THE ᴵRING-OPENING POLYMERIZATION OF CYCLOSILOXANES IN THE

PRESENCE OF

BIS(α,ω-AMINOPROPYL)-1,3-TETRAMETHYLDISILOXANE

by

Patricia M. ₕSormani⫽

Dissertation submitted to the Faculty of the

Virginia Polytechnic Institute and State University

in partial fulfillment of the requirements for the degree of

Ph. D.

in

Chemistry

APPROVED:

_____

James E. McGrath

_____   _____
Harold M. Bell   Thomas C. Ward

_____   _____
Garth L. Wilkes   James P. Wightman

February 1986

Blacksburg, Virginia

ACKNOWLEDGEMENTS

Sincere thanks and appreciation are extended to Professor J. E. McGrath for his guidance and support during the course of my graduate studies. The assistance of Professors Ward, Wilkes, Wightman, and Bell is also acknowledged.

There are many other people who must be acknowledged for contributions to the work contained in this dissertation: for DSC analysis and intrinsic viscosities respectively, Dr. Dinesh Tyagi for the WAXS measurements, Dr. Rajgopal Subramanian for the initial ^{29}Si NMR work, Dr. Mike Ogden for assistance with the initial capillary GC work, my fellow graduate students in the polymer synthesis and characterization groups for many helpful discussions. Finally, the assistance of   in making the figures contained in this dissertation is gratefully acknowledged.

Thanks go to all my friends who helped make my stay in Blacksburg enjoyable and especially to   for many enjoyable hours on the squash court. I also would like to thank my family for their love and support.

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1.0 INTRODUCTION

The preparation of well-defined functionally-terminated oligomers or prepolymers is of the utmost importance for the successful synthesis of a variety of high molecular weight block copolymers. It is desirable to have a knowledge of the molecular weight distribution of the functional oligomer and it is important to prepare exactly a difunctional system. Toward this end, studies of the fundamental processes by which functional oligomers are formed are of great interest.

An important class of polymers for the synthesis of interesting block copolymers are the polyorganosiloxanes. Functional polysiloxane oligomers are prepared by the anionic or cationic ring-opening polymerization of cyclic siloxanes. While the actual synthesis of these materials has been well-established, there has been relatively little fundamental work in this area, particularly in the area of functional polydimethyl-co-diphenylsiloxane oligomers. In this latter case, the reaction mechanism will play an important role in the sequence distributions of such co-oligomers, which in turn influences such properties as the glass transition temperature. An investigation of the processes occurring during these so-called equilibration reactions will yield useful information for the preparation of polysiloxane oligomers to be used in the synthesis of block or segmented copolymers.

2.0 LITERATURE REVIEW

2.1 INTRODUCTION

The field of siloxane chemistry has been of interest for quite some time and a number of comprehensive reviews are currently available [1-5]. This review will therefore attempt to present only the major aspects of organofunctional siloxanes as pertaining to this work.

Polyorganosiloxanes are probably the most important class of "semi-inorganic" polymers, so-called because of the inorganic backbone with organic structures attached. The backbone consists of alternating silicon oxygen bonds, with organic substituents such as methyl, phenyl, propyl, vinyl, cyanoalkyl, and so on, attached to the silicon atoms. Polysiloxanes possess a variety of interesting and unique properties such as good UV stability, lubricity, and a wide temperature use range, owing to the low glass transition temperature coupled with good thermal stability. A more complete listing of these properties is shown in Table 1.

Through the preparation of functionally terminated polysiloxane oligomers, these materials can be used to modify block copolymer properties. Polyesters, polycarbonates, polyimides and epoxy resins are a few examples of polymeric systems modifed by the incorporation of functionally-

terminated polysiloxanes [6-11]. Clearly then, it is of the utmost importance to prepare well-defined siloxane oligomers in the most efficient manner possible.

This work deals with different routes to functionally-terminated polysiloxane oligomers, the analytical techniques used to study these reactions, and the preparation of co-polymers from these materials.

Table 1.   Properties of Siloxanes

Thermal Stability
UV Stability
Biocompatibility
Lubricity
Low Glass Transition Temperature
High Gas Permeability
Low Surface Energy
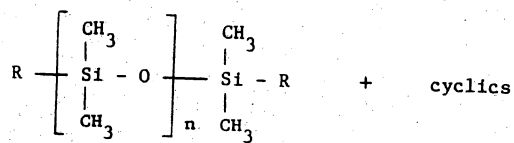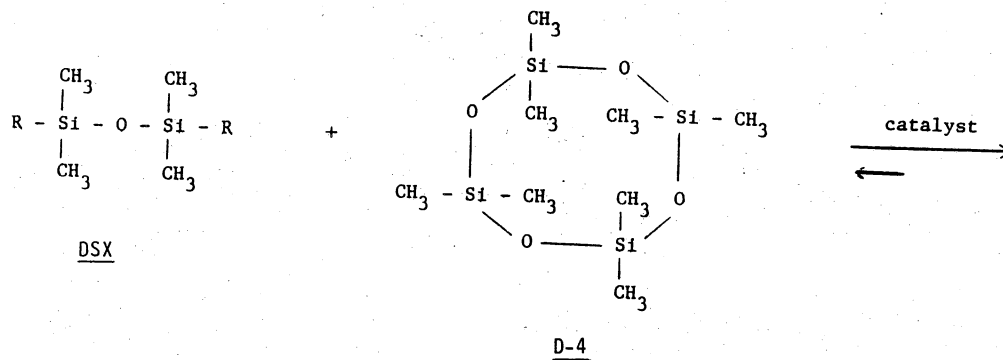
Figure 1. Synthesis of functionally-terminated polysiloxanes.

