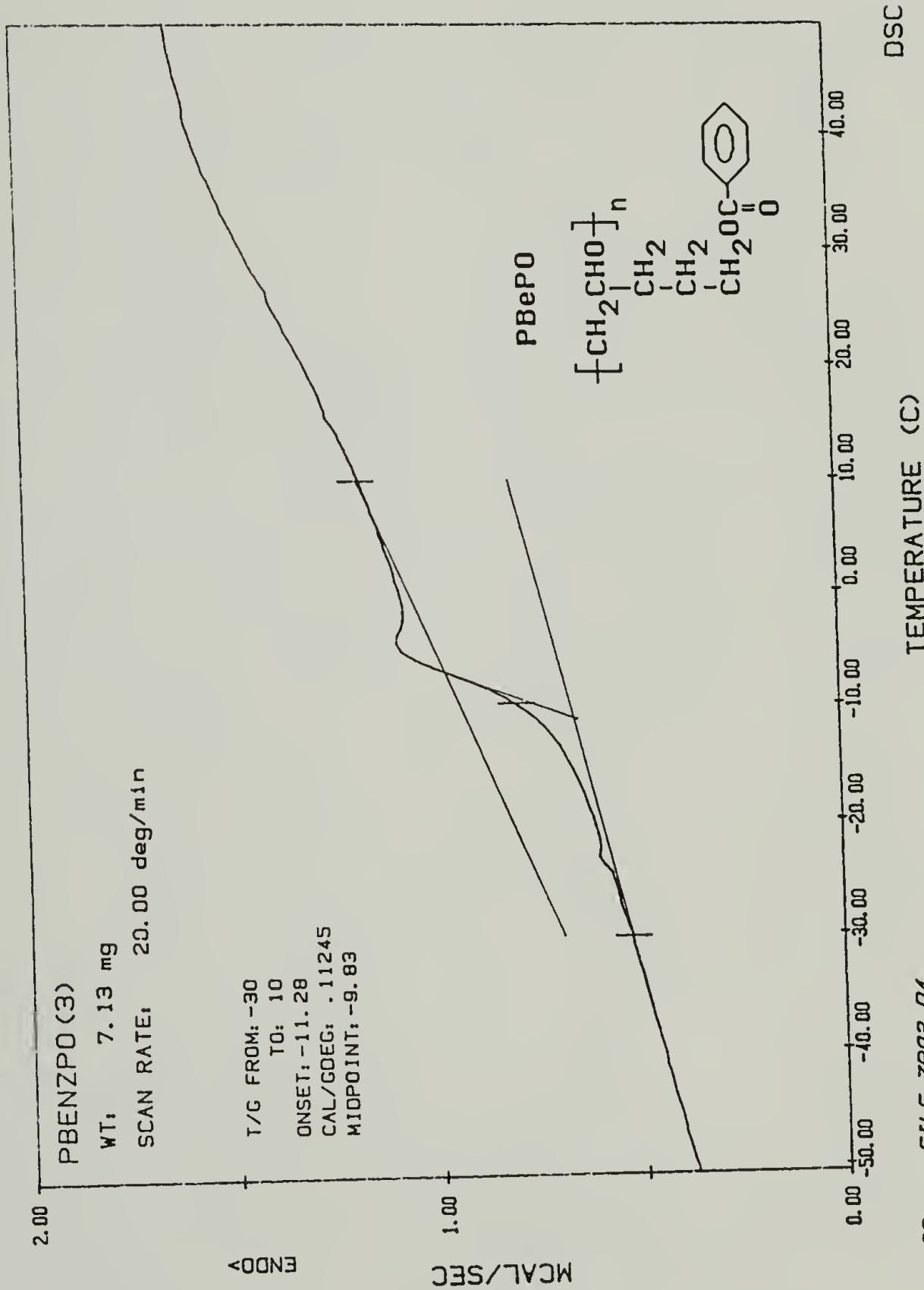

2.00
1.00
0.00
ENDO>
MCAL/SEC
WT: 7.20 mg
SCAN RATE: 20.00 deg/min
T/G FROM: -15
TO: 15
ONSET: 2.92
CAL/GDEG: 9.66976E-02
MIDPOINT: 5.67
PBeEO
-50.00
-40.00
-30.00
-20.00
-10.00
0.00
10.00
20.00
30.00
40.00
GS FILE: QSAVE.D4
TEMPERATURE (C)
DSC
DATE: 88/06/24 TIME: 16:54




POLY[(3-BENZOXYPROPYLOXIRANE)]




POLY[(3-BENZOXYPROPYLOXIRANE)]


PBePO
$+[CH_2CHO]+_n$
$CH_2$
$CH_2$
$CH_2OC$
O
PBENZPO(3)
WT: 7.13 mg
SCAN RATE: 20.00 deg/min
T/G FROM:-30
TO: 10
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1.00
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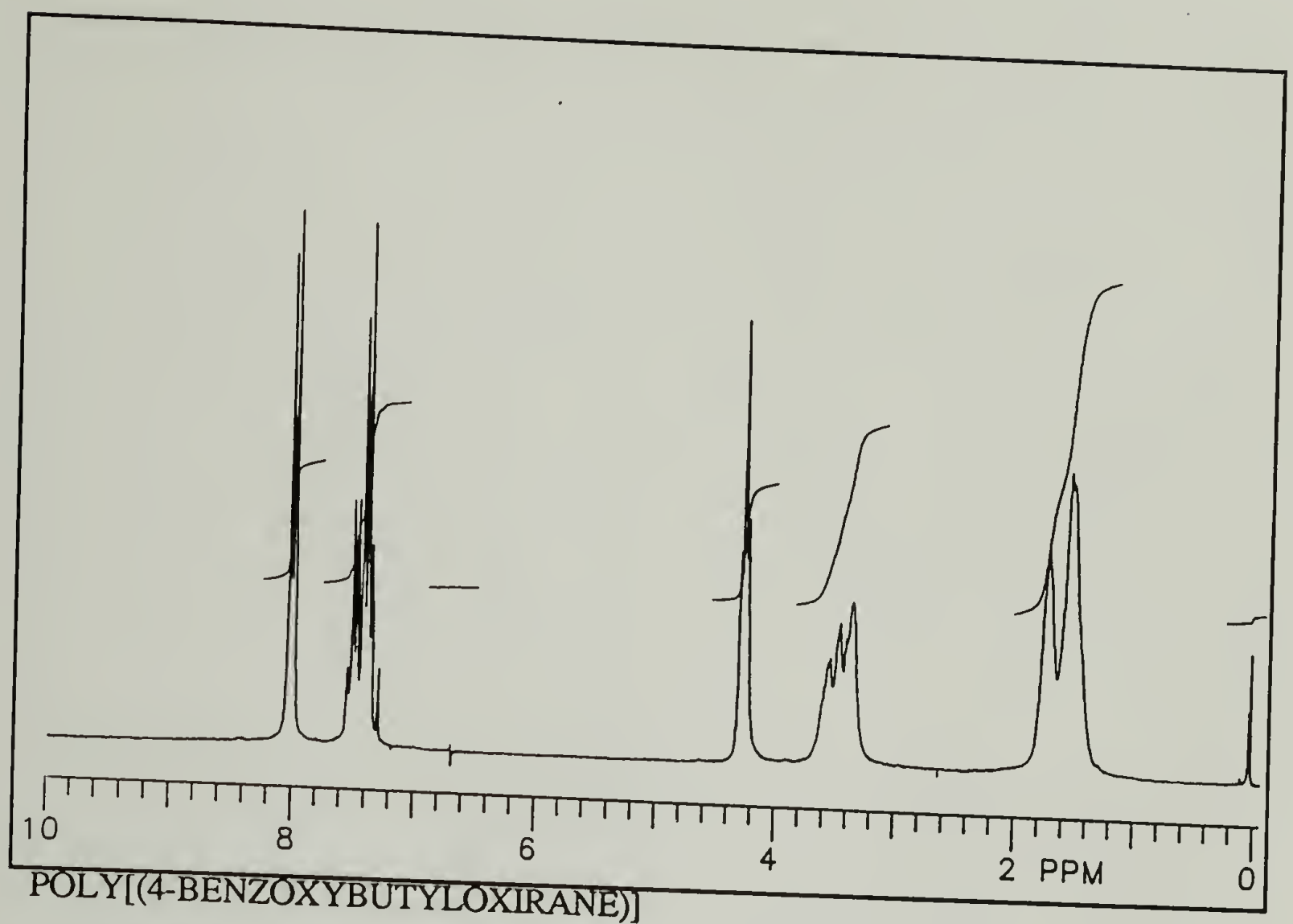
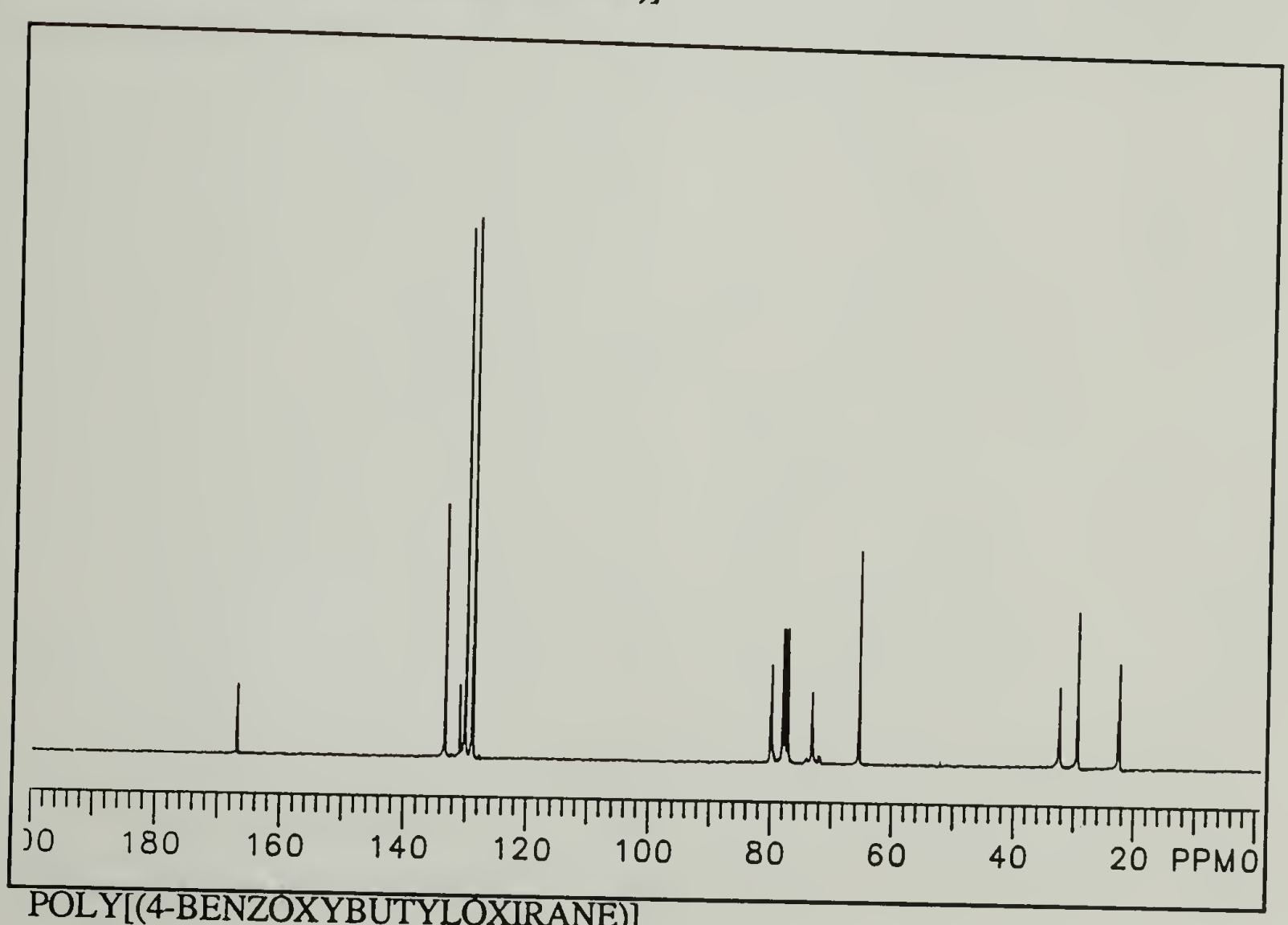
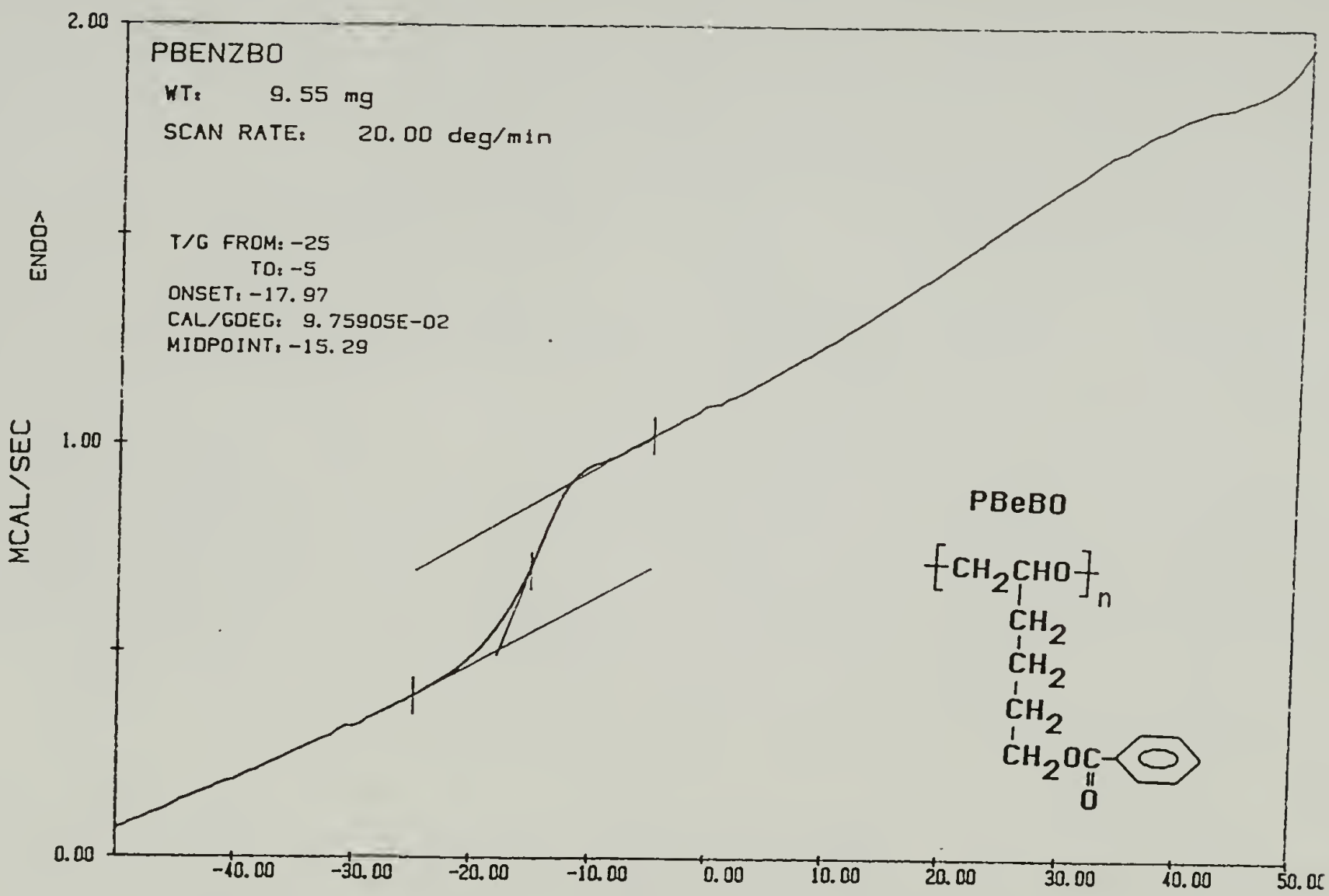
TEMPERATURE (C)
DSC
GS FILE: ZP03.04
DATE: 88/06/24 TIME: 16:03




POLY[(4-BENZOXYBUTYLOXIRANE)]




POLY[(4-BENZOXYBUTYLOXIRANE)]




GS FILE: QSAVE.04

DATE: 88/06/24 TIME: 17:15

# APPENDIX C.

## Reference Data and Spectra for the Analysis of Reactions .

Table A.1. Poly[(ω-chloroalkyl)oxirane] Reactions in DMAc.

| Reaction | Polymer | T (°C) | $[CH_2Cl]_0$ (mol/L) | $[TBAB]_0$ (mol/L) | k ($M^{-1}$ $s^{-1}$) |
|---|---|---|---|---|---|
| CR1 | PECH | 30 | 0.252 | 0.252 | $(4.9 \pm 0.5) \times 10^{-5}$ |
| CR2 | PECH | 40 | 0.250 | 0.250 | $(1.4 \pm 0.1) \times 10^{-4}$ |
| CR3 | PECH | 50 | 0.253 | 0.253 | $(3.6 \pm 0.4) \times 10^{-4}$ |
| CR4 | PECH | 60 | 0.257 | 0.255 | $(6.1 \pm 0.1) \times 10^{-4}$ |
| CR5 | PECH | 70 | 0.250 | 0.250 | $(1.2 \pm 0.2) \times 10^{-3}$ |
| CR6 | PCEO | 5 | 0.220 | 0.220 | $(6.1 \pm 0.8) \times 10^{-3}$ |
| CR7 | PCEO | 25 | 0.220 | 0.220 | $(3.5 \pm 0.3) \times 10^{-4}$ |
| CR8 | PCEO | 40 | 0.219 | 0.219 | $(1.3 \pm 0.1) \times 10^{-3}$ |
| CR9 | PCEO | 50 | 0.220 | 0.220 | $(2.5 \pm 0.2) \times 10^{-3}$ |
| CR10 | PCEO | 40 | 0.220 | 0.275 | $(1.4 \pm 0.1) \times 10^{-3}$ |
| CR11 | PCEO | 40 | 0.219 | 0.109 | $(1.3 \pm 0.2) \times 10^{-3}$ |
| CR12 | PCEO | 40 | 0.146 | 0.220 | $(1.4 \pm 0.2) \times 10^{-3}$ |
| CR13 | PCEO | 40 | 0.175 | 0.222 | $(1.4 \pm 0.2) \times 10^{-3}$ |
| CR14[a] | PCEO | 40 | 0.176 | 0.089 | $(1.3 \pm 0.1) \times 10^{-3}$ |
| CR15 | PCPO | 30 | 0.195 | 0.200 | $(8.6 \pm 0.8) \times 10^{-4}$ |
| CR16 | PCPO | 40 | 0.194 | 0.198 | $(1.9 \pm 0.1) \times 10^{-3}$ |
| CR17 | PCPO | 50 | 0.193 | 0.197 | $(3.5 \pm 0.6) \times 10^{-3}$ |
| CR18 | PCBO | 40 | 0.279 | 0.300 | $(1.8 \pm 0.1) \times 10^{-3}$ |
| CR19 | PCBO | 40 | 0.174 | 0.174 | $(1.7 \pm 0.2) \times 10^{-3}$ |

a. Included 0.137 g (0.46 mol) tetrabutylammonium chloride (TBACl) $[TBACl]_0$=0.089 mol/L.