2.2 EQUILIBRATION REACTIONS

2.2.1 PREPARATION OF POLYDIMETHYLSILOXANE OLIGOMERS

One of the most common methods of preparing polysiloxane oligomers is by an equilibration or "redistribution" process, performed in bulk. Various cyclic siloxanes may be reacted with an appropriate acidic or basic catalyst in the presence of a suitable functional disiloxane as is shown generally in Figure 1. There have been a variety of types of disiloxanes employed; both basic and acidic functionalities have been used. The disiloxane, whatever the functionality, functions to regulate the molecular weight of the oligomer formed since the trialkylsiloxane unit in the dimer is monofunctional [4, 12].

There are a number of "redistribution" reactions occur-ring in these ring-opening polymerizations, shown in scheme 1. Siloxane terminology makes use of the symbol D to refer to a dimethylsiloxane unit and M to refer to a trimethylsiloxane unit. Thus, D_4 refers to octamethyl-cyclotetrasiloxane, MM refers to hexamethyldisiloxane (a nonfunctional end blocker), and -Dx- refers to a dimethyl-siloxane unit in a chain. These various processes occur be-cause the silicon-oxygen bonds in the linear species are of similar reactivity to the silicon-oxygen bonds in the cyclics towards the catalyst. The first two reactions illustrated

result in changes in the number average molecular weight of the system, while the third and fourth reactions result in a change in the overall molecular weight distribution. The relative rates of each of the processes - opening of the cyclic siloxanes vs. incorporation of the end blocker, for example - depend upon the type of catalyst that is used, for reasons that will be discussed shortly.

(1) $-Dx-$ + D_4 $\longrightarrow$ $-D(x+4)-$

(2) $-Dx-$ + MM $\longrightarrow$ MDxM

(3) MDxM + MM $\longrightarrow$ MD(x-5)M + MD_5M

(4) MDxM + MDyM $\longrightarrow$ MD(x+w)M + MD(y-w)M
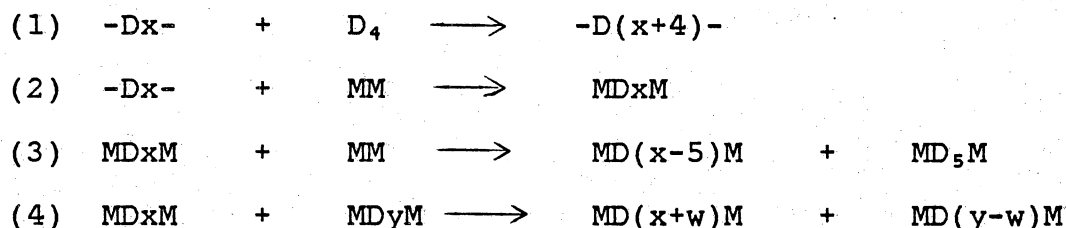
Scheme 1. Redistribution reactions occurring during a
         siloxane equilibration.

An alternative representation of the processes occurring during an equilibration reaction is shown in Figure 2. The reaction of a generalized siloxanolate catalyst with any cyclic siloxanes present, as well as with the functional disiloxane, is illustrated. Reactions 3 and 4 in scheme 1 are also illustrated here. Finally, the phenomenon of "backbiting" is also shown. Backbiting is that process by which the siloxanolate attacks a silicon-oxygen bond in the same chain on which it is located. This is possible due to

the flexible nature of the siloxane chain. One way to mini-
mize backbiting is to carry out the polymerization in bulk.
The addition of solvent will increase the amount of backbit-
ing that occurs, by decreasing the probability of the
siloxanolate encountering another chain or cyclic siloxane
to attack, and so increase the proportion of rings present
in the system.

In 1950 Stockmayer and Jacobsen published their now
classic paper which described the theory of molecular weight
distributions in ring-chain equilibrated polymer systems
[13]. This was the first paper which considered the presence
of cyclic structures. Details of the derivation will not be
repeated here. It was predicted that the rings formed are
small. It was also predicted that, while the actual concen-
tration of rings was not a function of dilution, the number
of rings should increase linearly with dilution, which makes
the proportion of rings in the system greater with increasing
dilution. Figure 3 illustrates their predicted distribution
for chain and ring species formed in an equilibrated polymer.

A flaw in Jacobson and Stockmayer's theory was found in
the case of unstrained small rings. Higher concentrations
were formed than were predicted by theory. Flory and co-
workers corrected the theory by adding a requirement that to
form a ring, two termini have to approach one another from a
specified direction [14, 15]. In the case of short chains
the probability of approach of two termini of one chain would

$\sim\!\!\sim\!\!\sim\overset{CH_3}{\underset{CH_3}{Si\!-\!O}}{}^{\ominus}\,{}^{\oplus}M$

$\left(\overset{CH_3}{\underset{CH_3}{Si\!-\!O}}\right)_n$

$\sim\!\!\sim\!\!\sim O^{\ominus}\,{}^{\oplus}M$
+
NEW CHAINS

TERMINATED OR
GROWING CHAIN

$\sim\!\!\sim\!\!\sim\overset{CH_3}{\underset{CH_3}{Si\!-\!O}}{}^{\ominus}\,{}^{\oplus}M$

CATALYST

$\overset{CH_3}{\underset{CH_3}{R\!-\!Si\!-\!O}}\overset{CH_3}{\underset{CH_3}{Si\!-\!R}}$

$\sim\!\!\sim\!\!\sim O\!-\!\overset{CH_3}{\underset{CH_3}{Si}}\!-\!R$

$\overset{CH_3}{\underset{CH_3}{R\!-\!Si\!-\!O}}{}^{\ominus}\,{}^{\oplus}M$

"BACKBITING"

$\sim\!\!\sim\!\!\sim\overset{CH_3}{\underset{CH_3}{Si\!-\!O}}{}^{\ominus}\,{}^{\oplus}M$
+
CYCLICS
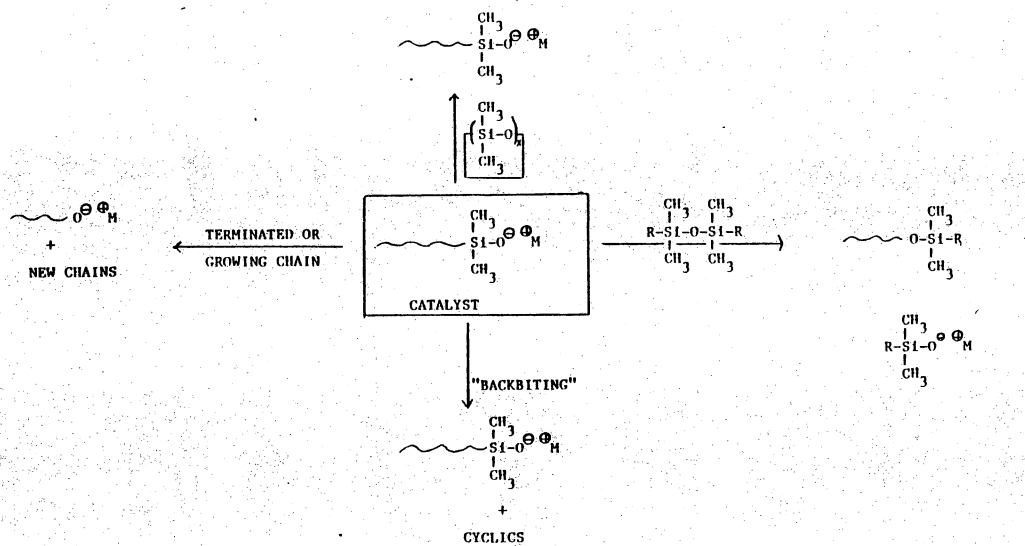
Figure 2.   Processes   occurring   during   a   polysiloxane
equilibration.

Literature Review
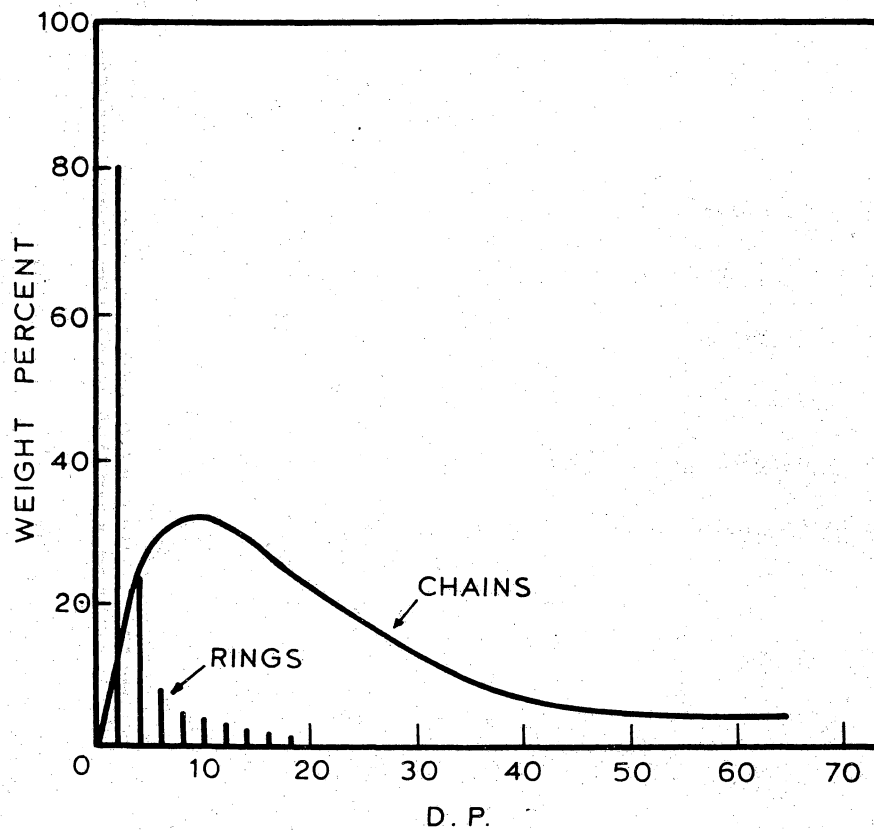
Figure 3. Ring-chain distribution in a polymer equilibrate.

depend on a variety of factors specific to the particular system, such as bond angles and steric factors.

There have been a number of studies since that time concerned with determining equilibrium distributions of cyclics and linears in polysiloxanes [see for example, 16-21, 28, 29, 30], all essentially agreeing with the Flory theory.

There are a variety of catalysts that can be successfully used to prepare organofunctional siloxane oligomers. Generally, protonic and Lewis acids and bases are useful catalysts. Since this work is concerned with the preparation of aminopropyl-terminated siloxane oligomers, only the subject of basic catalysts will be treated here. The reader interested in acid-catalyzed equilibrations is referred to the excellent review by Wright [2]. The decision of whether to use an acidic or a basic catalyst depends on the type of functional siloxane that is being prepared. A disiloxane with a basic functionality, aminopropyl, for example, would require a basic catalyst. Otherwise, the acidic catalyst might first react with the amine, rather than the siloxane bond.