Table A.2. Poly[(ω-bromoalkyl)oxirane] Reactions in DMAc.

| Reaction | Polymer | T (°C) | $[CH_2Br]_0$ (mol/L) | $[TBAB]_0$ (mol/L) | k ($M^{-1}$ $s^{-1}$) |
|---|---|---|---|---|---|
| BR1[a] | PBMO | 20 | 0.137 | 0.143 | $(2.9 \pm 0.3) \times 10^{-3}$ |
| BR2 | PBMO | 10 | 0.169 | 0.171 | $(1.2 \pm 0.2) \times 10^{-3}$ |
| BR3 | PBMO | 5 | 0.171 | 0.171 | $(9.9 \pm 0.8) \times 10^{-4}$ |
| BR4 | PBMO | 0 | 0.137 | 0.139 | $(7.1 \pm 1.3) \times 10^{-4}$ |
| BR5 | PBEO | 5 | 0.432 | 0.200 | $(3.8 \pm 0.5) \times 10^{-3}$ |
| BR6 | PBEO | -10 | 0.186 | 0.186 | $(3.2 \pm 0.3) \times 10^{-3}$ |
| BR7 | PBEO | -10 | 0.232 | 0.172 | $(3.0 \pm 0.5) \times 10^{-3}$ |
| BR8 | PBEO | -10 | 0.309 | 0.162 | $(3.3 \pm 0.8) \times 10^{-3}$ |
| BR9 | PBEO | -10 | 0.385 | 0.158 | $(3.4 \pm 0.7) \times 10^{-3}$ |

Table A.3. Composition of 1-Chloropentane Reactions in DMAc.

| Reaction | T (°C) | $[CH_2Cl]_0$ (mol/L) | $[TBAB]_0$ (mol/L) | k ($M^{-1}$ $s^{-1}$) |
|---|---|---|---|---|
| SR1 | 50 | 0.164 | 0.170 | $(8.1 \pm 0.2) \times 10^{-3}$ |
| SR2 | 40 | 0.163 | 0.163 | $(4.3 \pm 0.2) \times 10^{-3}$ |
| SR3 | 35 | 0.164 | 0.154 | $(2.7 \pm 0.1) \times 10^{-3}$ |
| SR4 | 30 | 0.219 | 0.228 | $(1.9 \pm 0.2) \times 10^{-3}$ |

Table A.4. $^{13}C$ NMR Chemical Shift for Selected Carbons Of Functionalized Polyethers in DMAc at 50° C.[a]

| Polymer | -$CH_2$- Backbone | -CH- Backbone | -$CH_2$- ω-Pendant | Aromatic Carbons o | m | p |
|---|---|---|---|---|---|---|
| PECH | 67.9 | 77.6 | 42.8 | - | - | - |
| PBMO | 69.0 | 77.2 | | - | - | - |
| PBeMO | 68.3 | 76.2 | 63.1 | 127.8 | 128.3 | 131.9 |
| PCEO | 70.5 | 75.2 | 40.6 | - | - | - |
| PBEO | 71.5 | 76.2 | 34.6 | - | - | - |
| PBeEO | 71.1 | 75.1 | 60.4 | 127.3 | 128.1 | 131.8 |
| PCPO | 71.0 | 77.3 | 44.1 | - | - | - |
| PBPO | 70.9 | 77.3 | 33.5 | - | - | - |
| PBePO | 71.0 | 77.8 | 63.9 | 127.4 | 128.1 | 131.8 |
| PCBO | 71.1 | 77.0 | 44.0 | - | - | - |
| PBeBO | 71.2 | 77.9 | 63.5 | 127.4 | 128.1 | 131.8 |
| P3CMO | 67.9 | 40.8 | 42.4 | - | - | - |
| P3BeMO | 68.1 | 38.5 | 62.1 | 127.4 | 128.2 | 131.9 |
| P2CMO | 33.8(68.1)[b] | 73.5 | 41.5 | - | - | - |
| P3CO | 70.9 | 57.1 | ---- | - | - | - |
| P3BeO | 71.0 | 67.2 | ---- | 127.2 | 128.0 | 132.0 |

a. All chemical shifts in ppm's referenced to acetamide methyl group from DMAc as 19.63 PPM.

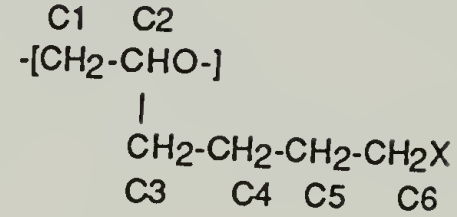
b. Low field resonance arises from methylene attached to oxygen in backbone

Table A.5. T1[a] Data for Alkyl Carbons of Oxirane Polymers

| POLYMER\|CARBON C1[b] | C2 | C3 | C4 | C5 | C6 |
|---|---|---|---|---|---|
| -Methyl | | | | | |
| Chloro | 0.262±0.013 | 0.437+0.015 | 0.244±0.008 | | |
| Bromo | 0.378±0.018 | 0.676±0.023 | c | | |
| Benzoxy | 0.170±0.018 | 0.262±0.020 | 0.145±0.008 | | |
| -Ethyl | | | | | |
| Chloro | 0.311±0.006 | 0.523±0.006 | c | 0.618±0.015 | |
| Bromo | 0.269±0.017 | 0.436±0.017 | 0.489±0.023 | 0.412±0.068 | |
| Benzoxy | 0.168±0.020 | 0.256±0.016 | 0.176±0.012 | 0.220±0.014 | |
| -Propyl | | | | | |
| Chloro | 0.301±0.016 | 0.432±0.016 | 0.373±0.022 | 0.703±0.042 | 1.104±0.050 |
| Bromo | 0.227±0.007 | 0.384±0.016 | 0.306±0.014 | 0.623±0.018 | 0.990±0.024 |
| Benzoxy | 0.143±0.038 | 0.233±0.033 | 0.157±0.026 | 0.281±0.033 | 0.291±0.038 |
| -Butyl | | | | | |
| Chloro | 0.231±0.008 | 0.364±0.008 | 0.280±0.011 | 0.585±0.017 | 1.058±0.029 1.232±0.010 |
| Bromo | | | | | |
| Benzoxy | 0.150±0.012 | 0.250±0.008 | 0.140±0.044 | 0.200±0.020 | 0.282±0.040 0.387±0.013 |

[a]All T1 values in sec. Error values are those given by the T1 calculation program.

[b]Numbering starts with methylene carbon in backbone as C1 with the methine as C2 and then consecutively out the pendant chain as shown for a substituted butyl oxirane




[c]Not recorded due to solvent interference.

Table A.6. $^{13}C$ $T_1$ Data[a] for Selected Benzoate Carbons

| Benzoate[b]\Carbon | para | meta | ortho |
|---|---|---|---|
| $Bu_4N^+$ | 2.897±0.103 | 1.323±0.109 | 2.968±0.102 |
| $C_5H_{11}$ | 2.924±0.232 | 4.492±0.121 | 4.499±0.114 |
| PBenzMO | 0.347±0.017 | 0.685±0.029 | 0.694±0.030 |
| PBenzEO | 0.418±0.009 | 0.915±0.006 | 0.908±0.016 |
| PBenzPO | 0.458±0.041 | 0.930±0.045 | 0.971±0.041 |
| PBenzBO | 0.579±0.020 | 1.163±0.009 | 1.200±0.024 |

a All T1 values given in seconds

b $Bu_4N^+$= Tetrabutyl ammonium benzoate; PBenzMO= Poly(benzoxymethyloxirane); PBenzEO= Poly(benzoxyethyloxirane); PBenzPO= Poly(benzoxypropyloxirane); PBenzBO= Poly(benzoxybutyloxirane).

Table A.7. NOE Factors Used in Quantitative Interpretation of $^{13}C$ NMR Spectra.

| Polymer | Carbon[a] | Factor Unreacted | Factor Reacted |
|---|---|---|---|
| PECH | A | 2.5 | 2.2 |
| PCEO | A | 2.4 | 2.7 |
| PCPO | A | 3.0 | 2.7 |
| PCBO | A | 3.0 | 2.8 |
| P3CO | A | 2.7 | 2.8 |
| P3CMO | A | 2.8 | 2.8 |
| PBMO | B | 2.6 | 2.4 |
| PBEO | B | 2.5 | 2.2 |

a. A - Terminal Pendant Methylene. B - Backbone Methine.

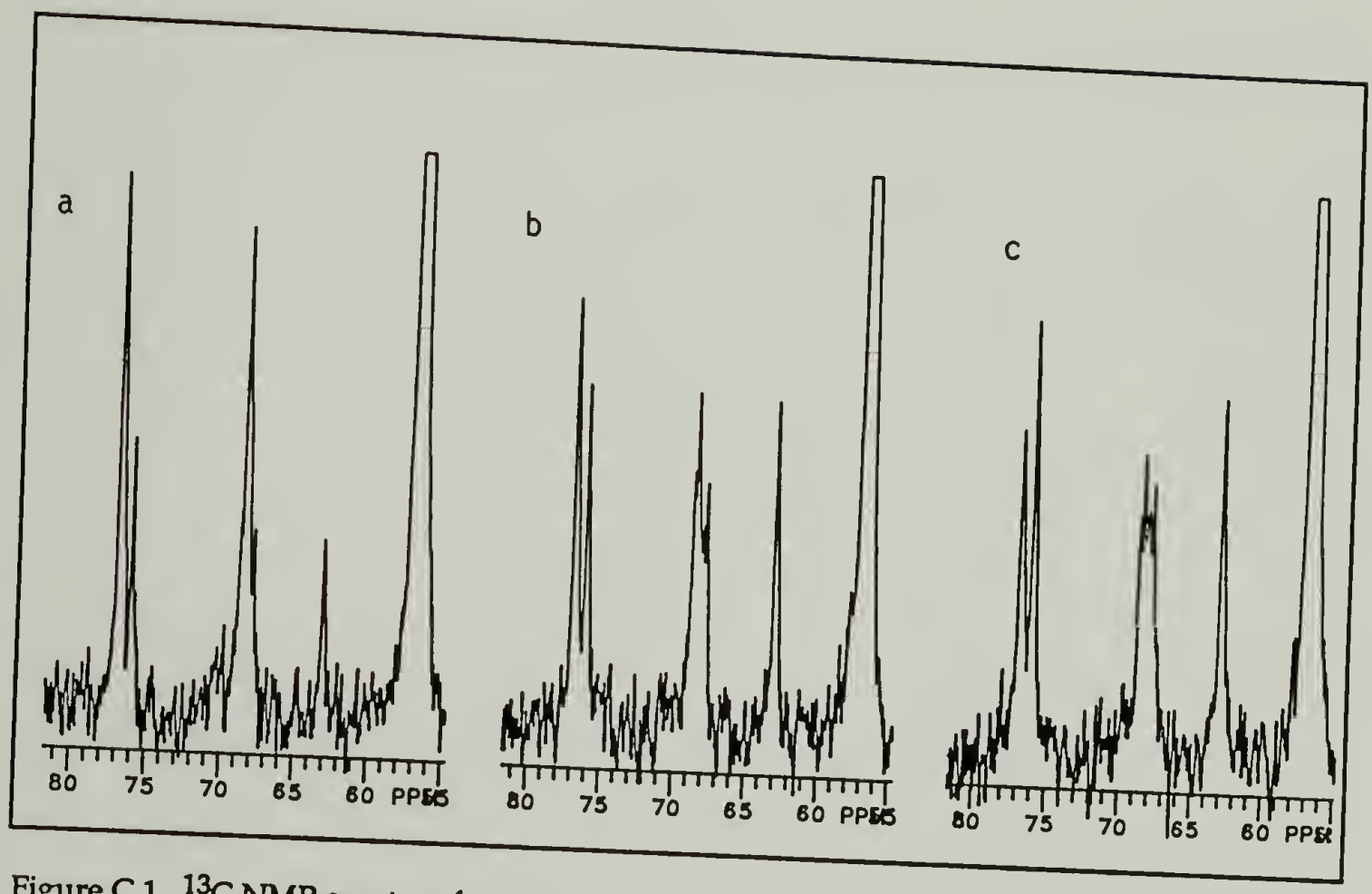



Figure C.1. $^{13}C$ NMR spectra of reaction mixture of PBMO and TBAB at 10°C in DMAc at 26, 66 and 106 minutes of reaction time (a-c respectively).

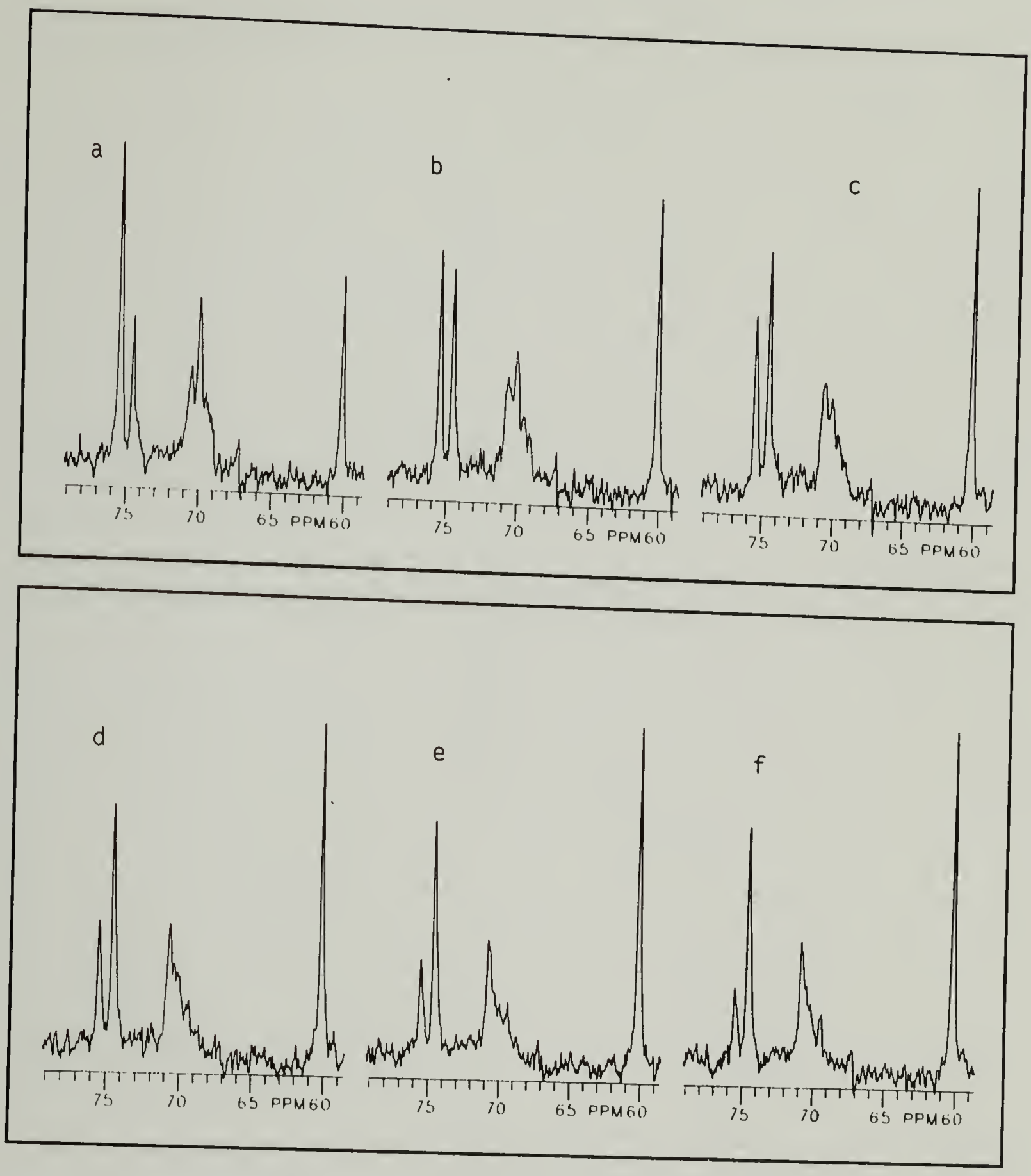



Figure C.2. $^{13}C$ NMR spectra of reaction mixture of PBEO and 1 equiv TBAB at -10°C in DMAc at 7, 17, 27, 47, 90 and 130 minutes of reaction time (a-f respectively).

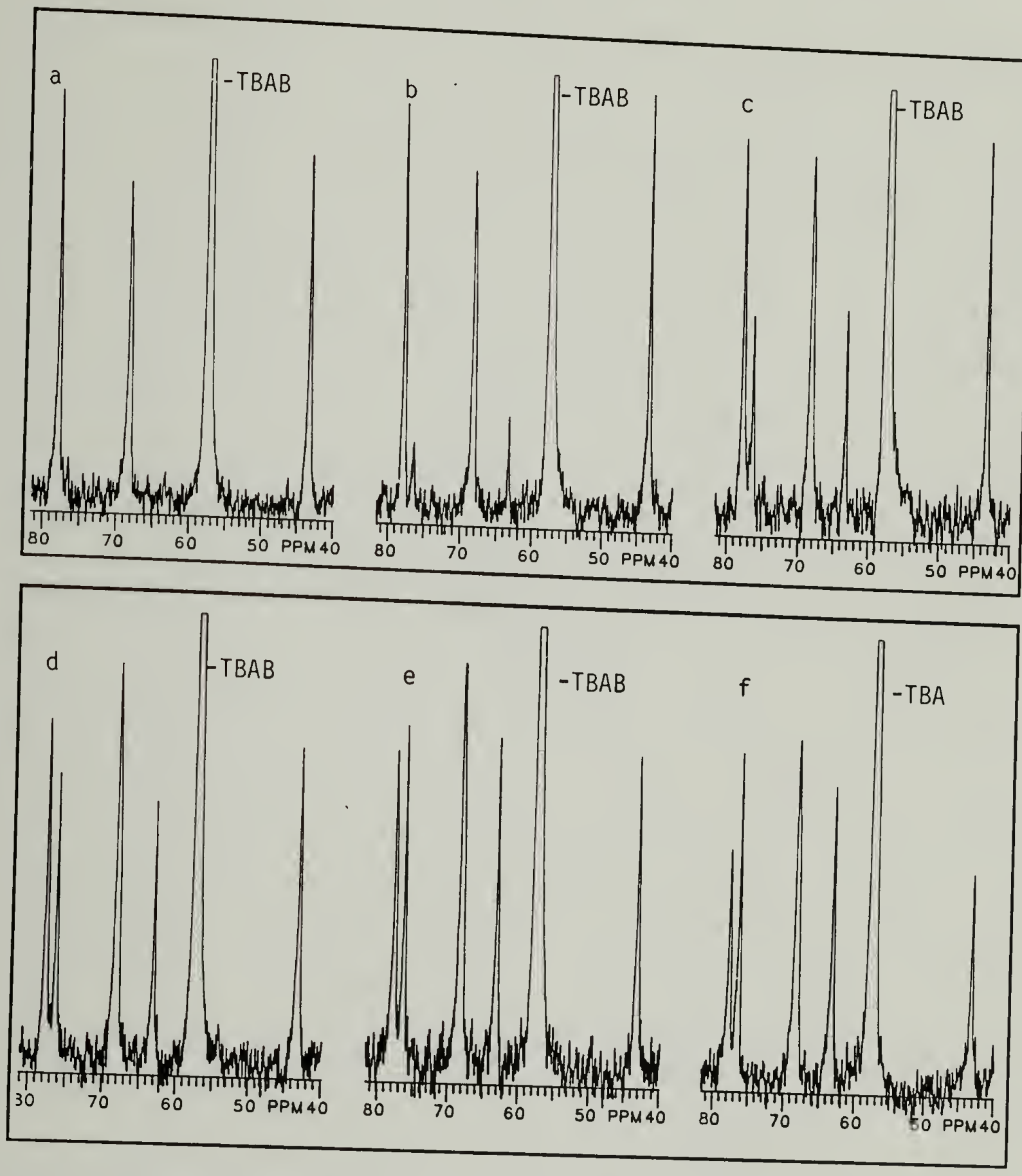



Figure C.3. Spectra of reaction mixture of PECH and TBAB at 40°C in DMAc at 29, 80, 171, 352, 472 and 653 minutes of reaction time (a-f respectively).