Bases such as alcoholates, hydroxides, phenolates of the alkali metals, quaternary ammonium and phosphonium bases, as well as the corresponding siloxanolates and fluorides have all been used as equilibration catalysts [1-4]. It is believed that all these generate the siloxanolate in situ; alternatively the siloxanolate may be prepared separately prior

to use in the equilibration reaction, as is discussed in chapter 5. It is the siloxanolate which attacks the silicon-oxygen bond in either the cyclic or linear species present.

Among the alkali metal hydroxides and siloxanolates, the activity decreases in the order Cs > Rb > K > Li [22]. Potassium hydroxide is perhaps one of the most commonly used. The use of potassium hydroxide as an equilibration catalyst allows the reaction to be conducted at high temperatures, if desired. Temperatures as high as 160°C have been used [51]. This type of catalyst is a non-transient catalyst. In order to obtain a thermally stable polymer at the end of the polymerization - an important consideration - the catalyst must be removed or neutralized.

Alternatively, a so-called transient catalyst may be employed. A transient catalyst is one which decomposes upon heating to products which are not catalytically active to-wards siloxane equilibration. Important examples of these include the tetraalkyl-phosphonium and -ammonium bases. Tetramethylammoniumhydroxide is a commonly used transient catalyst. Upon heating above 130°C this catalyst decomposes to trimethylamine, which is volatile at these temperatures, and methanol or methoxy-terminated siloxane [23, 39], none of which are effective equilibration catalysts. One unat-tractive feature of this particular catalyst is the lingering odor of the trimethylamine, which is difficult to remove

completely. The quaternary phosphonium bases, also effective transient catalysts [23], decompose to phosphine oxides and hydrocarbons, which do not have as disagreeable an odor as the amine products. These materials, however, have not been as extensively studied as the quaternary ammonium bases.

The question of the process by which these reactions proceed has been investigated by a variety of techniques [3, 12, 16, 24, 25]. The formation of polymer has usually been studied rather than the disappearance of starting materials. Kantor and co-workers, for example, made viscosity measurements as a function of time, which indicated the formation of polymeric species and yielded some mechanistic information as well [12]. In a base-catalyzed equilibration, an increase in viscosity is initially observed, followed by a decrease in viscosity. The opposite effect, a slow increase in viscosity to some approximately constant value, is observed in an acid-catalyzed equilibration. In the base-catalyzed process, the initial increase in viscosity corresponds to the opening up of the D_4 ring - an increase in the molecular weight of the system. The decrease in viscosity corresponds to the incorporation of the disiloxane, which is a slower process, corresponding to a decrease in the higher moment molecular weight averages. The reason for the faster reaction of D_4 compared to a disiloxane in a basic equilibration lies in the electron density of the silicon atom in each case. In the D_4 ring the silicon atom has two

oxygen atoms directly bound, resulting in a more
electropositive silicon atom and therefore a silicon-oxygen
bond which is more readily attacked by a nucleophile. A
silicon atom in a disiloxane is not as electropositive since
only one oxygen atom is attached. Therefore, that silicon-
oxygen bond is not as easily broken by a nucleophile. In an
acid-catalyzed equilibration the less electropositive
silicon atom would be more readily attacked by the
electrophilic catalyst, hence the faster reaction of the
disiloxane and slower reaction of D_4 leading to a gradual
increase in the molecular weight of the system. The order
of reactivity for dimethylsiloxane equilibration in a base-
catalyzed process was found by Kantor et al. to be $D_3 > D_4 >$
$MD_2M > MDM > MM$ [12].

A number of mechanisms have been proposed for the base-
catalyzed process [12, 22, 26]. While Hurd and co-workers
observed that inductive effects play some role in accounting
for reactivities in this process [22], Kantor and co-workers
[12] assumed that nucleophilic attack on the silicon atom by
the siloxanolate anion is the crucial step:

$$
\begin{array}{c}
\overset{R}{\underset{|}{\;}}\;\overset{R}{\underset{|}{\;}} \\
\end{array}
$$

R R   R R   R R   R R   R R   R R
 \ /   \ /   \ /   \ /   \ /   \ /
—Si—O$^{\ominus}$ +   —Si—O—Si—   →   —Si—O—Si— + $^{\ominus}$O—Si—
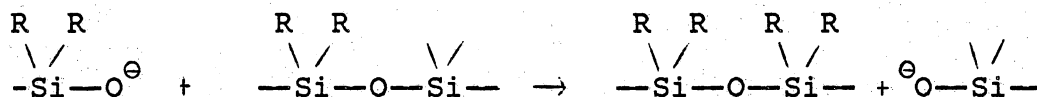
Hurd et al. found that KNH_2 and KOH were equally effective in promoting these reactions [22]. This indicated that the hydroxide or amide anions do not participate in the reaction after the initiation step.

Grubb and Osthoff [24] performed some early kinetic work on the reaction of D_4 with potassium hydroxide and potassium siloxanolate catalysts. Their technique was to monitor the vapor pressure of the reaction mixture and compare that with the vapor pressure over mixtures of polymer and known amounts of D_4 It was found that the reaction was first order in D_4 concentration and 1/2 order in catalyst concentration. Their conclusions on the mechanism are illustrated in equations 5 through 7.

$$(5) \quad -\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}- \ + \ KOH \longrightarrow -\overset{|}{\underset{|}{Si}}-O^{\ominus}{}^{\oplus}K \ + \ HO-\overset{|}{\underset{|}{Si}}-$$

$$(6) \quad -\overset{|}{\underset{|}{Si}}-O^{\ominus}{}^{\oplus}K \longrightarrow -\overset{|}{\underset{|}{Si}}-O^{\ominus} \ + \ {}^{\oplus}K$$

$$(7) \quad -\overset{|}{\underset{|}{Si}}-O^{\ominus} \ + \ \underset{\underset{O}{\diagdown \diagup}}{Si \quad Si} \longrightarrow -\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}\sim\sim\sim-\overset{|}{\underset{|}{Si}}-O^{\ominus}$$
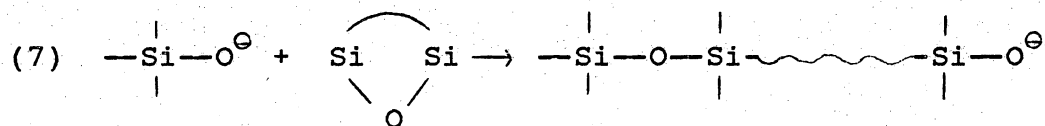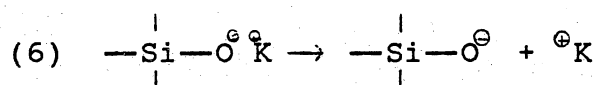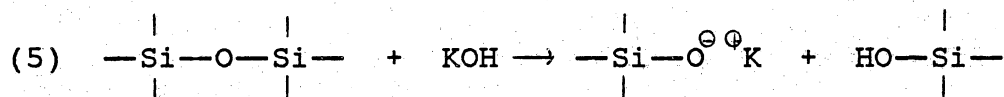
The nature of the ion pair in equation 6 is still in question. Russian workers have noted a deviation from linearity at high catalyst concentrations in a plot of catalyst concentration

vs. degree of polymerization [27] and postulated the forma-
tion of stable associates of the type shown below.
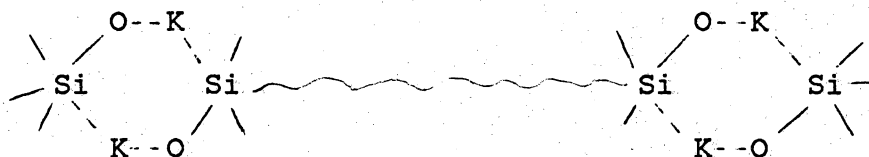
In addition, Mazurek and Chojnowski have suggested [25] ad-
ditional aggregation of the types shown below.
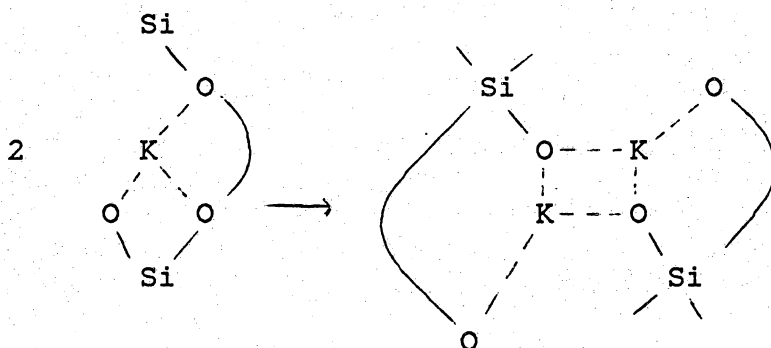
   It seems likely that the siloxanolate anion must be
"free" in order to participate in the polymerization, rather
than bound up in a complex. Along this line, work has been
done with the addition of polar additives to increase the
rate of reaction, presumably by shifting the equilibrium more
toward the unassociated siloxanolate [31-38]. There is still
room for exploration of the mechanism by which these
siloxanolate catalysts function.

2.2.2 PREPARATION OF POLYDIMETHYL-CO-DIPHENYLSILOXANES

Polydimethyl-co-diphenylsiloxanes have also been of considerable interest and are treated in some detail in The Siloxane Bond [3]. There are several methods of preparing these materials. One route involves the use of cyclic siloxanes where some of the silicon atoms in the ring are dimethyl substituted and some are diphenyl substituted [40-42]. Alternatively, cyclic siloxanes may be used in which the silicon atoms in the ring have both a methyl and a phenyl substituent attached [43,44]. The use of this type of cyclosiloxane allows exactly a 50/50 molar methyl/phenyl oligomer to be prepared. However, these types of cyclics are typically difficult to prepare.

A fairly common way of preparing these co-oligomers is to copolymerize octaphenylcyclotetrasiloxane, D_4'', with D_4. This system has been studied fairly well, but again the polymer formation as a function of time has apparently always been the technique used to study the reaction. Initial work [50] seemed to indicate that the D_4'' ring was exclusively polymerized at the expense of the D_4 early in the reaction. Subsequent work [47, 49] revealed some slight polymerization of D_4 early in the reaction when the polymerization was carried out with potassium tetraphenylsiloxanediolate as catalyst, although the product obtained was still enriched in diphenylsiloxane units compared with the feed composition.

As the amount of D_4'' in the charge increased, the rate of polymer formation and the equilibrium yield decreased [47].

Andrianov and co-workers also observed the formation of "mixed cyclics", which have both dimethylsiloxane and diphenylsiloxane units present in the same ring, fairly early in the polymerization [47]. Values for the reactivity ratios by the Mayo-Lewis method indicated a tendency towards alternation of the siloxane units. Quantitative results could not be strictly obtained since there was a strong tendency for chain-transfer to the polymer. Considering the alternation of the dimethyl- and diphenylsiloxane units, and recalling the backbiting process, it is not surprising to observe the formation of mixed cyclics.