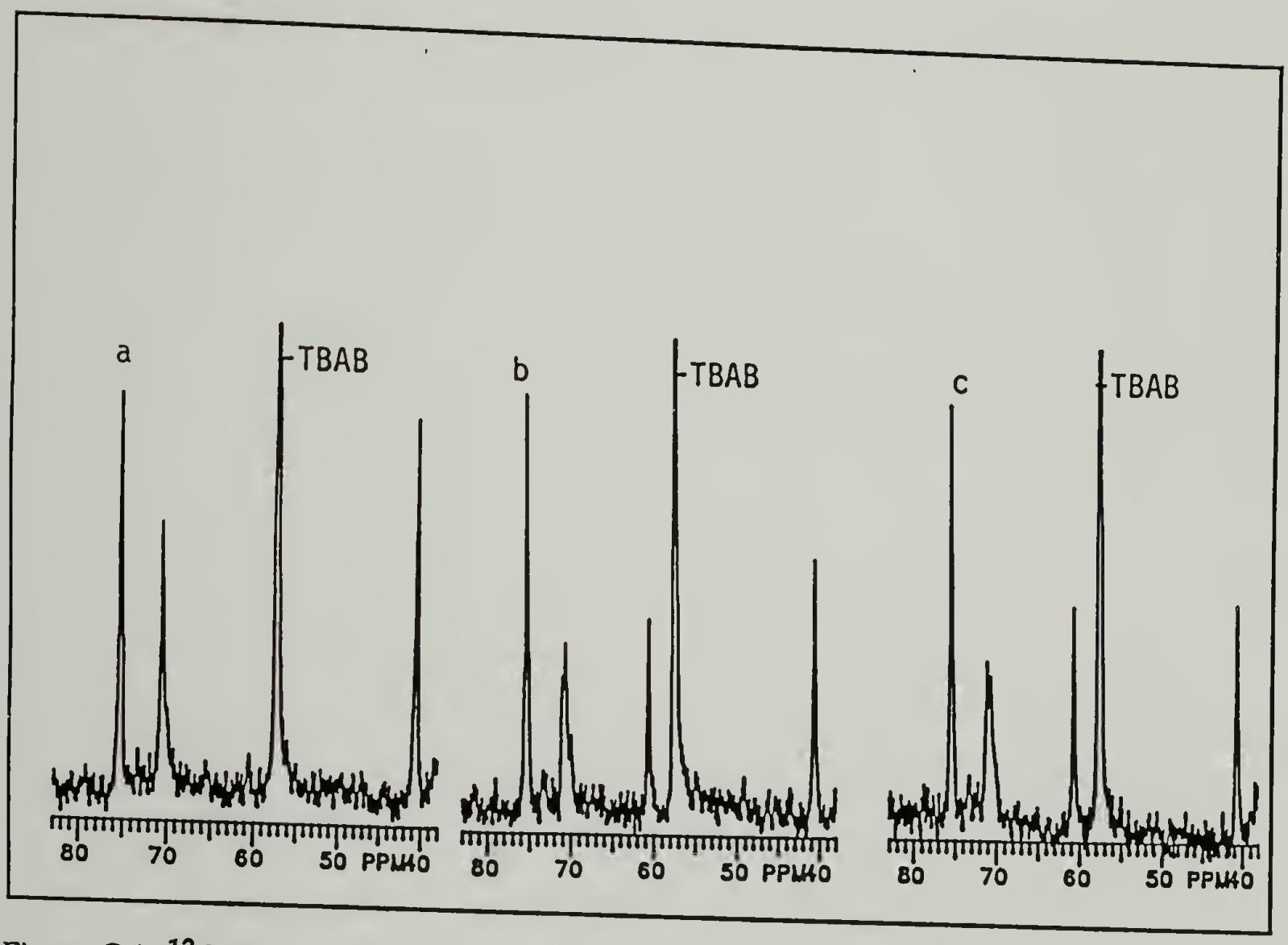



Figure C.4. $^{13}C$ NMR spectra of reaction mixture of PCEO and TBAB at 50°C in DMAc at 7,50 and 125 minutes of reaction time (a-c respectively).

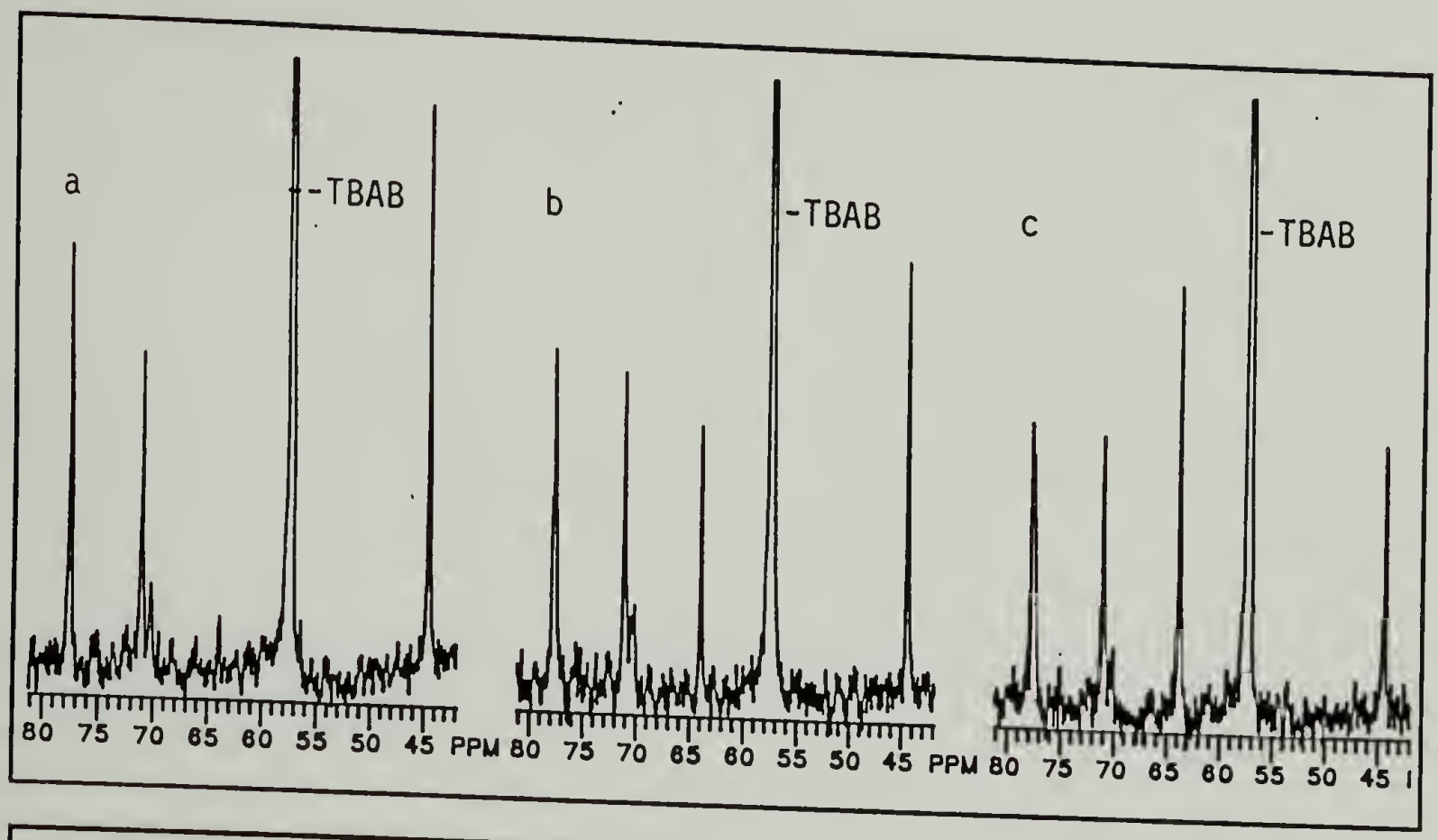



Figure C.5. $^{13}C$ NMR spectra of reaction mixture of PCPO and TBAB at 40°C in DMAc at 8, 28, 89, 209, 299 and 420 minutes of reaction time (a-f respectively).

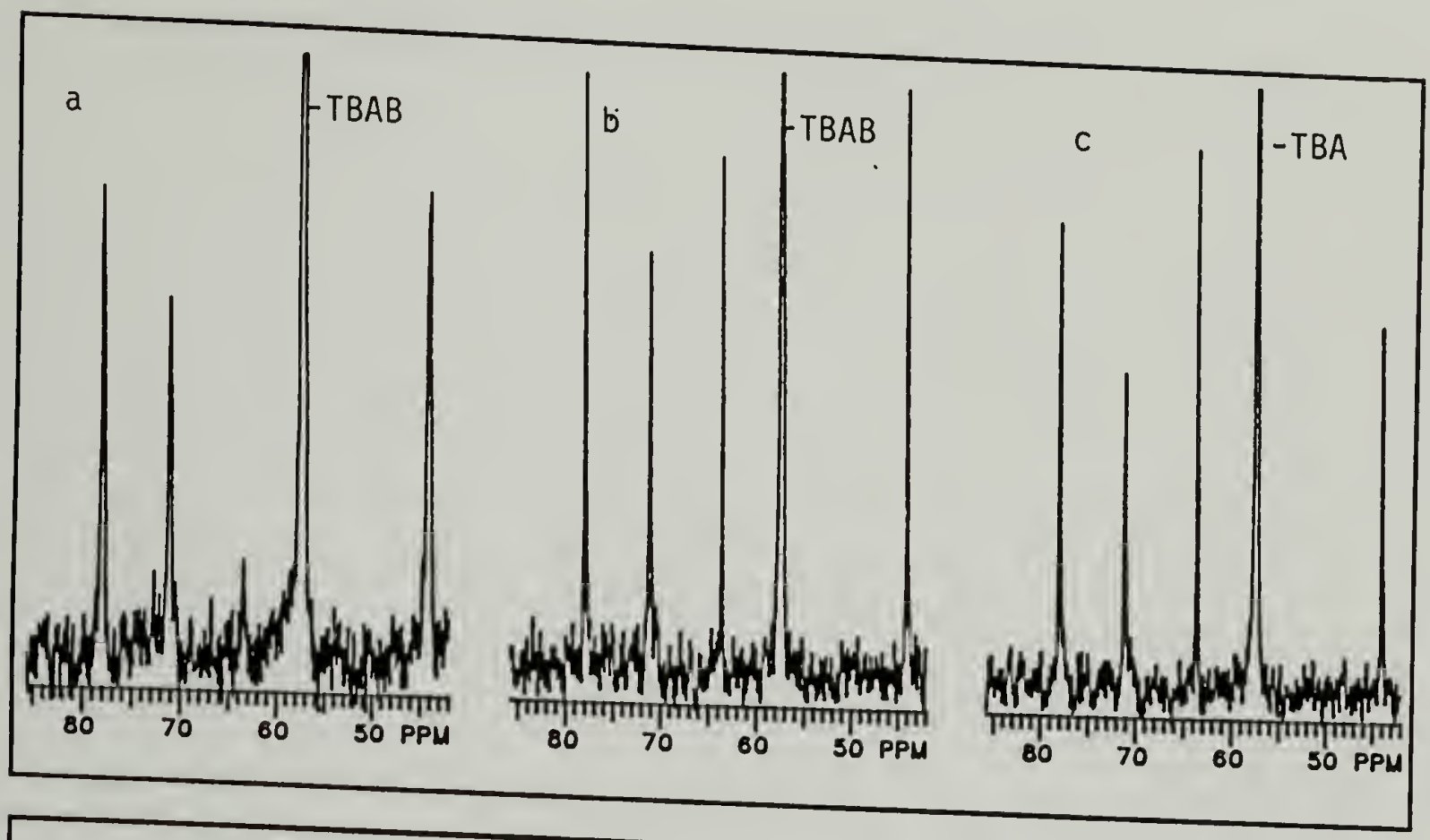



Figure C.6. $^{13}C$ NMR spectra of reaction mixture of PCBO and TBAB at 40°C in DMAc at 7, 27, 47,118, 238 and 438 minutes of reaction time (a-f respectively).

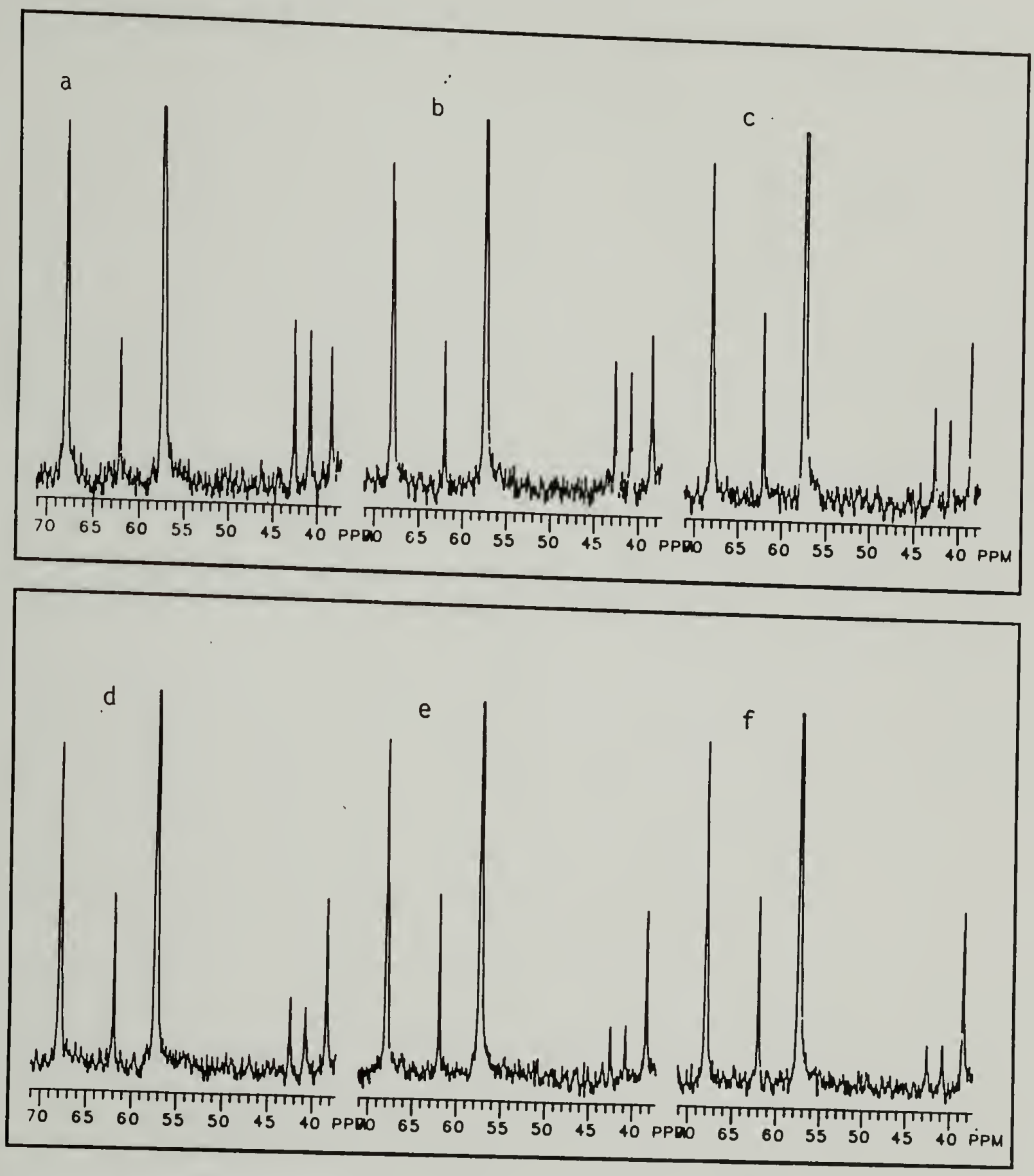



Figure C.7. $^{13}C$ NMR spectra of reaction mixture of P3MCO and TBAB at 50°C in DMAc at 85, 119, 209, 270, 390 and 480 minutes of reaction time (a-f respectively).

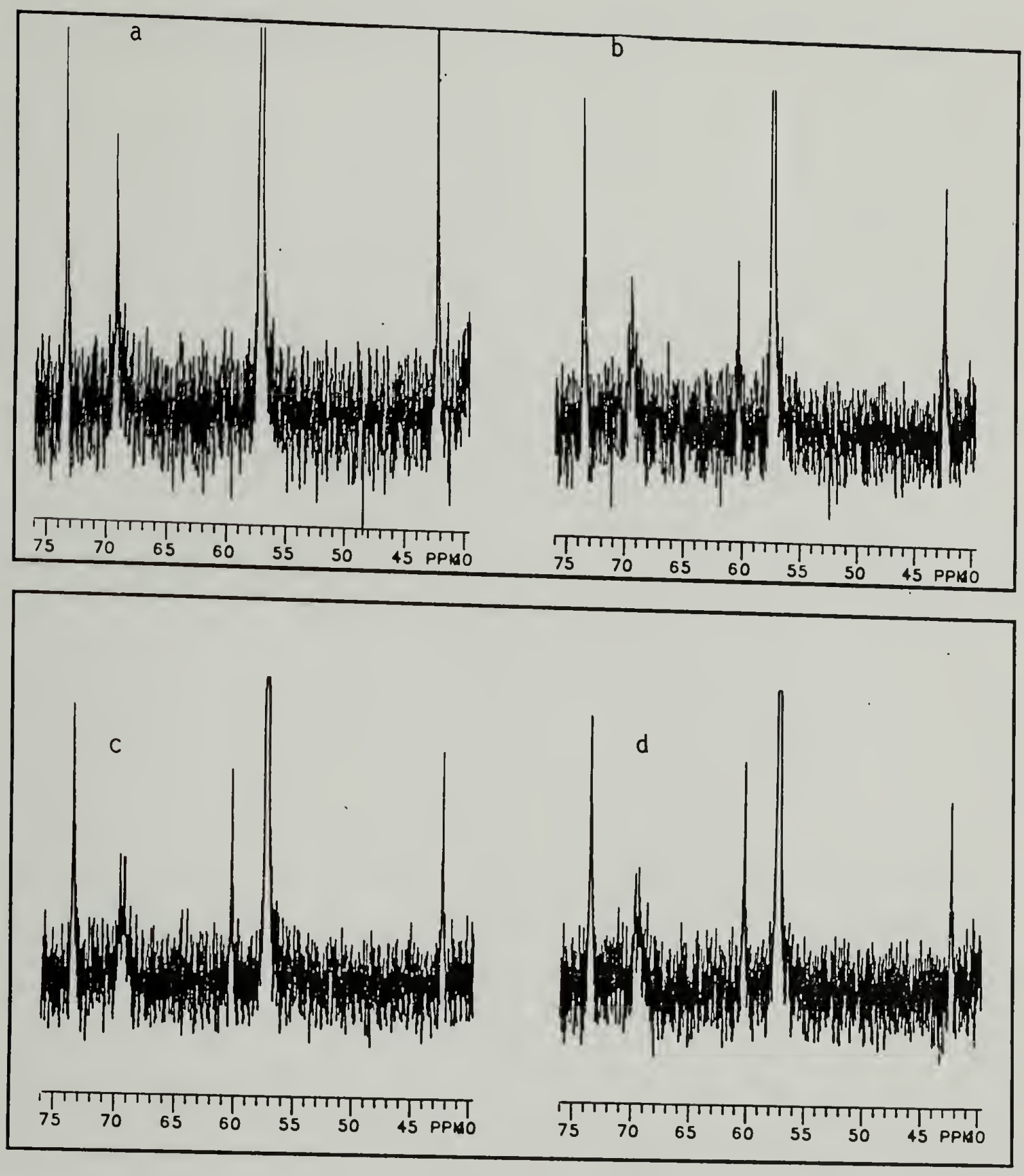



Figure C.8. $^{13}C$ NMR spectra of reaction mixture of P2CMO and TBAB at 50°C in DMAc at 15, 175, 250 and 335 minutes of reaction time (a-d respectively).

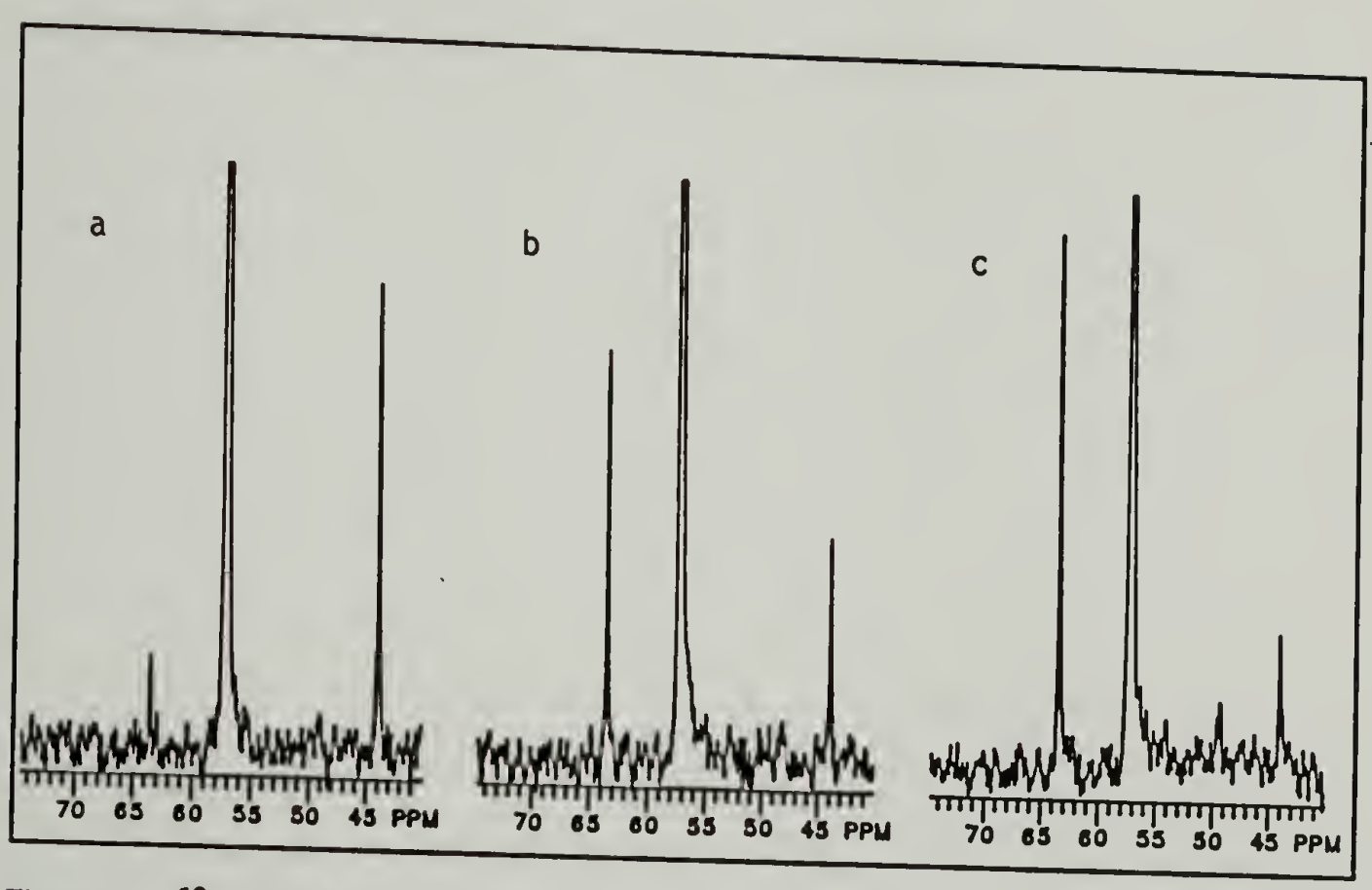



Figure C.9. $^{13}C$ NMR spectra of reaction mixture of 1-chloropentane and TBAB at 40°C in DMAc at 7, 48 and 88 minutes of reaction time (a-c respectively).

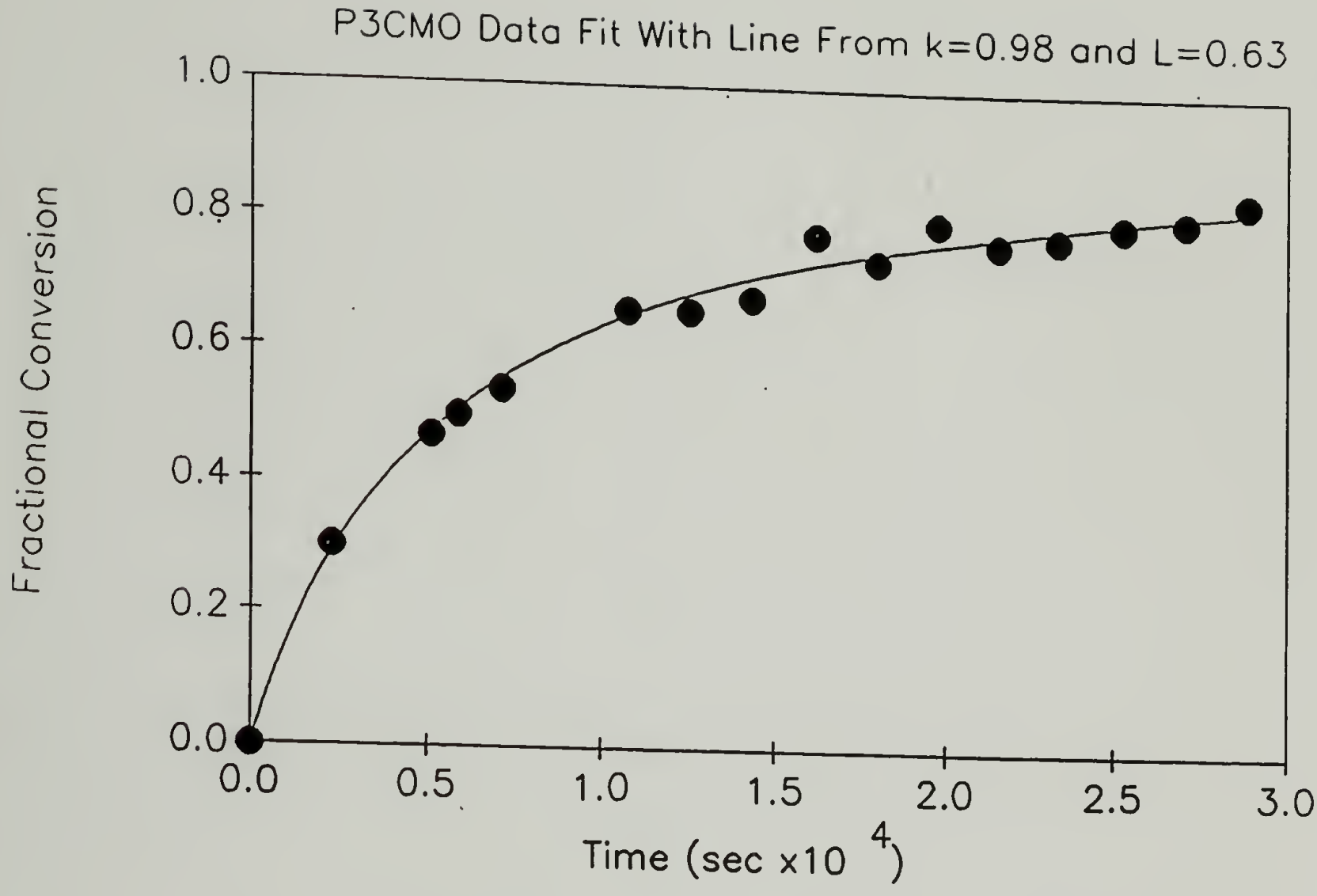



Figure C.10. Plot of conversion vs time for the reaction of P3CMO with an equivalent amount of TBAB in DMAc at 50°C. Data points indicate observed values and the solid line is the best fit calculated using K and L values obtained from Figure C.24.

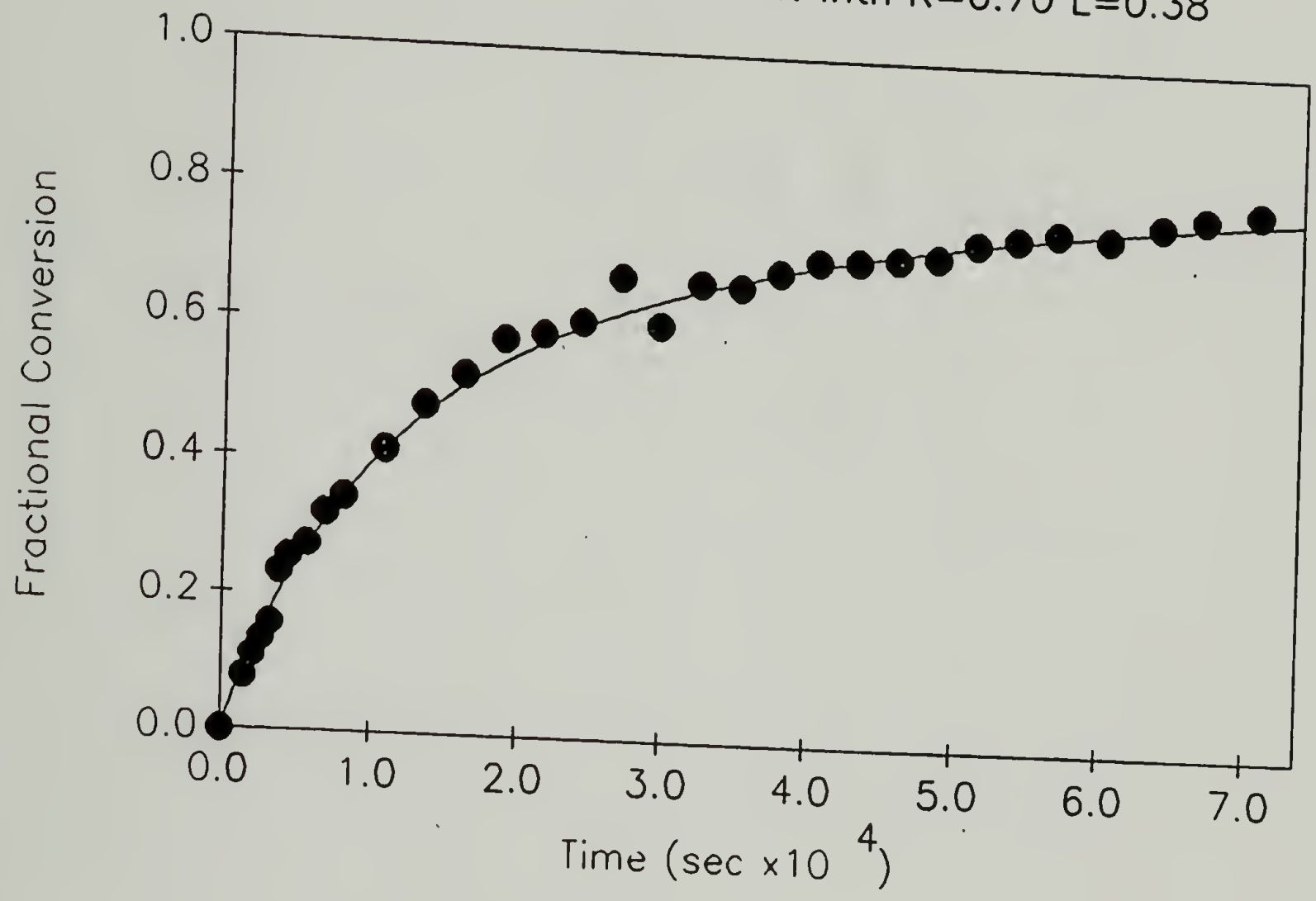



Figure C.11. Plot of conversion vs time for the reaction of PBEO with an equivalent amount of TBAB in $CDCl_3$ at 45°C. Data points indicate observed values and the solid line is the best fit calculated using K and L values obtained from Figure C.12.

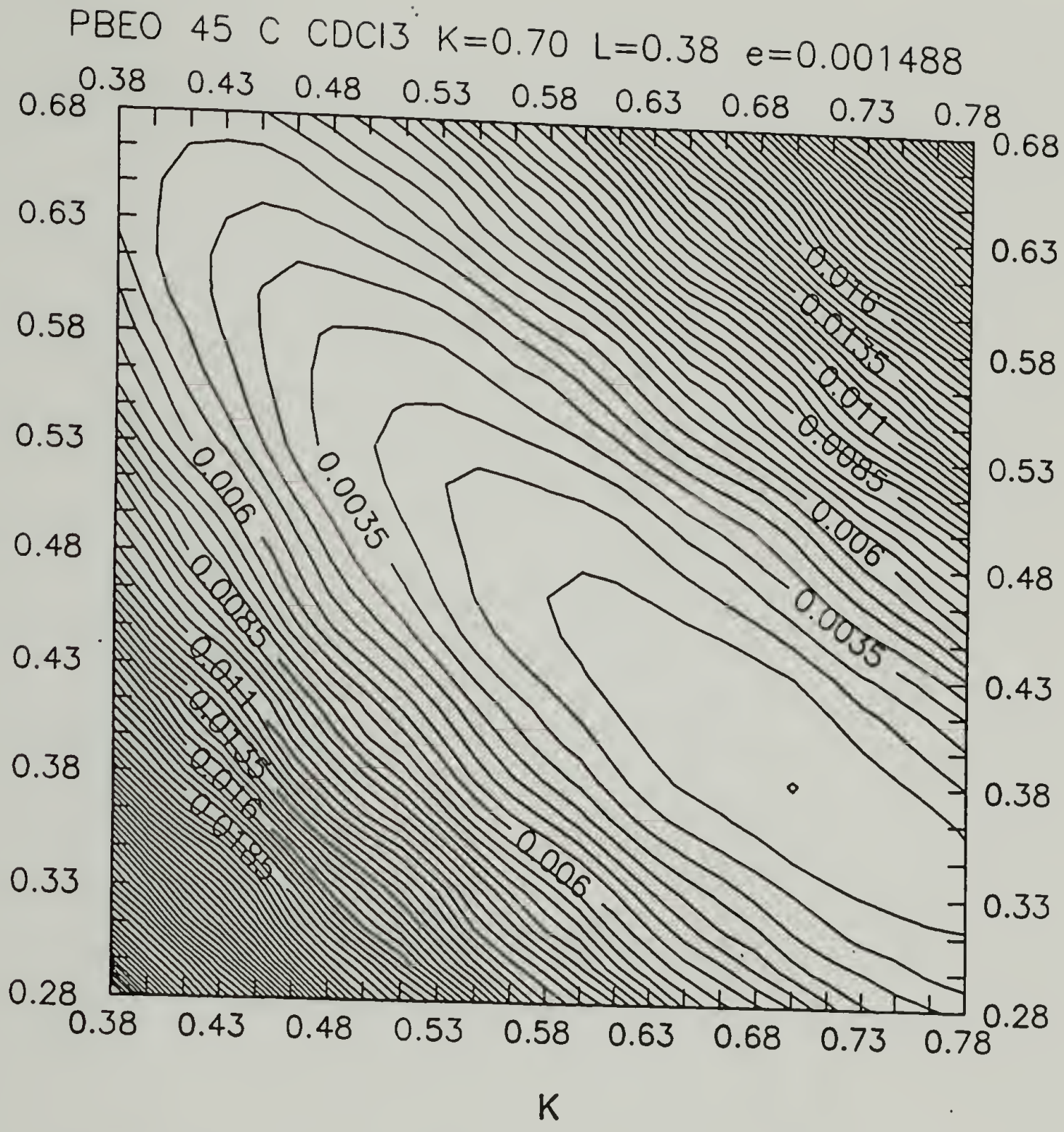



Figure C.12. Contour plot of the sum of the squares of the difference between measured conversion curve and the curve calculated using different K and L valuesfor the reaction of PBEO and TBAB in $CDCl_3$ at 45° C

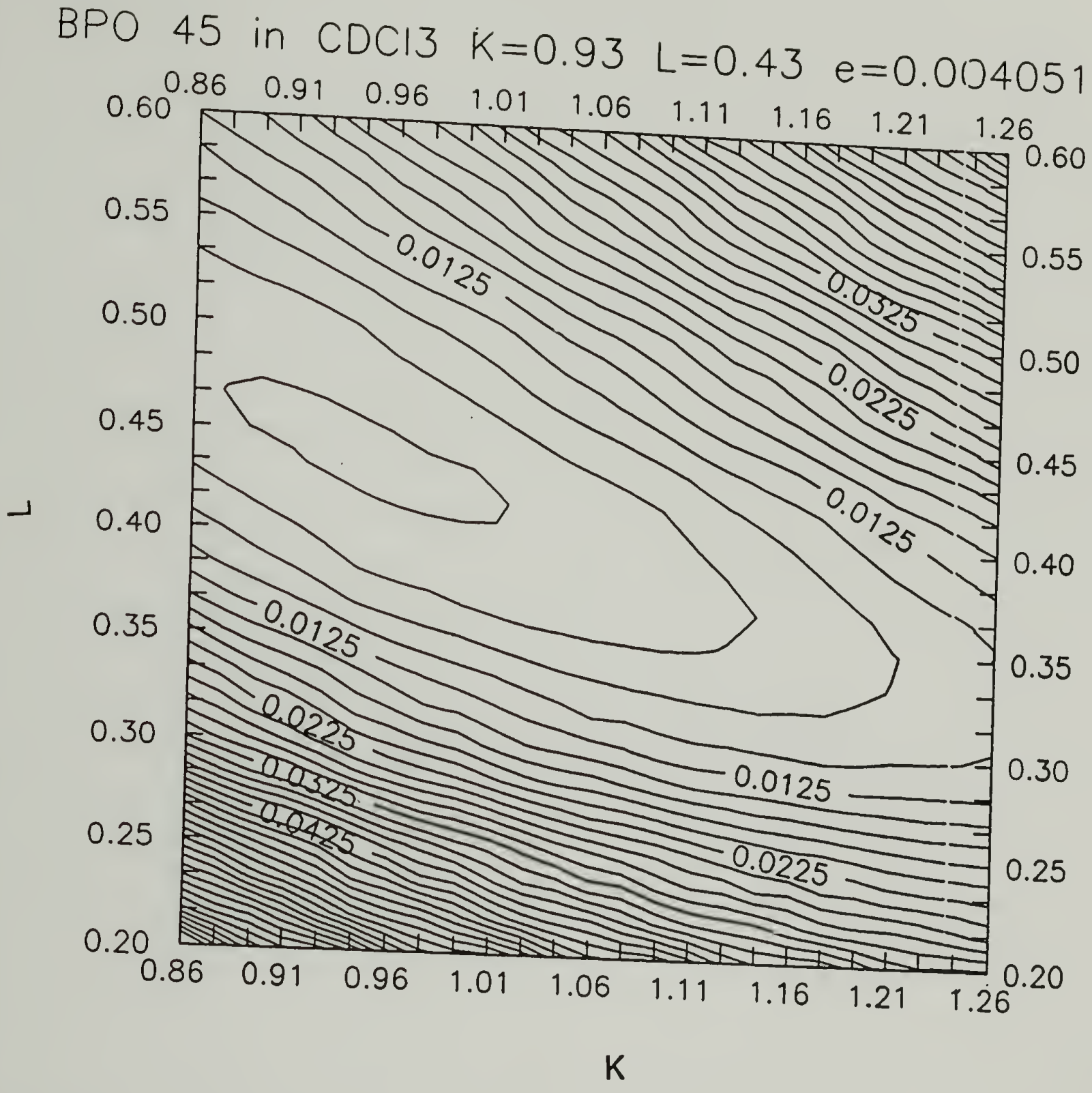



Figure C.13. Contour plot of the sum of the squares of the differences between measured conversion curve and the curve calculated using different K and L values for the reaction of PBPO and TBAB in $CDCl_3$ at 45° C.

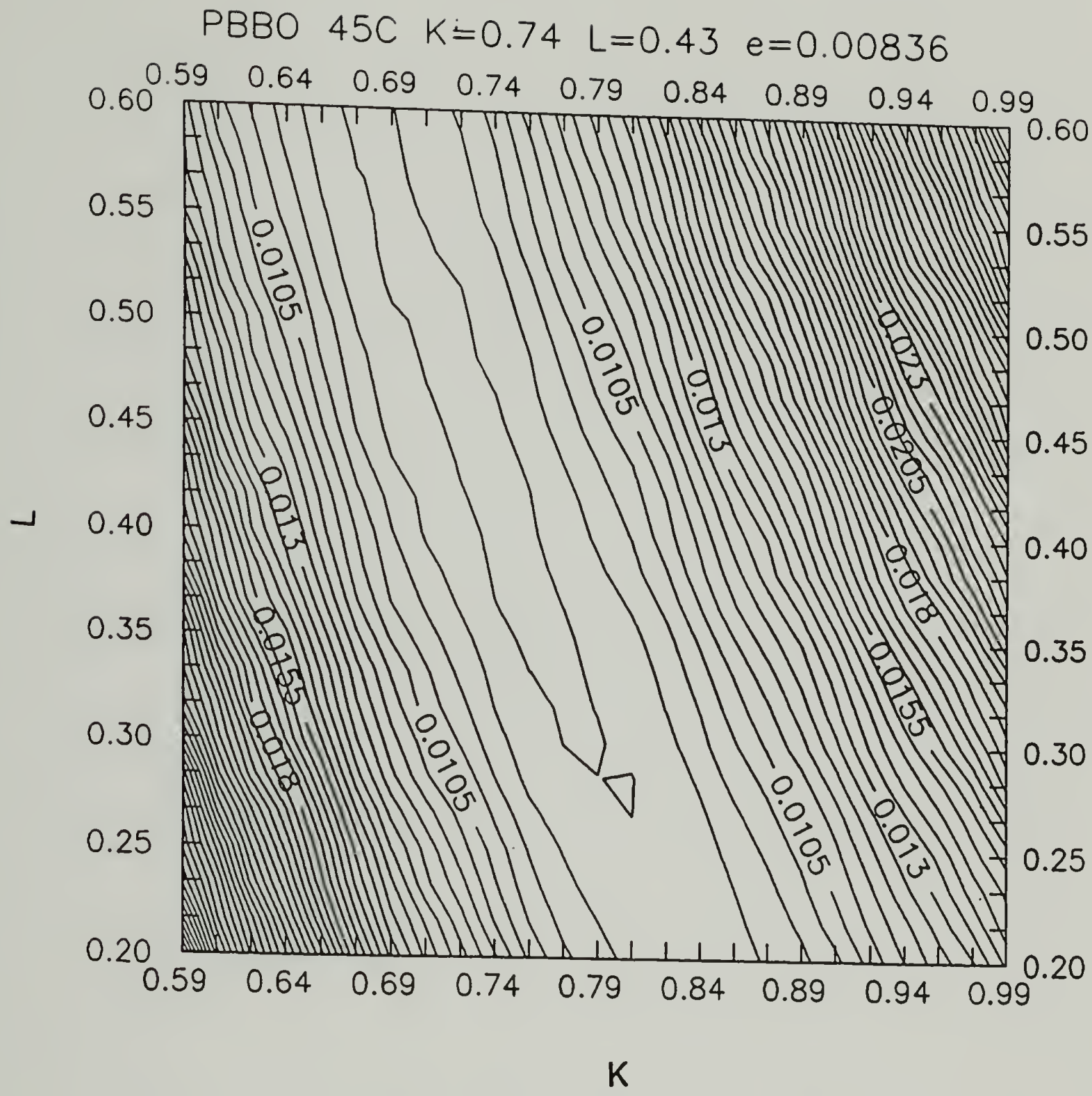



Figure C.14. Contour plot of the sum of the squares of the differences between measured conversion curve and the curve calculated using different K and L values for the reaction of PBBO and TBAB in $CDCl_3$ at 45° C.