The reason for the faster incorporation of the D_4'' ring compared with the D_4 ring again is concerned with the electron density of the silicon atom in the ring. In the D_4'' ring, the electron-withdrawing phenyl substituents make the silicon atom more electropositive and cause the ring to be opened more easily by a basic catalyst. However, once the ring is opened and a new siloxanolate anion is formed, the phenyl substituents act to stabilize the negative charge. This siloxanolate anion is therefore a weaker nucleophile and the reaction then proceeds more slowly. This is a clear case of electronic effects playing a much greater role in determining the course of a reaction than steric effects. In general, the substitution of electron-acceptor substituents

speeds up the base-catalyzed equilibration reaction of cyclic siloxanes.

2.3 ANALYTICAL TECHNIQUES

2.3.1 HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

The applications of high performance liquid chromatography (HPLC) in polymer characterization are well established [52-70, 80, 81]. However, most studies have been in the area of gel permeation (or size exclusion) chromatography [71-74, for example]. Polymer characterization results obtained from gel permeation chromatography (GPC) represent a portion of many papers that focus principally on synthetic polymer chemistry.

In spite of the popularity of GPC analysis, the technique suffers from relatively poor resolution and a limited peak capacity as compared with conventional liquid chromatography. Recent developments in packing methods for GPC have improved this situation somewhat [see ref. 71 for example]. However, for moderately low molecular weight oligomers HPLC, whether normal-phase or reversed-phase, appears to be the preferred technique.

Polystyrene oligomers have probably been the most widely studied by HPLC [52-56]. Analysis of a polystyrene standard with a molecular weight of $\simeq$ 600 g/mole on a reversed-phase

column (C_{18}) revealed the presence of 11 peaks [54] while the same material analyzed by conventional GPC would presumably give only one peak. Both gradient as well as isocratic liquid chromatography may be used to give adequate resolution. Normal-phase as well as reversed-phase materials give adequate resolution with reasonable analysis times.

Another example of the use of HPLC in polymer chemistry is work done by Krajnik and co-workers [69,70]. These workers studied the presence of cyclic oligomers in the polymerization of lactams. The cyclics were extracted from the polymer and successfullly separated by reversed-phase HPLC. No attempt was made to separate the linears from the cyclics by HPLC.

Finally, work has been done by Sormani and co-workers [78, 79] dealing with the ring-opening polymerization of octamethylcyclotetrasiloxane. Reversed-phase HPLC again was the preferred technique over GPC analysis. In fact, GPC was not a viable option here due to the $1°$ amine functionality of the polysiloxane, which would cause adsorption of the oligomer onto many GPC columns, such as microstyrogel.

Reversed-Phase HPLC is clearly a technique which deserves further attention from polymer chemists, particularly in the characterization of low molecular weight functional oligomers. For details of the theory involved and some practical aspects of modern HPLC the reader is referred to

the excellent books by Krstulovic and Brown [82] and Molnar [83].

2.3.2 GAS CHROMATOGRAPHY

Gas Chromatography is a chromatographic technique that has, understandably, not received much attention in the area of polymer characterization. However, Kleinert and Weschler [28] did use gas chromatography-mass spectrometry to identify cyclic siloxanes produced in the pyrolysis of some polydimethylsiloxanes. Carmichael and co-workers [16, 17] were able to separate cyclic and linear siloxanes in an equilibrated material up to a molecular weight of 2530 g/mole. Packed columns, with a diphenyldimethylsiloxane stationary phase, were used up to 400°C [17].

With the increasing popularity of capillary gas chromatography, more possibilities for the application of GC to oligomer characterization are opened up. Capillary GC offers a number of advantages over packed column chromatography [89]. Capillary GC allows longer column lengths, increased sensitivity, and faster analysis times, for example.

However, capillary GC is also limited in terms of the molecular weight of the materials that can be studied due to the volatility requirement. Sormani and co-workers [78, 79] have successfully used capillary GC to monitor the disap-

pearance of the functional end blocker in a siloxane equilibration. Presumably, as packing materials with higher temperature limits become more available, the molecular weight limit should become less of a problem and make capillary GC an even more useful technique for oligomer characterization.

2.3.3 ^{29} SI NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

INTRODUCTION

^{29} Si NMR is potentially an extremely powerful tool for the structural characterization of organosilicones. Lauterbur's review [99] in 1962 was one of the first to report the direct observation of the ^{29} Si nucleus in liquids. Since that time, and especialy with the advent of Fourier-Transform NMR, the field of ^{29} Si NMR has grown tremendously. A number of reviews have been published in this area [90-92, 99]. This review presents the important features of ^{29} Si NMR, the terminology in common use, and those facets of the technique of particular importance for the analysis of functional siloxane co-oligomers.

FEATURES OF ^{29} SI NMR

There are several properties of the ^{29} Si nucleus which must be considered at the outset, listed in Table 2. The ^{29} Si nucleus suffers from a low natural abundance, low sensitivity

and negative magnetogyric ratio. The situation is comparable to that for the ^{13}C nucleus. The problem of low sensitivity has been largely helped by the advent of Fourier-Transform NMR, FT-NMR. The theory of FT-NMR has been well documented [see, for example, Farrar and Becker, 100] and will not be duplicated here. In addition, the [29]Si nucleus has a long spin-lattice relaxation time, T_1, that is greater than 20 seconds. This requires long delays between pulses in an FT-NMR experiment. The negative magnetogyric ratio means that, when ^{1}H decoupling is employed, a negative Nuclear Overhauser Effect (NOE) is observed, resulting in negative or nulled peaks. This problem may be overcome by the addition of a small amount ($\simeq 0.02$ M) of a shiftless relaxation agent such as chromium triacetylacetonate [101, 102]. A paramagnetic relaxation agent such as this reduces the T_1 to only a few seconds by replacing other relaxation mechanisms with electron-nuclear dipole-dipole interactions, which are highly efficient, and removes the NOE. Since there are other techniques for reducing T_1 values and enhancing the sensitivity (selective population transfer [103], and cross-polarization [104], for example), it is important to define the experimental conditions used very precisely.

At the present time, the known range over which [29]Si resonances appear is > 550 ppm, although most appear within a 250 ppm range. The [29]Si nuclei in functionally-terminated polydimethyl- and polydimethyl-co-diphenylsiloxanes appear

over approximately a 60 ppm range. There are extensive tabulations of these chemical shift data published [92, for example]. It is important to clearly define the scale and reference used since there is no universally accepted standard, although tetramethylsilane, TMS, is a fairly commonly used reference. The choice of an appropriate reference depends largely on the silicone compounds to be analyzed, the solvent and the temperature used in the NMR experiment. When TMS is used as the reference, chemical shifts are reported in ppm with positive values to high frequency (and low field) and negative values to low frequency (high field).

Common terminology in this field makes use of the letters M, D, T, and Q, which represent $R_3SiO_{1/2}$, $R_2Si(O_{1/2})_2$, $RSi(O_{1/2})_3$ and $Si(O_{1/2})_4$ units respectively. R represents either aliphatic or aromatic substituents, such as methyl, hydrogen, and phenyl. Shown in Figure 4 is the range of chemical shifts for the various types of structural units in siloxanes [90, 95]. Substituents other than methyl are indicated as superscripts. For example, "D" represents a dimethylsiloxane unit, "D^{PH}" a methylphenylsiloxane unit and "D^{PH_2}" a diphenylsiloxane unit. The ability of ^{29}Si NMR between D, T, and Q structures has been clearly demonstrated [93, 94].

Table 2. ^{29}Si Characteristics

Spin = 1/2

Abundance = 4.7 %

Rel. Sensitivity = 7.84 x 10^3

Magnetic Moment = -0.961

Magnetogyric Ratio = -5.3 x 10^7

Negative NOE with ^{1}H decoupling

Long spin lattice relaxation (T_1 > 20 sec.

Chemical shift range > 550 ppm
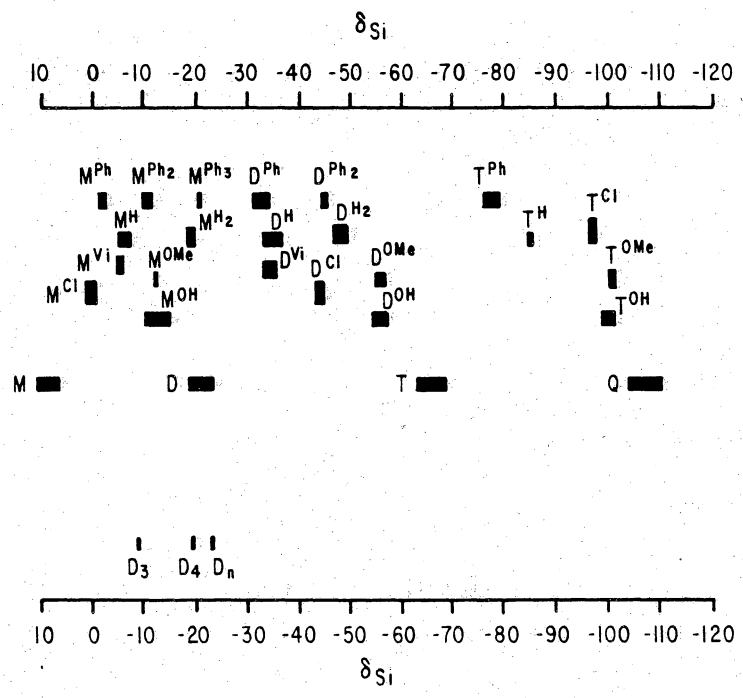
Figure 4.   Chemical shifts of different structural units
            in ^{29}Si NMR.

The power of ^{29}Si NMR over ^{1}H and ^{13}C NMR in the study
of polysiloxanes is illustrated in Figure 5 [90]. The ^{1}H NMR
spectrum of a dimethylsiloxane oligomer, MD$_3$M, provides no
structural information. While the ^{13}C and ^{29}Si NMR spectra
differentiate between the "M" silicon atom and "D" silicon
atom, the ^{29}Si NMR spectrum also distinguishes between the
two different types of D units. In fact, individual reso-
nance lines have been reported for each silicon atom up to a
10 unit oligomer [91, 94, 96, 97]. In addition, specific end
group effects have been observed. That is, the type of M unit
will affect the position of the chemical shift of that
silicon atom. For example, a trimethylsiloxane unit on the
end of an oligomer appears at 7.07 ppm [96] while a silicon
atom in the group $NH_2(CH_2)_3Si(CH_3)_2$ appears at 7.35 ppm (see
chapter 5), a significant and reproducible difference. The
type of silicon nucleus adjacent to the silicon in the M
group will also affect the chemical shift of the M silicon.
This suggests that in a siloxane co-oligomer, dimethyl-co-
diphenyl for example, different types of end group silicon
peaks could be observed, depending on whether the first D
unit, and the second, and so on, was a dimethyl-substituted
silicon or a diphenyl-substituted silicon.