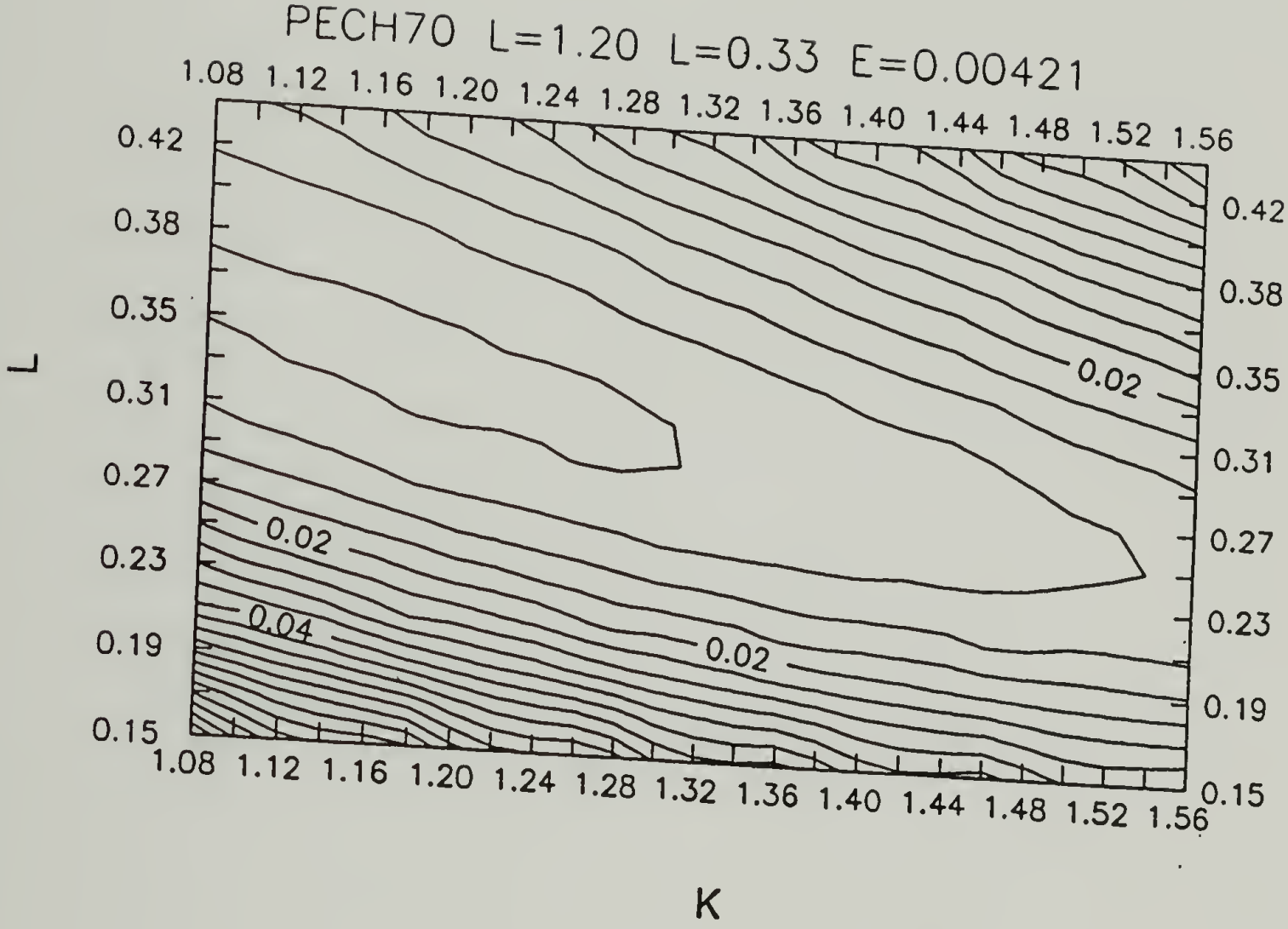



Figure C.15. Contour plot of the sum of the squares of the differences between measured conversion curve and the curve calculated using different K and L values for the reaction of PECH and TBAB in DMAc at 70° C.

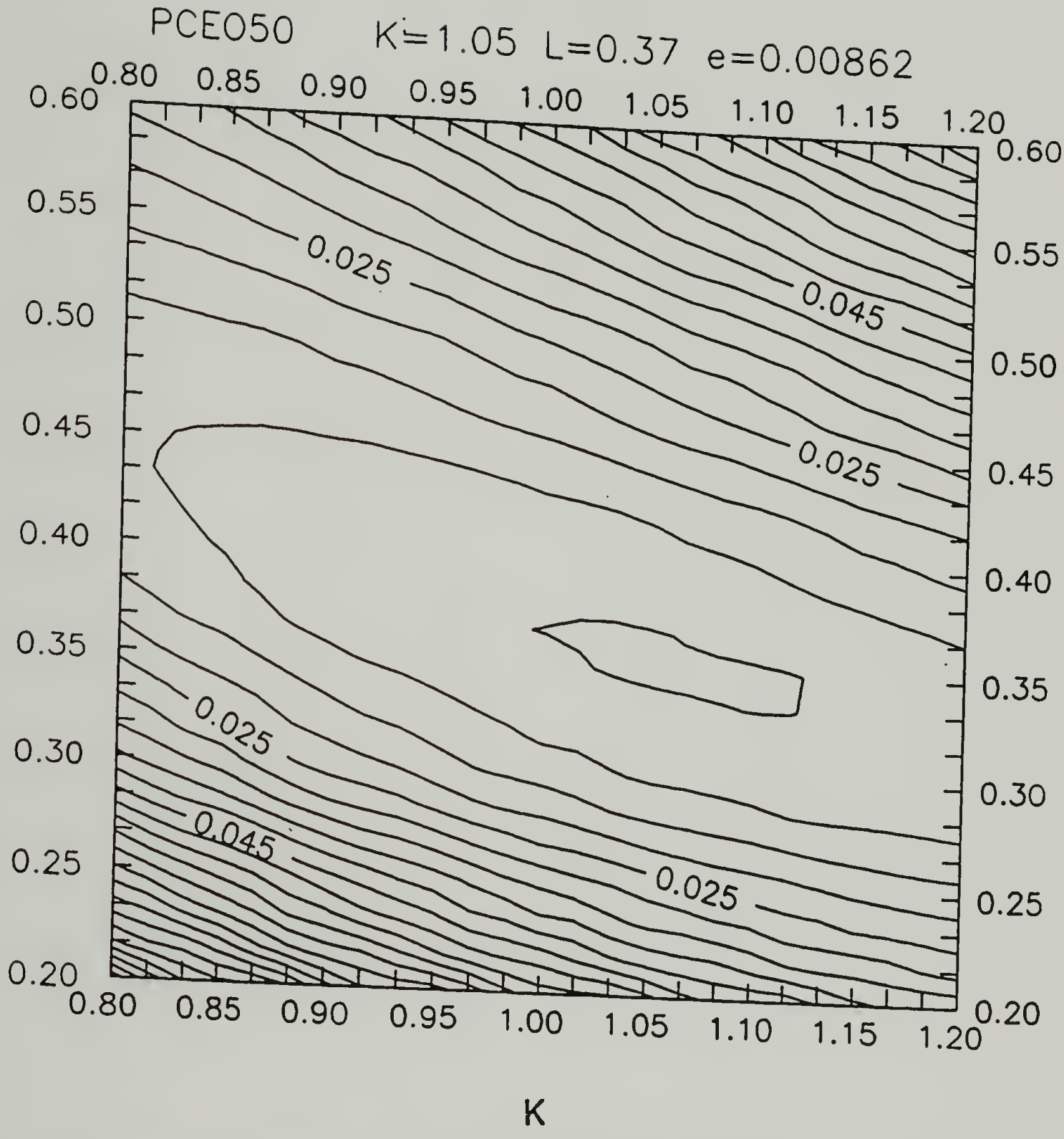



Figure C.16. Contour plot of the sum of the squares of the differences between measured conversion curve and the curve calculated using different K and L values for the reaction of PCEO and TBAB in DMAc at 50° C.

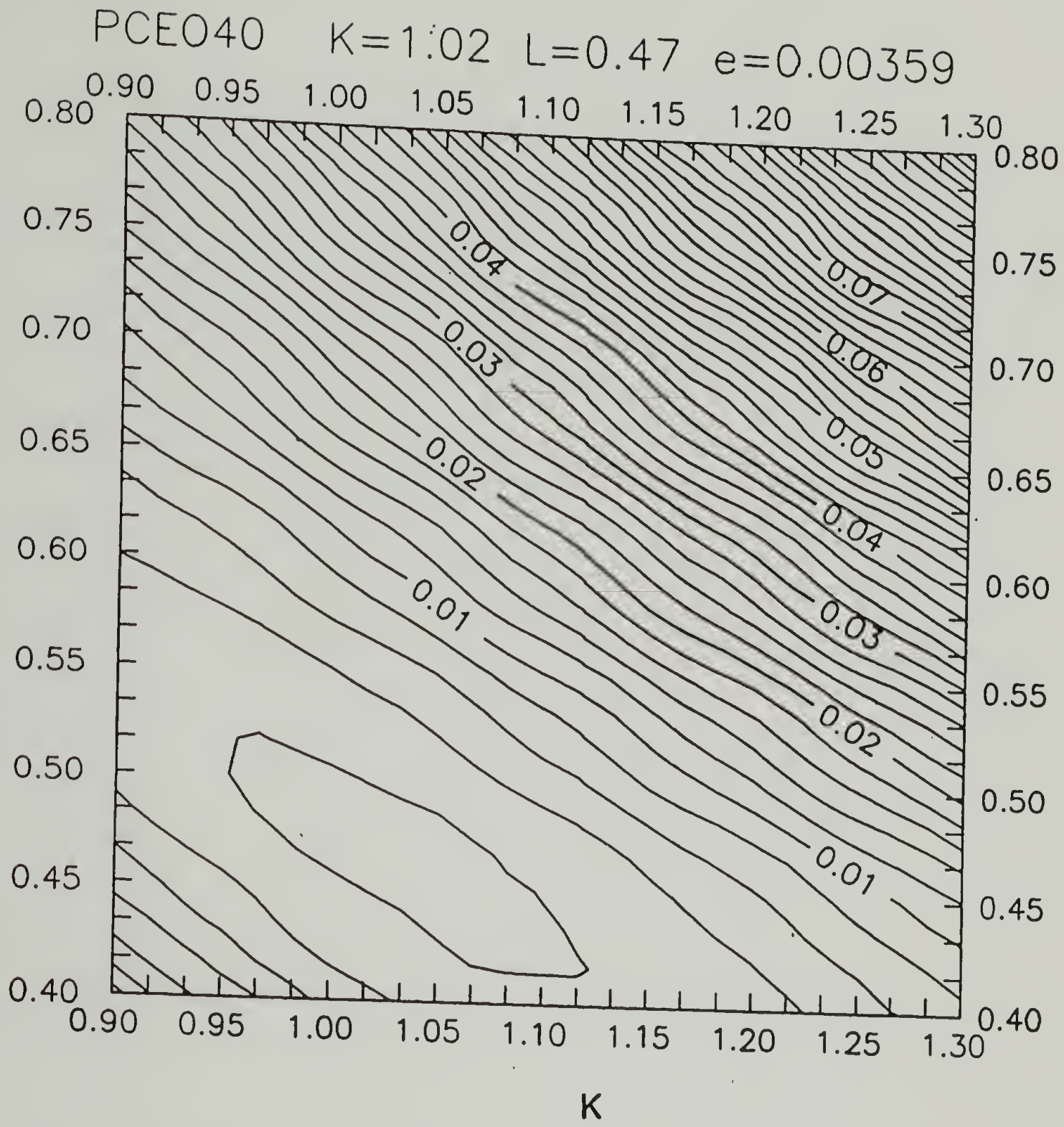



Figure C.17. Contour plot of the sum of the squares of the differences between measured conversion curve and the curve calculated using different K and L values for the reaction of PCEO and TBAB in DMAc at 40° C.

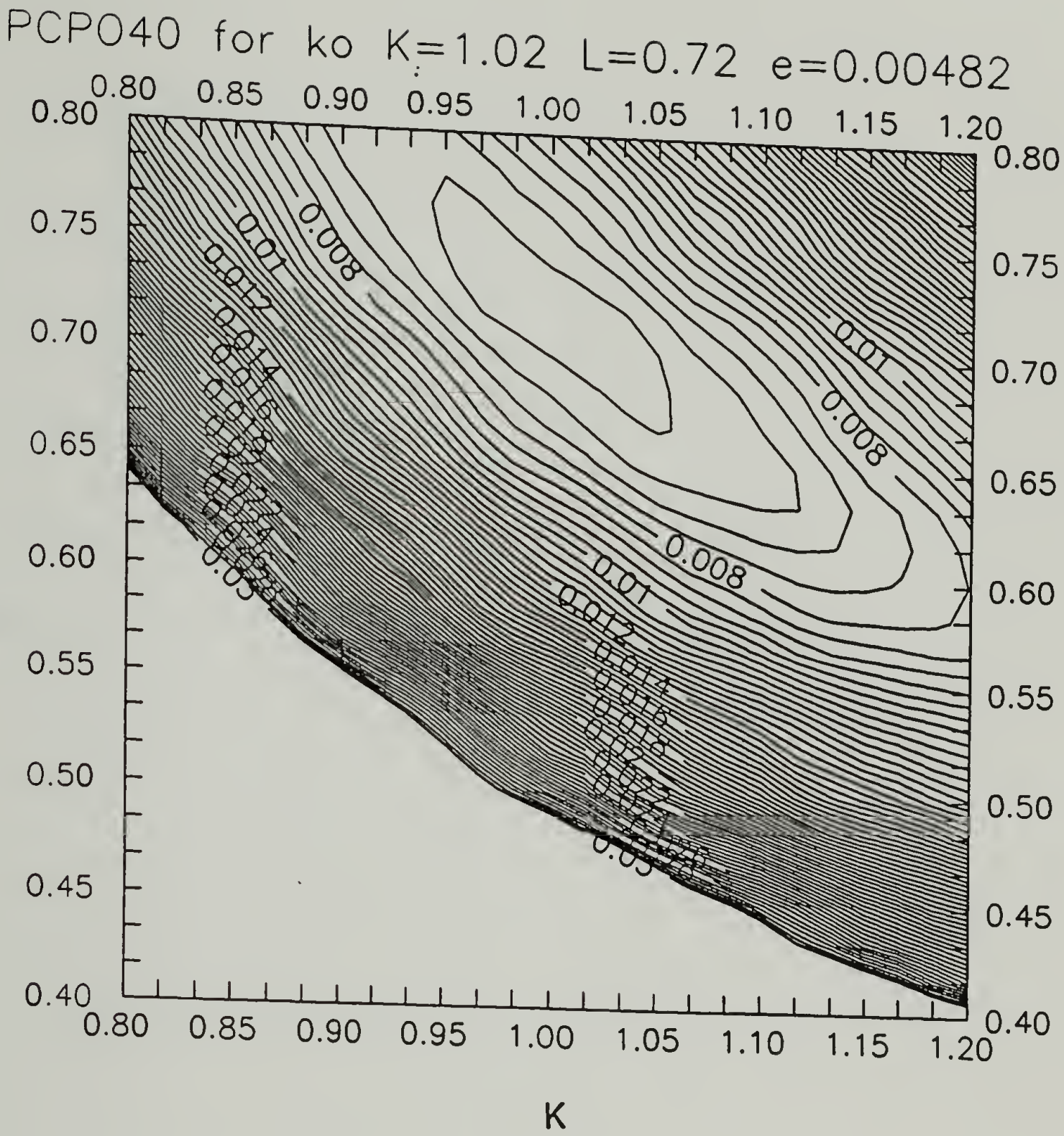



Figure C.18. Contour plot of the sum of the squares of the differences between measured conversion curve and the curve calculated using different K and L values for the reaction of PCPO and TBAB in DMAc at 40° C.

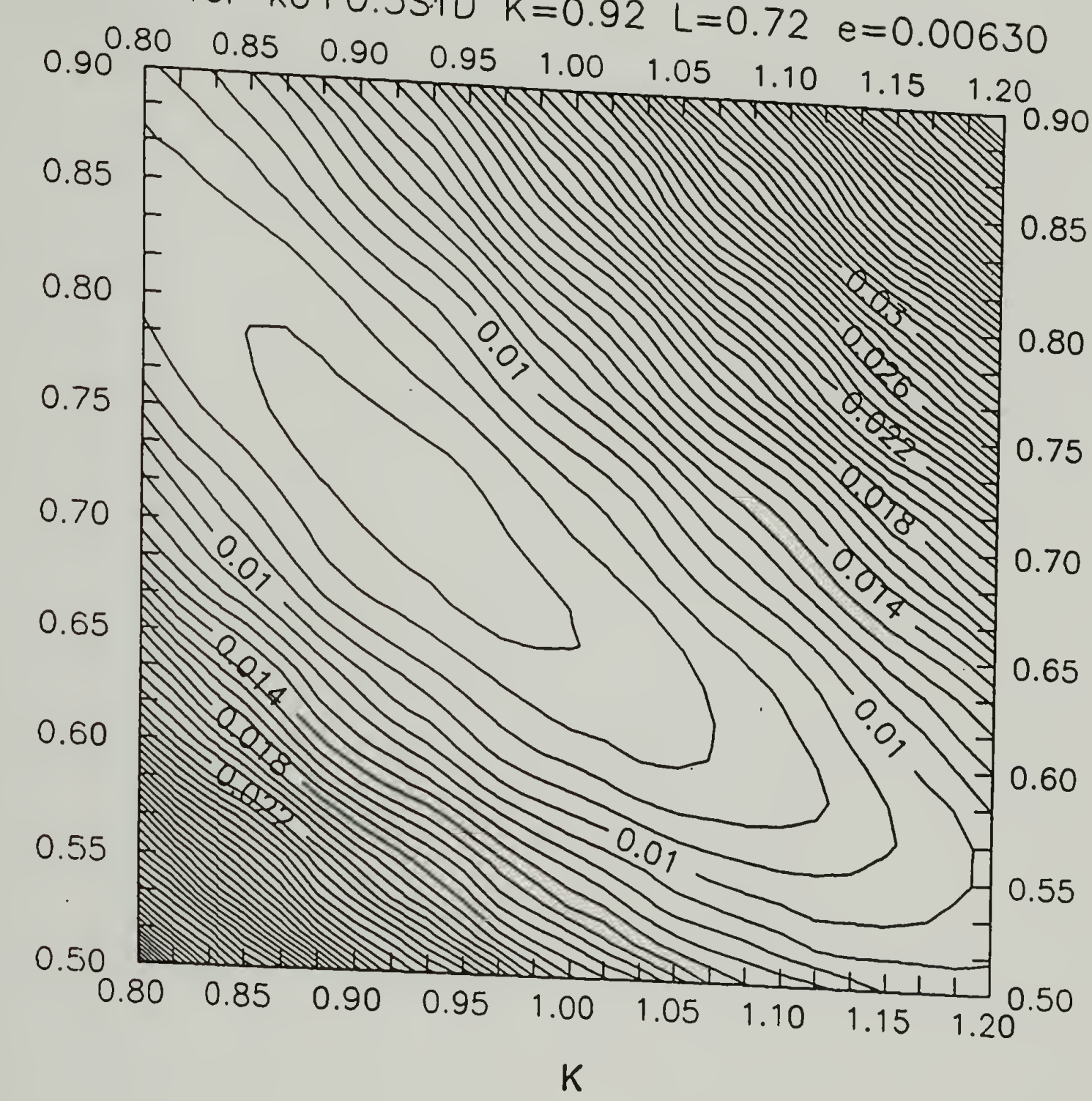



Figure C.19. Contour plot of the sum of the squares of the differences between measured conversion curve and the curve calculated using different K and L values for the reaction of PCPO and TBAB in DMAc at 40° C.

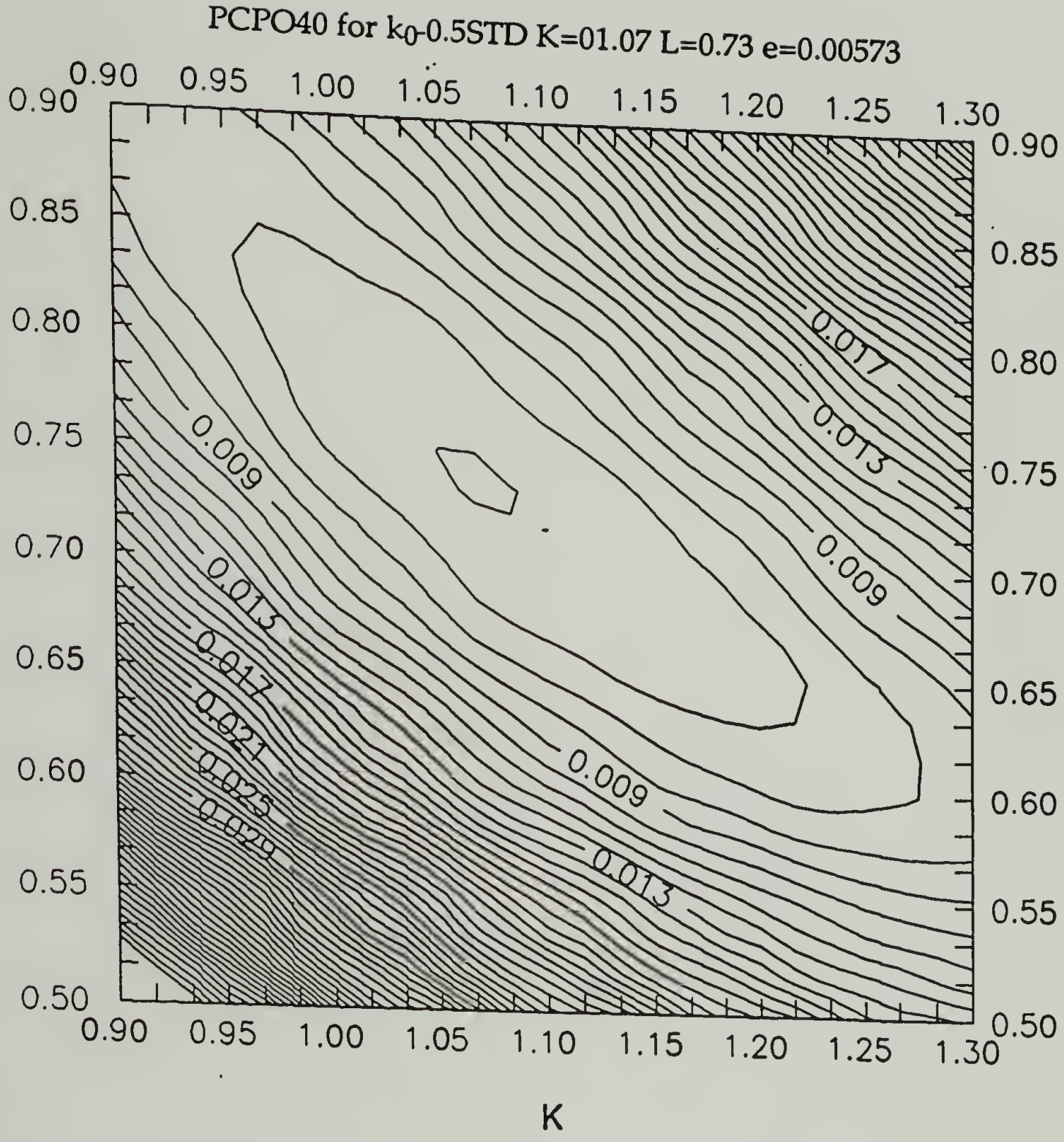



Figure C.20. Contour plot of the sum of the squares of the differences between measured conversion curve and the curve calculated using different K and L values for the reaction of PCPO and TBAB in DMAc at 40° C.

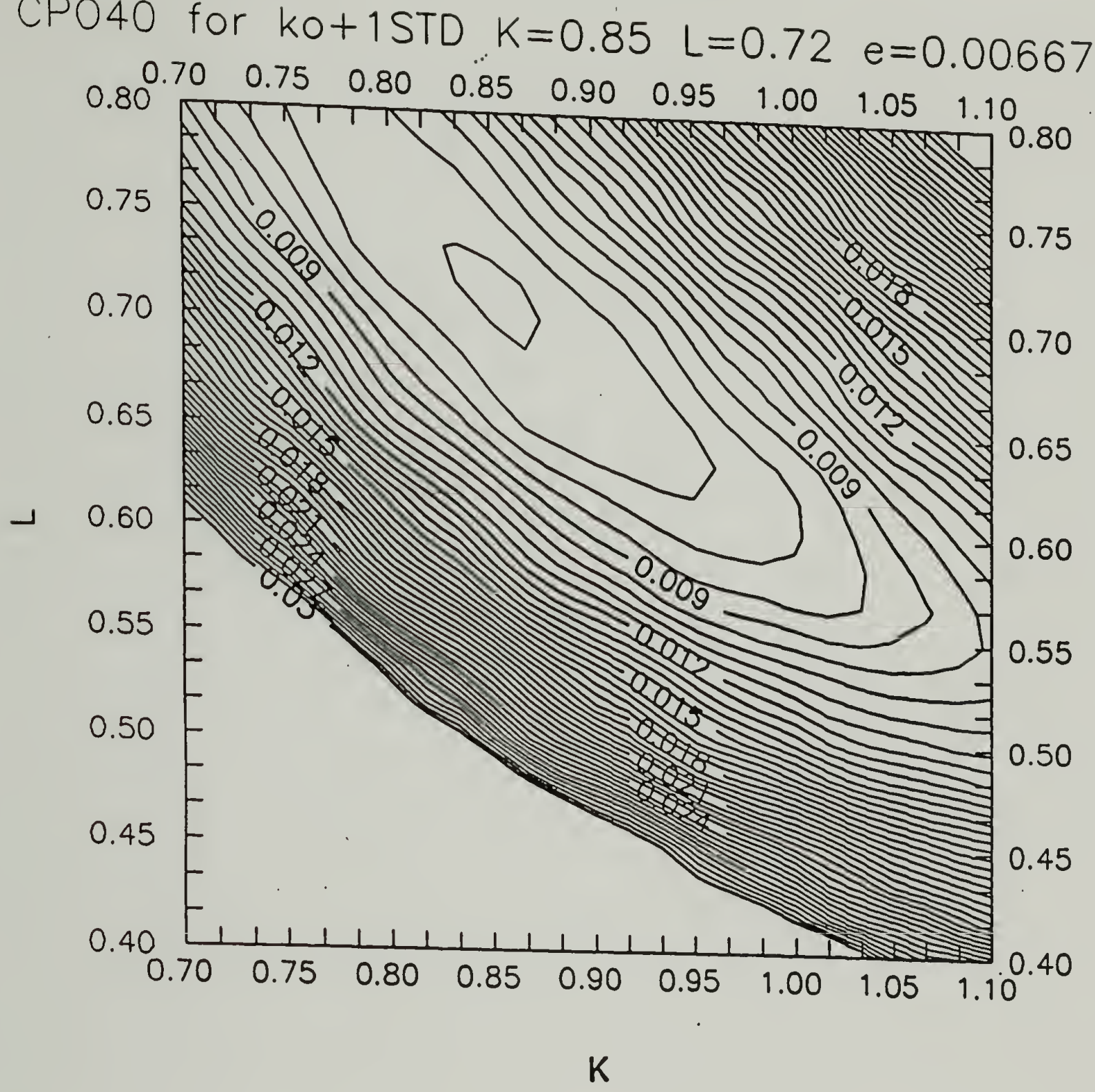



Figure C.21. Contour plot of the sum of the squares of the differences between measured conversion curve and the curve calculated using different K and L values for the reaction of PCPO and TBAB in DMAc at 40° C.

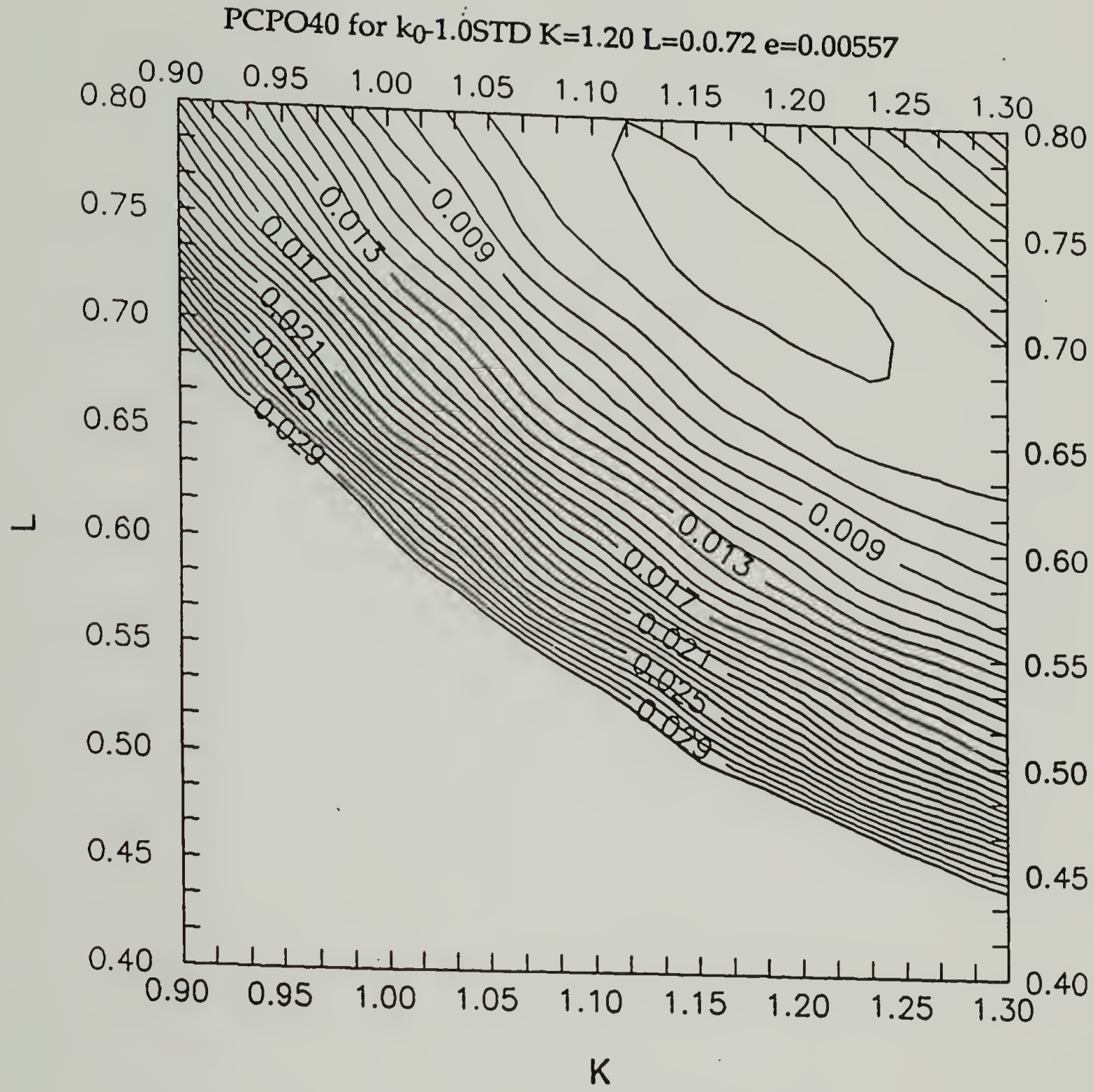



Figure C.22. Contour plot of the sum of the squares of the differences between measured conversion curve and the curve calculated using different K and L values for the reaction of PCPO and TBAB in DMAc at 40° C

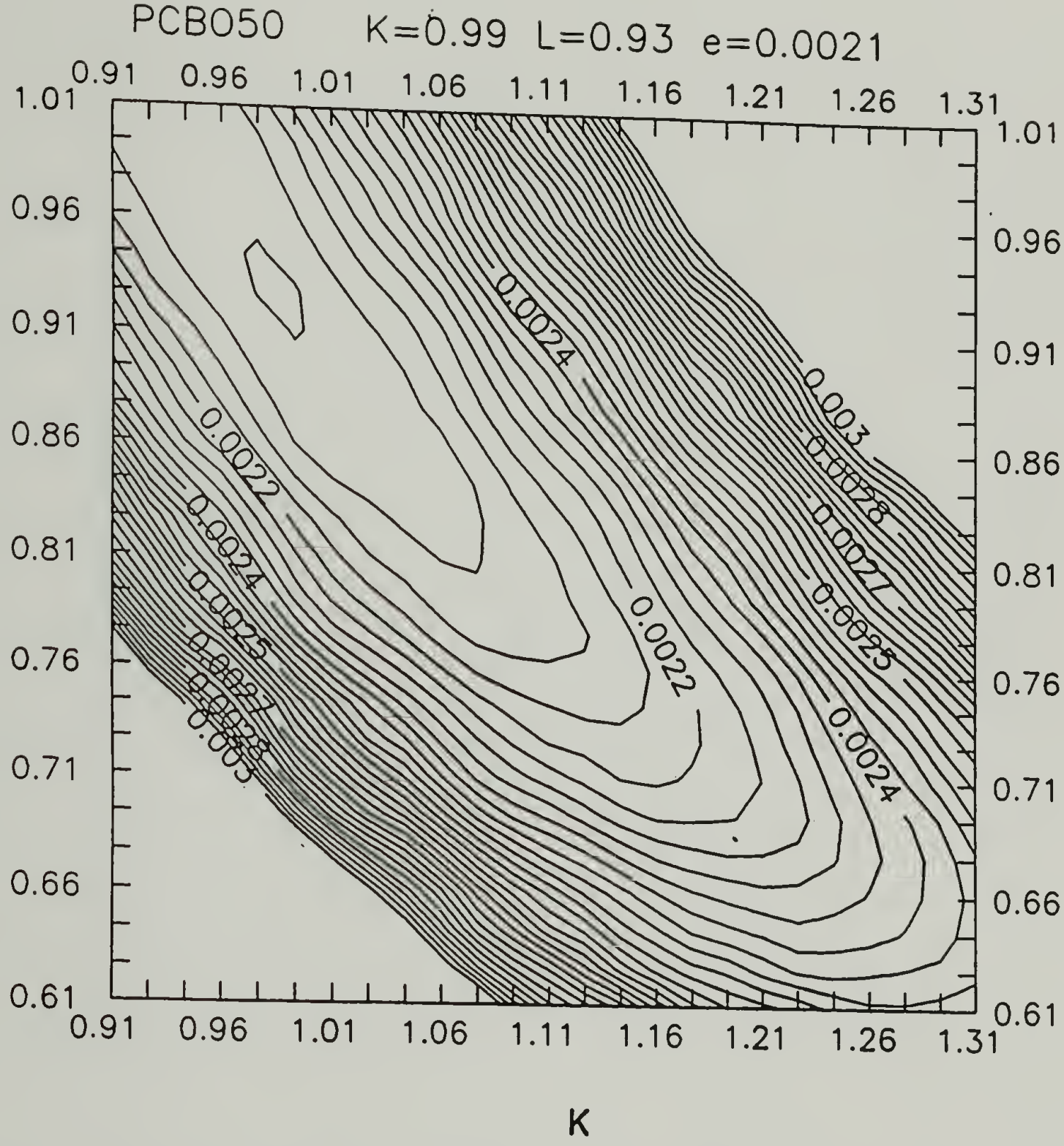



Figure C.23. Contour plot of the sum of the squares of the differences between measured conversion curve and the curve calculated using different K and L values for the reaction of PCBO and TBAB in DMAc at 40° C.

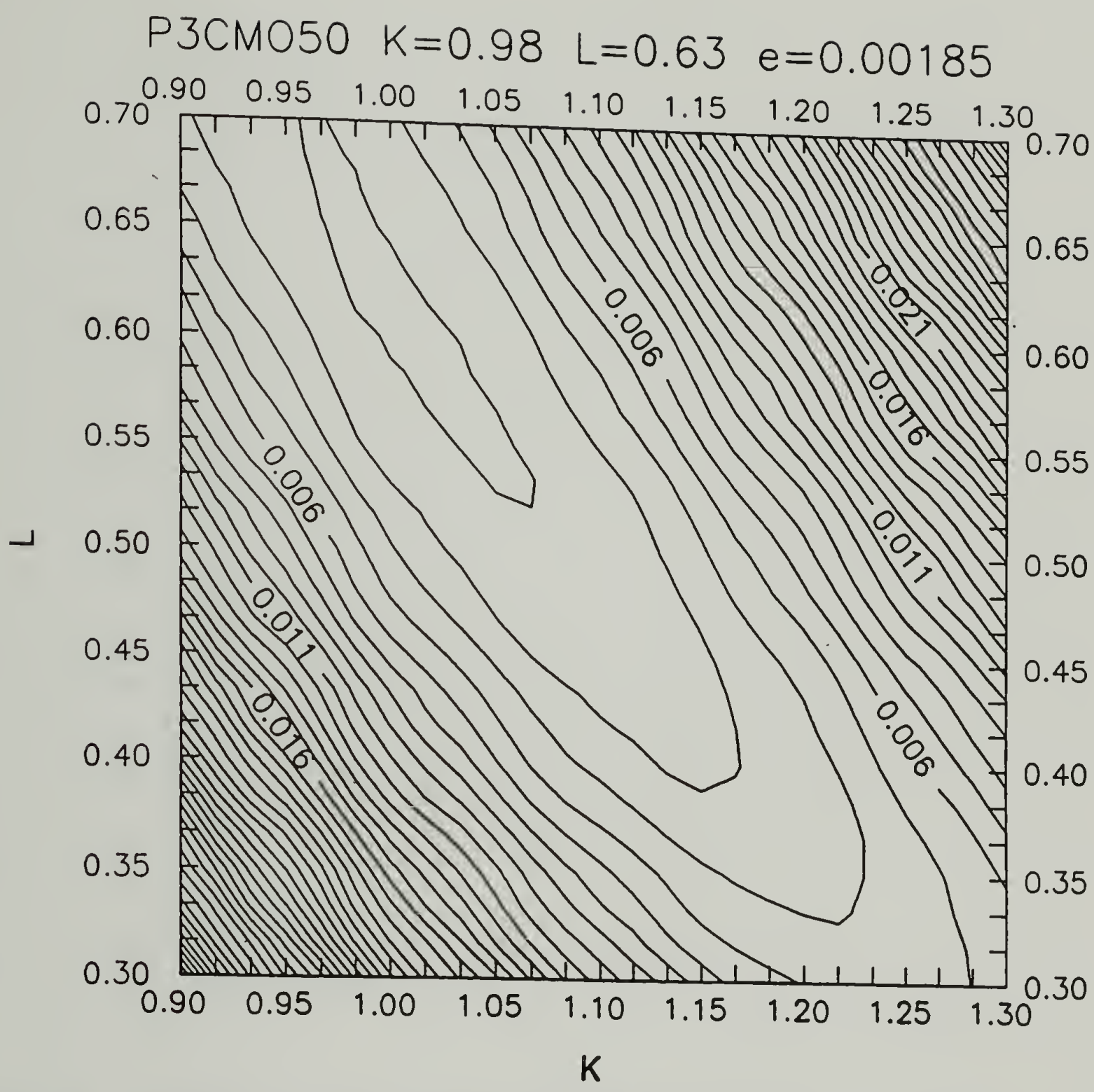



Figure C.24. Contour plot of the sum of the squares of the differences between measured conversion curve and the curve calculated using different K and L values for the eaction of P3CMO and TBAB in DMAc at 50° C

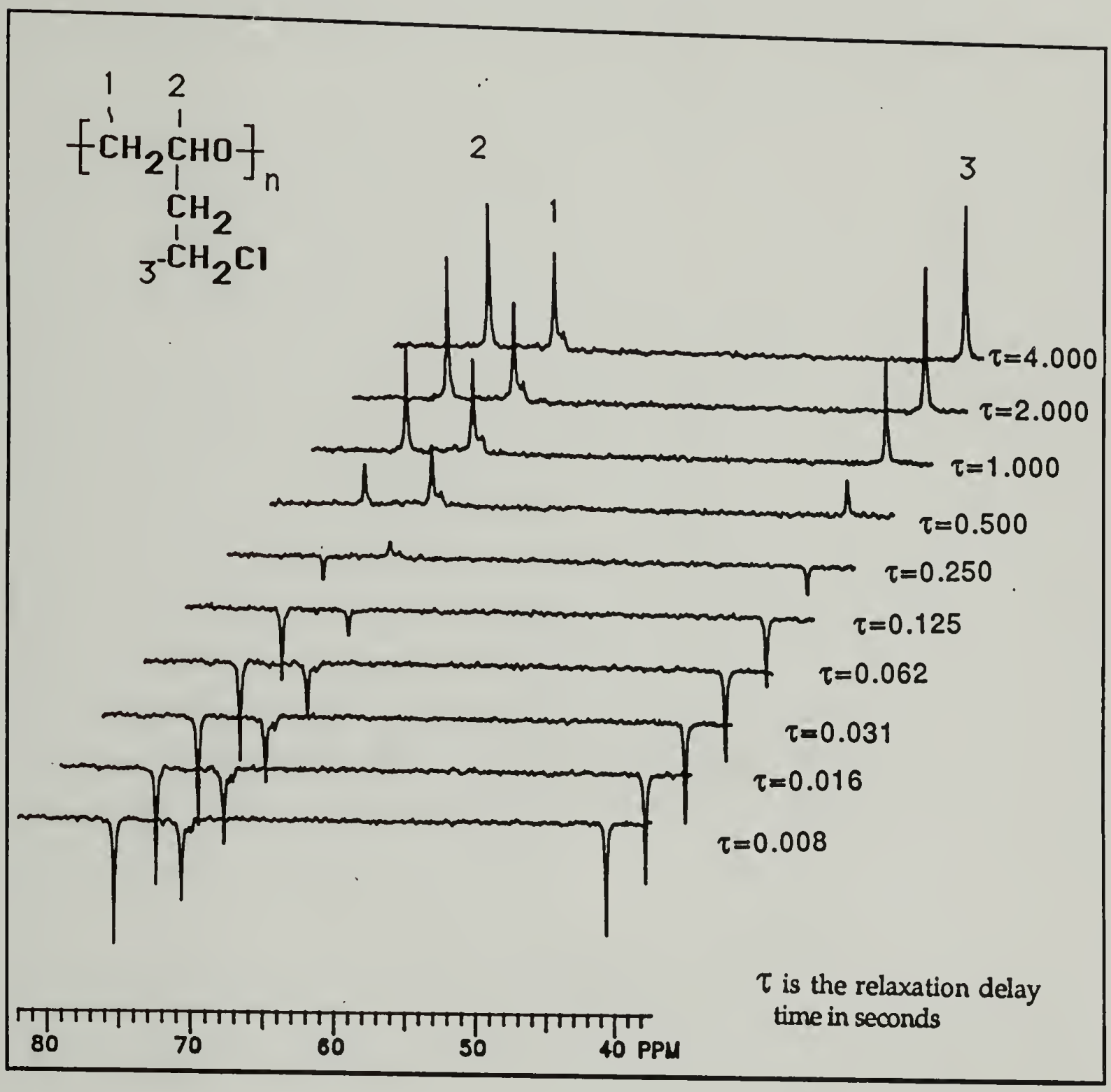



Figure C.25. Example of $^{13}C$ NMR $T_1$ experiment spectra at 50° C in DMAc for the backbone methylene, methine and ω-pendant methyleneon PCEO.

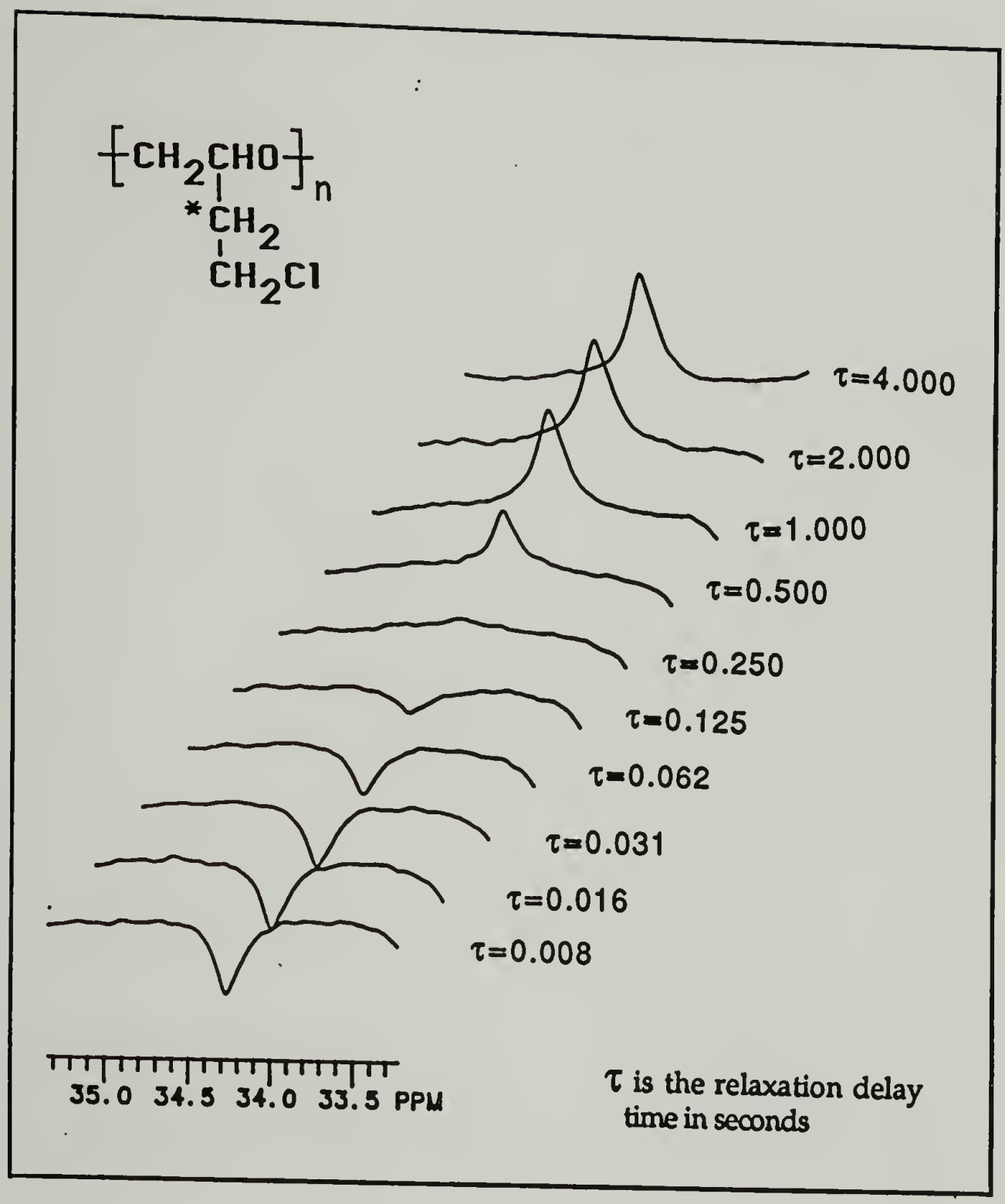



Figure C.26. Example of $^{13}C$ NMR $T_1$ experiment spectra at 50° C in DMAc for the pendant chain methylene on PCEO.

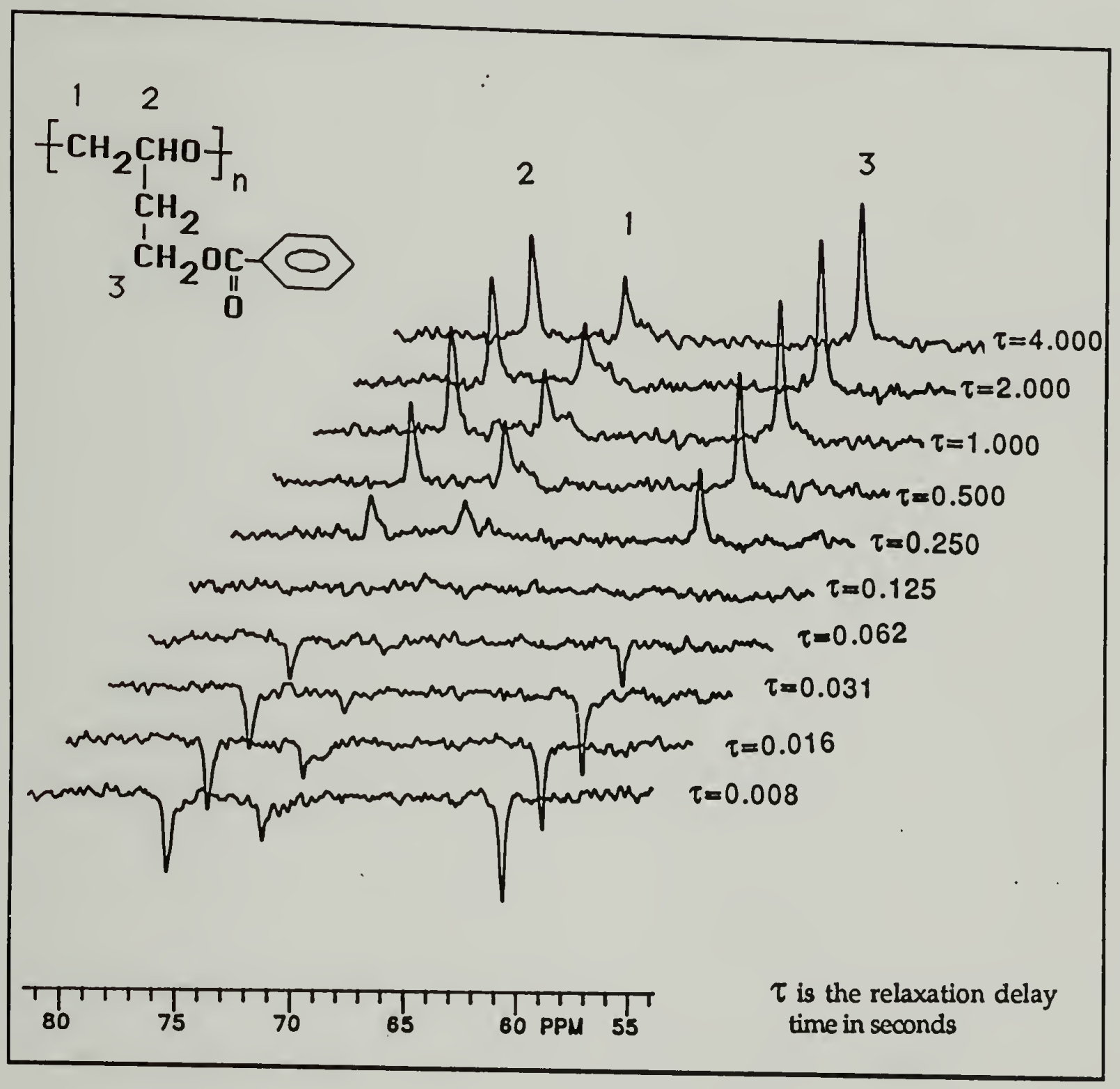



Figure C.27. Example of $^{13}C$ NMR $T_1$ experiment spectra at 50° C in DMAc for the backbone methylene, methine and ω-pendant methyleneon PBeEO.

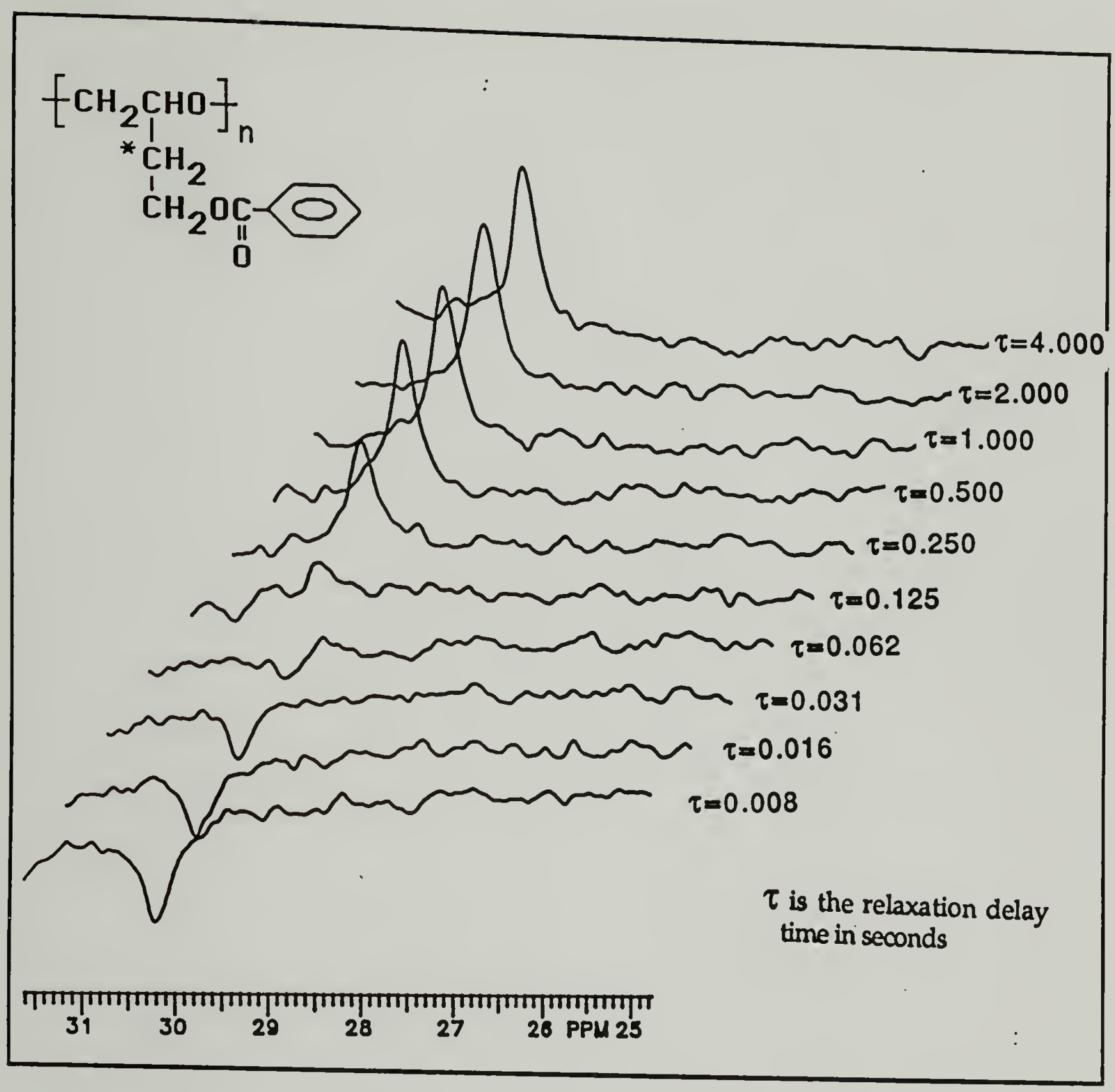



Figure C.28. Example of $^{13}C$ NMR $T_1$ experiment spectra at 50° C in DMAc for the pendant chain methylene on PBeEO.

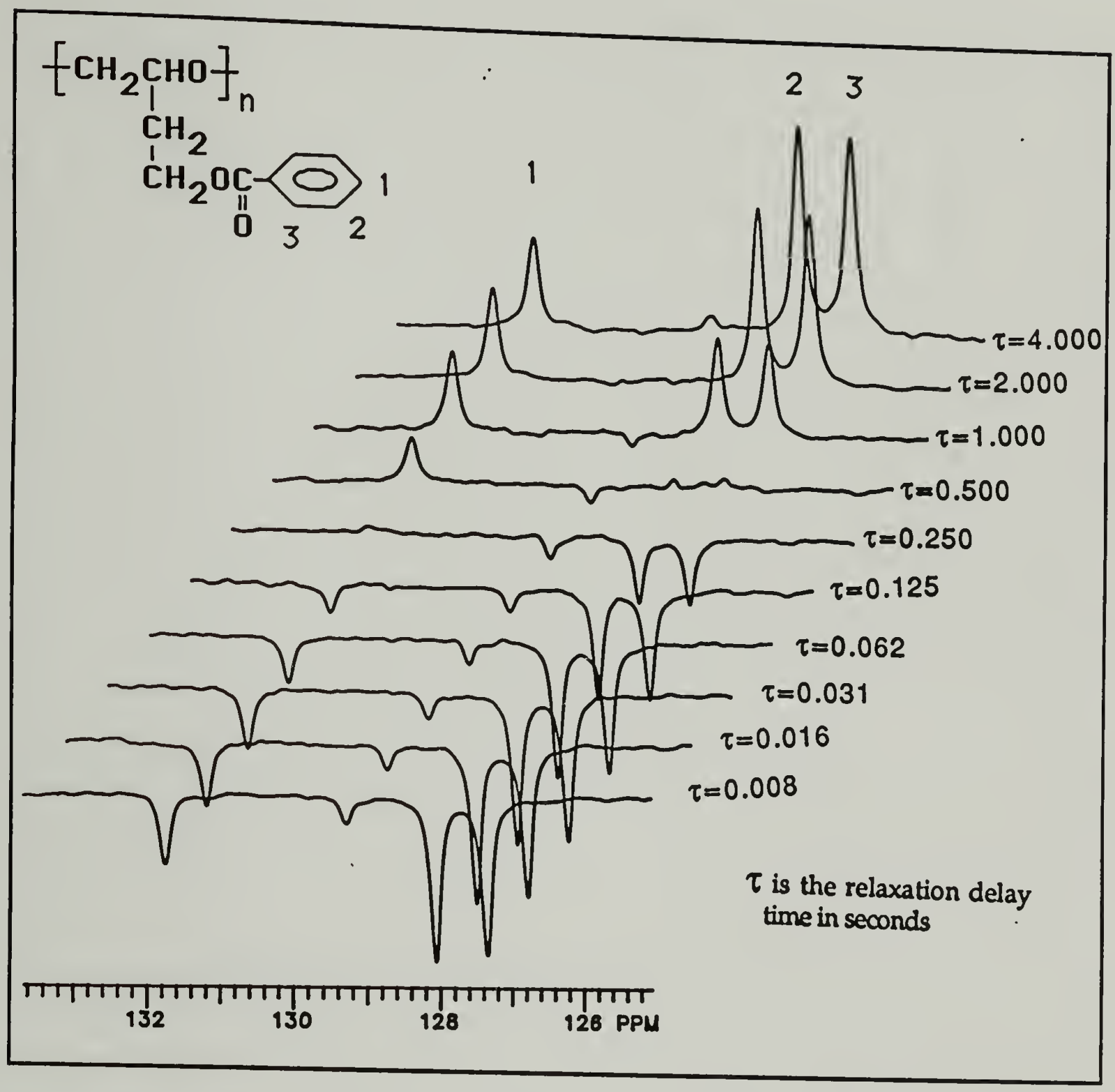



Figure C.29. Example of $^{13}C$ NMR $T_1$ experiment spectra at 50° C in DMAc for the protonated aromatic carbons in PBeEO.

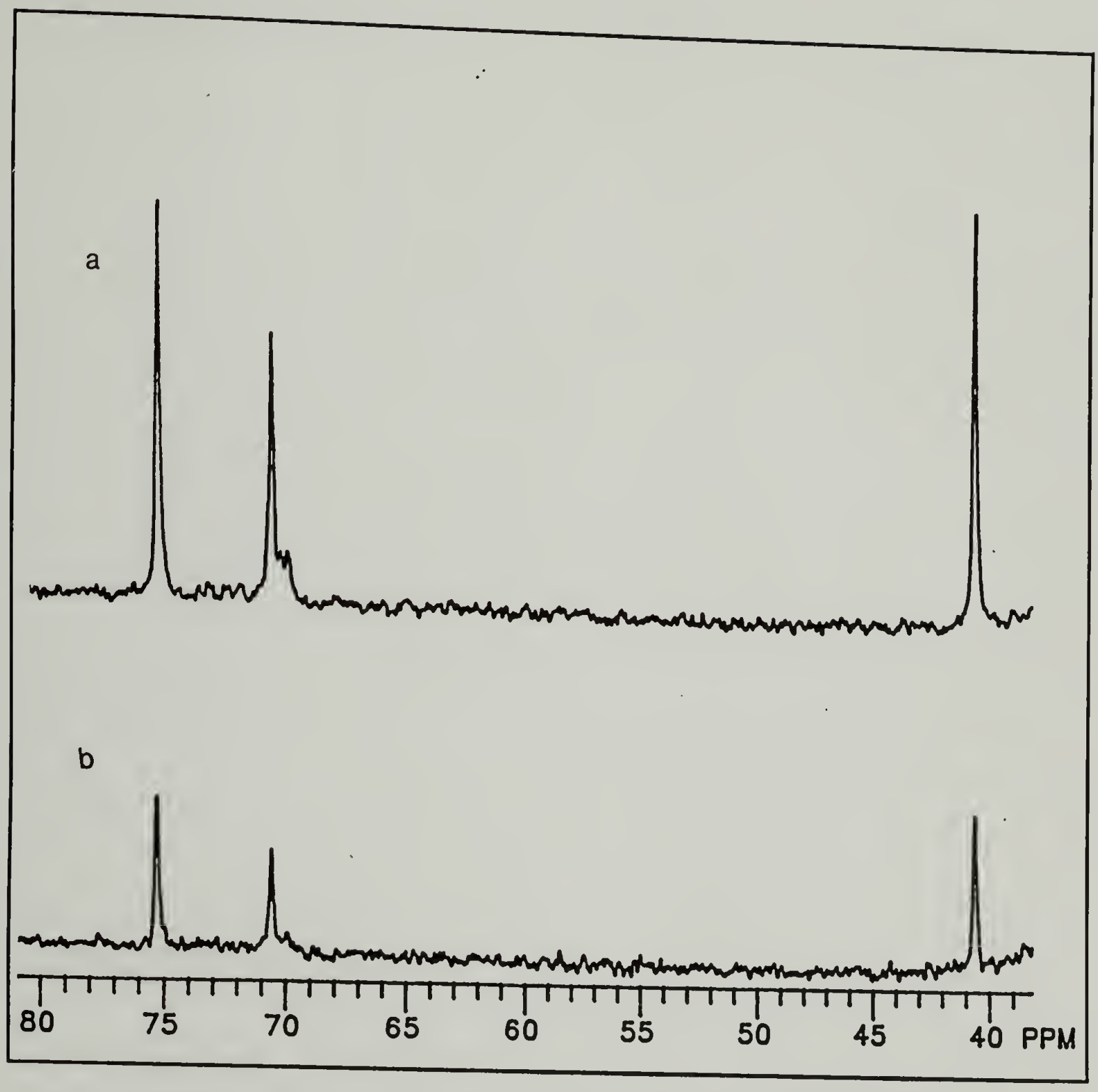



Figure C.30. $^{13}C$ NMR spectra of PCEO at 50° C in DMAc used for the determination of NOE factors for backbone carbons and pendant ω-methylene. Spectrum a was obtained with continuous decoupling and b with gated decoupling.

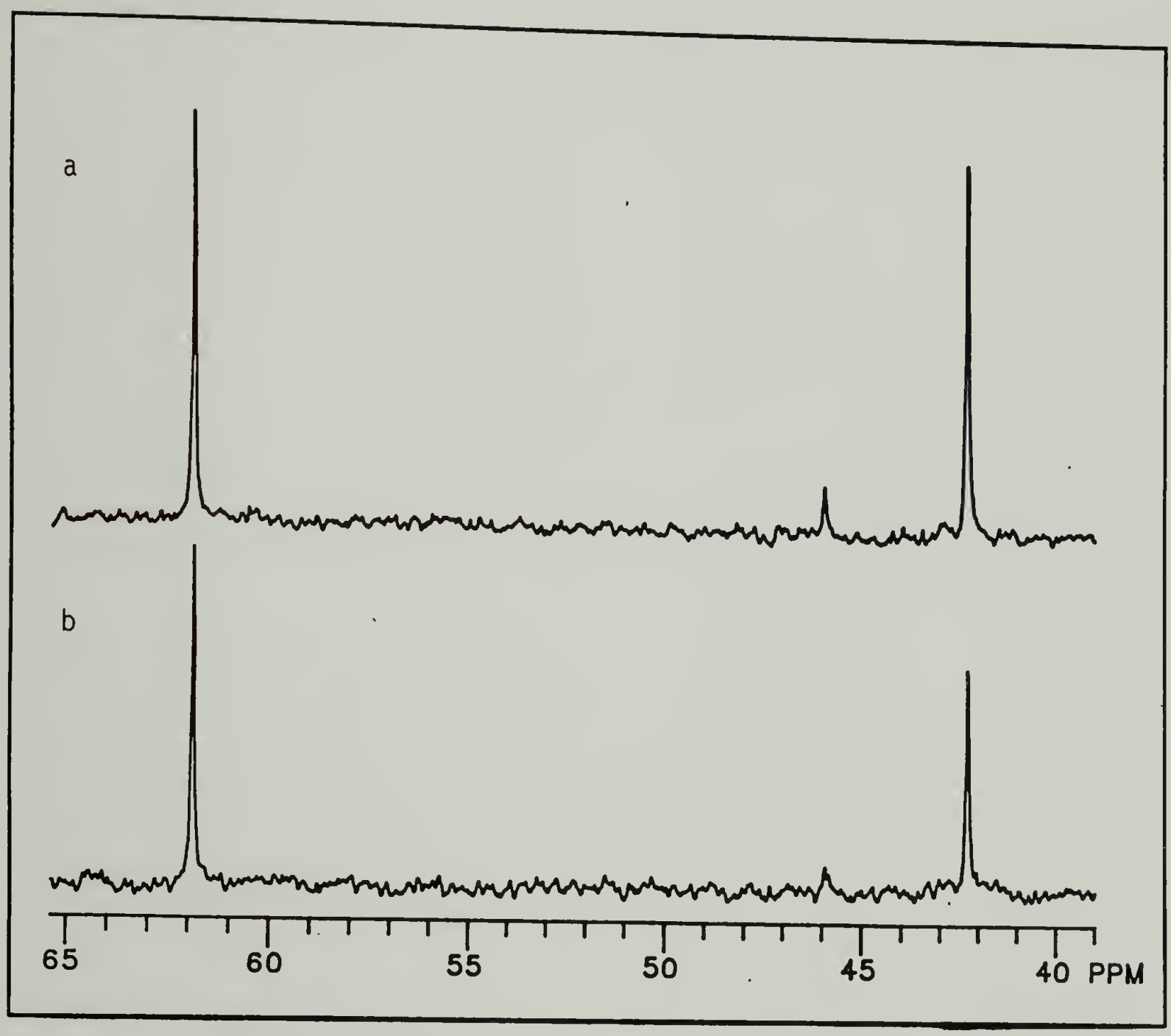



Figure C.31. $^{13}C$ NMR spectra of a mixture of 1-chloropentane and 1-benzoyloxypentane at 50° in DMAc showing the terminal methylene resonances obtained using delay times of 75 sec (a) and 2 sec (b).

# APPENDIX D

FORTRAN programs, Kinet and Contour, Used for the Evaluation of K and L in the Kinetics of Reaction Studies.

```
      PROGRAM KINET
C-----------------------------------------------------------------------
C  KINET-PROGRAM FOR CALCULATING CONVERSION CURVE BASED ON BOUCHER'S
C       EQUATION (SEE E.A. BOUCHER, PROGR. POLYM. SCI., 6, 63 (1978))
C       GIVEN ESTIMATES FOR K AND L.
C
C       CODE WRITTEN BY BRIAN DEVLIN, UMASS 1988.
C
C  REQUIRED INPUT:
C       1)  COEFFICIENTS FOR FIFTH ORDER FIT OF 1-FRAC CONV FOR OBSERVED
C           DATA.
C       2)  RATE CONSTANT-K0.
C       3)  CONCENTRATION OF POLYMER REPEAT UNITS AT TIME 0
C       4)  MEASURED TIME AND CONVERSION VALUES
C-----------------------------------------------------------------------
C
C       ****DECLARATIONS****
C
      CHARACTER*64 FNAME
      CHARACTER*20 DEVICE,XLAB,YLAB,OUTFIL
      CHARACTER*1 RESPON
      REAL KZERO
      EXTERNAL FUNC,SITWO,CUREQU
      COMMON AA,BB,CC,DD,EE,FF,BIGK,BIGL
      DIMENSION TIME(100),SI(100),TIMINT(101),SICAL(101),ALPHA(101),
     *   PTXCAL(101),PTYCAL(101),PTX(100),PTY(100)
      PARAMETER(X=0.0, Y=0.0, XMAX=639.0, YMAX=199.0, XOR=110.0,
     *   YOR=45.0,XLIM=510.0,YLIM=175.0,YLABX=60.0,YLABY=70.0,
     *   XLABX=290.0,XLABY=15.0,ITH=1,ITW=1,ITC=1,ITZ=0,B=9.999E-1)
C
C       ****PROMPT AND PROCESS INPUT DATA****
C
      WRITE(*,50)
50    FORMAT(' INPUT DATA FILE NAME-'\)
      READ(*,75) FNAME
75    FORMAT(A)
      OPEN(5,FILE=FNAME)
      READ(5,*) AAA,BBB,CCC,DDD,EEE,FFF
      READ(5,*) KZERO,CONCR
      DO 100 I=1,100
            READ(5,*,END=200) TIME(I),SI(I)
            NP=I
100   CONTINUE
200   CONTINUE
C
C       ****CALCULATE INTEGRAL COEFFICIENTS****
C
      CLOSE(5)
      AA=AAA/6.0
      BB=BBB/5.0
      CC=CCC/4.0
      DD=DDD/3.0
      EE=EEE/2.0
      FF=FFF
C
C       ****GET ESTIMATES FOR K AND L****
C
      WRITE(*,210)
      READ(*,*) BIGK
210   FORMAT(' Input K constant- '\)
      WRITE(*,220)
220   FORMAT(' Input L constant- '\)
      READ(*,*) BIGL
```

```
C
C
C       ****CALCULATE TIME INTERVAL****

        SIZINT=TIME(NP)/20.0
        DO 300 I=1,21
                IF (I.EQ.1) THEN
                        TIMINT(1)=0.0
                ELSE
                        TIMINT(I)=FLOAT(I-1)*SIZINT
                ENDIF
300     CONTINUE
C
C
C       ****CALCULATE ALFA FROM INPUT EQUATION****

        DO 400 I=1,21
                ALPHA(I)=ALFINT(TIMINT(I),KZERO,CONCR)
400     CONTINUE
C
C
C       ****CALCULATIONS****

        DO 500 I=1,21
                CALL QROMB(FUNC,ALPHA(I),B,SONE)
                CALL QROMB(SITWO,ALPHA(I),B,STWO)
                SICAL(I)=1.0-((2.0*BIGK*ALPHA(I)**BIGL)*SONE+
     *  (2.0*ALPHA(I)**BIGL)*STWO+SCONST(ALPHA(I)))
                WRITE(*,450) I
450     FORMAT('+DATA POINT CALCULATED-->',I2)
500     CONTINUE
        DEVICE = '/HALOIBME.DEV/'
        CALL SETDEV(DEVICE)
c
c-----------------------------------------------------------------------
c       Init graphics
c-----------------------------------------------------------------------
        CALL INITGR( 1 )
        CALL SETIEE(1)
        YLAB='/% CONVERSION/'
        XLAB='/TIME (sec)/'
        CALL SETWOR(X,Y,XMAX,YMAX)
        CALL BOX(XOR,YOR,XLIM,YLIM)
        CALL INITTC(IH,IW,IC)
        CALL SETTEX(ITH,ITW,ITC,ITZ)
        CALL MOVTCA(YLABX,YLABY)
        CALL TEXT(YLAB)
        CALL MOVTCA(XLABX,XLABY)
        CALL SETTEX(ITH,ITW,ITZ,ITZ)
        CALL TEXT(XLAB)
        CALL MOVTCA(XSCLAB,XZLAB)
        CALL DELTCU
        CALL INITMA(INDEX,ICODE)
        DO 800 N=1,NP
                PTX(N)=TIME(N)*400.0/TIME(NP) + 110.0
                PTY(N)=SI(N)*130.0 + 45.0
                CALL PTABS(PTX(N),PTY(N))
```

```
800     CONTINUE
        DO 850 K=1,21
                PTXCAL(K)=TIMINT(K)*400.0/TIMINT(21) + 110.0
                PTYCAL(K)=SICAL(K)*130.0 + 45.0
                CALL PTABS(PTXCAL(K),PTYCAL(K))
850     CONTINUE
        DO 870 I=1,2500000
        DO 860 J=1,40000000
860     CONTINUE
870     CONTINUE
        pause
        CALL CLOSEG
C
C       ****SAVE FILE****
C
        WRITE(*,900)
900     FORMAT(' Do you want the fitted line data output to a file?-'\)
        READ(*,'(A1)') RESPON
        IF ((RESPON.EQ.'y').OR.(RESPON .EQ.'Y'))THEN
                WRITE(*,1000)
1000            FORMAT(' INPUT FILE NAME-'\)
                READ(*,1001) OUTFIL
1001            FORMAT(A)
                OPEN(6,FILE=OUTFIL,STATUS='NEW')
                DO 1100 I=1,21
                        WRITE(6,*) TIMINT(I),SICAL(I)
1100            CONTINUE
                CLOSE(6)
        ENDIF
        END
C
C       ****SUBROUTINES***
C
C       ****CALCULATE ALFA****
C
        FUNCTION ALFINT(TIMPAR,KZERO,CONCR)
        REAL KZERO
        COMMON AA,BB,CC,DD,EE,FF,BIGK,BIGL
        ALFINT=EXP(KZERO*CONCR*(- AA*(TIMPAR**6)
     *     -BB*(TIMPAR**5)-CC*(TIMPAR**4)-DD*(TIMPAR**3)-EE*(TIMPAR**2)
     *     -FF*TIMPAR))
        END
C
C       ****NUMERICAL SOLVE COMPONENTS OF 1-SI EQUATIONS****
C
        FUNCTION FUNC(U)
        COMMON AA,BB,CC,DD,EE,FF,BIGK,BIGL
        FUNC=(1.0-U)**2.0*U**(2.0*BIGK-BIGL-1.0)*EXP(-2.0*(1.0-BIGK)*
     *  (1.0-U))
        END
C
        FUNCTION SITWO(U)
        COMMON AA,BB,CC,DD,EE,FF,BIGK,BIGL
        SITWO=(1.0-U)*U**(2.0*BIGK-BIGL)*EXP(-2.0*(1.0-BIGK)*(1.0-U))
        END
C
        FUNCTION SCONST(ALP)
        COMMON AA,BB,CC,DD,EE,FF,BIGK,BIGL
        SCONST=EXP((1-BIGK)*(1.0-ALP)*(-2.0))*(2.0-ALP)*ALP**(2.0*BIGK)
        END
```

```
      PROGRAM CONTOUR
C-----------------------------------------------------------------
C       CONTOUR-PROGRAM FOR JUDGING THE GOODNESS OF FIT BETWEEN
C         THE BEST FIT LINE OF OBSERVED DATA AND CURVES CALCULATED
C         USING BOUCHER'S EQUATION (SEE KINET).  GENERATES OUTPUT
C         FILE WHICH CONTAINS 400 COMBINATIONS OF K AND L BASED ON
C         ESTIMATE OF LOWEST K AND L VALUES, AND THE SUM OF SQUARES
C         OF THE DIFFERECE BETWEEN CALCULATE DATA POINTS AND OBSERVE
C         VALUES.
C
C       CODE WRITEEN BY BRIAN DEVLIN, UMASS 1988.
C
C  REQUIRED INPUT:  SAME AS KINET
C
C  OUTPUT CAN BE EVALUATED AS A TABLE OF NUMBERS OR CAN BE TRANSFERRED
C     TO A XYZ GRAPHING PROGRAM FOR PLOTTING.
C-----------------------------------------------------------------
C
C       ****DECLARATIONS*******
C
      CHARACTER*64 FNAME,ONAME
      REAL KZERO, kmin, lmin
      EXTERNAL FUNC,SITWO,CUREQU
      COMMON AINT,BINT,CINT,DINT,EINT,FINT,BIGK,BIGL
      DIMENSION TIME(50),SI(50),TIMINT(21),ALPHA(21),
     *   BIGLA(20),BIGKA(20),SIEQU(21)
      DIMENSION ERROR(20,20)
      PARAMETER(B=9.999E-1)
C
C       ******INPUT*****
C
      WRITE(*,50)
      READ(*,75) FNAME
50    FORMAT(' INPUT DATA FILE NAME-'\)
75    FORMAT(A)
      OPEN(5,FILE=FNAME)
      READ(5,*) AEQ,BEQ,CEQ,DEQ,EEQ,FEQ
      READ(5,*) KZERO,CONCR
      DO 100 I=1,100
            READ(5,*,END=200) TIME(I),SI(I)
            NP=I
100   CONTINUE
200   CONTINUE
      CLOSE(5)
C
C       *****GET INTEGRAL COEFFICIENTS*****
C
      AINT=AEQ/6.0
      BINT=BEQ/5.0
      CINT=CEQ/4.0
      DINT=DEQ/3.0
      EINT=EEQ/2.0
      FINT=FEQ
C
C       ****SET INTERVAL FOR EVALUATION***
C
      SIZINT=TIME(NP)/20.0
      DO 300 I=1,21
            IF (I.EQ.1) THEN
                  TIMINT(1)=0.00
            ELSE
                  TIMINT(I)=FLOAT(I-1)*SIZINT
            ENDIF
300   CONTINUE
```

```
C
C       ***1-SI FROM FIT EQUATION*****
C
        DO 350 I=1,21
                SIEQU(I)=CUREQU(TIMINT(I),AEQ,BEQ,CEQ,DEQ,EEQ,FEQ)
350     CONTINUE
C
C       *****ALPHA FROM CURVE INTEGRAL*****
C
        DO 400 I=1,21
                ALPHA(I)=ALFINT(TIMINT(I),KZERO,CONCR)
400     CONTINUE
C
C       ******VARY K AND L******
C
        write(*,420)
        read(*,*) kmin
        write(*,430)
        read(*,*) lmin
420     format(' in put kmin')
430     format(' in put lmin')
        DO 700 KONE=1,20
                BIGKA(KONE)=kmin+FLOAT(KONE-1)*0.4/19.0
                BIGK=BIGKA(KONE)
        DO 600 KTWO=1,20
                BIGLA(KTWO)=lmin+FLOAT(KTWO-1)*0.4/19.0
                BIGL=BIGLA(KTWO)
                ERR=0.0
C
C       ****CALCULATIONS******
C
        DO 500 I=1,21
                CALL QROMB(FUNC,ALPHA(I),B,SONE)
                CALL QROMB(SITWO,ALPHA(I),B,STWO)
     *  SICAL=(2.0*BIGK*ALPHA(I)**BIGL)*SONE+
        (2.0*ALPHA(I)**BIGL)*STWO+SCONST(ALPHA(I))
        ERR=ERR+(ABS(SICAL-SIEQU(I)))**2
500     CONTINUE
        ERROR(KONE,KTWO)=ERR
        NCNT=(KONE-1)*20 +KTWO
        WRITE(*,550)NCNT
550     FORMAT('+',I3,' CONSTANT PAIRS ANALYZED')
600     CONTINUE
700     CONTINUE
        WRITE(*,710)
710     FORMAT(' INPUT FILE FOR ERROR VALUES--'\)
        READ(*,720)ONAME
720     FORMAT(A)
        OPEN(3,FILE=ONAME,STATUS='NEW')
        DO 800 I=1,20
                DO 750 K=1,20
                        WRITE(3,*) BIGKA(I),BIGLA(K),ERROR(I,K)
750             CONTINUE
800     CONTINUE
        CLOSE(3)
        END
        FUNCTION ALFINT(TIMPAR,KZERO,CONCR)
        REAL KZERO
        COMMON AINT,BINT,CINT,DINT,EINT,FINT,BIGK,BIGL
        ALFINT=EXP(KZERO*CONCR*(- AINT*(TIMPAR**6)-BINT*(TIMPAR**5)
     *    -CINT*(TIMPAR**4)-DINT*(TIMPAR**3)-EINT*(TIMPAR**2)
     *    -FINT*TIMPAR))
        END
```

```
C
      FUNCTION FUNC(U)
      COMMON AINT,BINT,CINT,DINT,EINT,FINT,BIGK,BIGL
      FUNC=(1.0-U)**2*U**(2.0*BIGK-BIGL-1.0)*EXP(-2.0*(1.0-BIGK)*
     *  (1.0-U))
      END
C
      FUNCTION SITWO(U)
      COMMON AINT,BINT,CINT,DINT,EINT,FINT,BIGK,BIGL
      SITWO=(1.0-U)*U**(2.0*BIGK-BIGL)*EXP(-2.0*(1.0-BIGK)*(1.0-U))
      END
C
      FUNCTION SCONST(ALP)
      COMMON AINT,BINT,CINT,DINT,EINT,FINT,BIGK,BIGL
      SCONST=EXP((1-BIGK)*(1.0-ALP)*(-2.0))*(2.0-ALP)*ALP**(2.0*BIGK)
      END
C
      FUNCTION CUREQU(T,A,B,C,D,E,F)
      CUREQU=A*T**5+B*T**4+C*T**3+D*T**2+E*T+F
      END
```

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MSD Isotopes LTD,*Deuterated NMR Solvents*-Handy Reference Data, circular .

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