There have also been differences in chemical shift ob-
served for linear vs. cyclic siloxanes. Table 3 shows the
^{29}Si chemical shift for a series of cyclic dimethylsiloxanes
and linear polydimethylsiloxanes [91]. Hexamethyl-
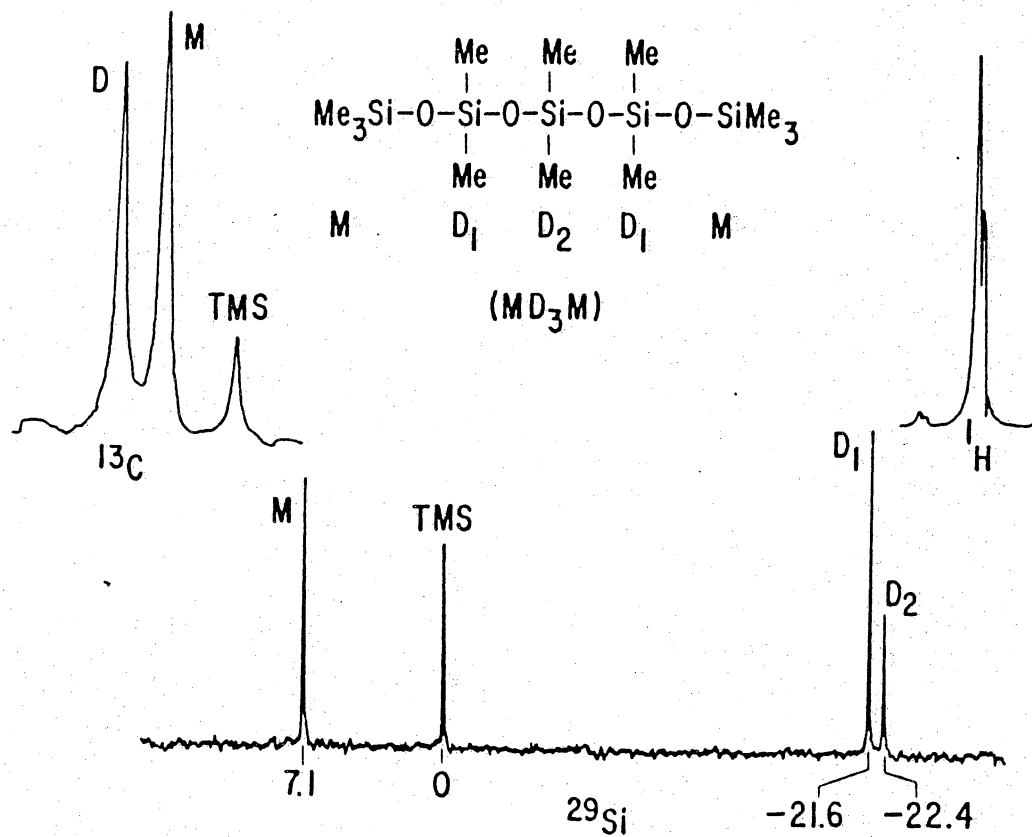
Figure 5. Comparison of ^{1}H, ^{13}C, and ^{29}Si NMR spectra of dodecamethylsiloxane [90].

cyclotrisiloxane, D_3, and D_4 have signals which are shifted
to higher frequency than the linear siloxanes due to ring
strain effects. The same trend occurs when groups other than
methyl are attached to silicon.

There have been a number of studies dealing with the
observed ^{29}Si NMR spectra of siloxane co-oligomers [95, 96,
98, 105]. For example, Engelhardt and Jancke [95] studied
methylphenylsiloxane copolymers. It had been shown by model
compound studies [106] that increasing numbers of phenyl- or
diphenyl-substituted silicon nuclei in the neighborhood of a
given silicon nucleus led to higher-frequency chemical
shifts. Shown in Figure 6 is a schematic representation of
the assignment for an expected theoretical distribution of a
copolymer of A and B units, of 50/50 molar composition [95].
A "triplet of triplets" is observed, due to nearest neighbor
effects, in the A and B region of the spectrum. Therefore,
the experimentally obtained ^{29}Si NMR spectrum should yield
valuable information on the sequence distribution of siloxane
copolymers. This will be discussed more fully in chapter 5.

δ Si (ppm from TMS)					
Compound	M	D^1	D^2	D^3	D^4
MM	6.79				
MDM	6.70	-21.5			
MD_2M	6.80	-22.0			
MD_3M	6.90	-21.8	-22.6		
MD_4M	7.00	-21.8	-23.4		
MD_5M	7.0	-21.8	-22.4	-22.3	
MD_6M	7.0	-21.8	-22.3	-22.2	
MD M	7.0	-21.89	-22.49	-22.33	-22.29
MD_8M	6.93	-21.86	-22.45	-22.3	-22.2
D_3		-9.12			
D_4		-19.5			
D_5		-21.93			
D_6		-22.48			

SEQUENCE

```
            A           B  B     A        B  A  A           B  A  A        B  B     A        B  A  A
   B  B  |--A--|     |--A--A--|  A     |--A--A--A--|     B  A  A     |--B--B--|  A     B  B  |--A--A--|  A
B--A  B--A  B  A  B--A  A  B  A--A  B--A--A  A  B  A--A  B--B--A  B--B  A--B  A  B--A--A  A  B--B--A  B--A--A
|  |  |  |  |--|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
B     B     A     B     A     A     B     B     A     B     B     A     A     A     B     B     A
```

NMR
SPECTRUM


```
[22][21][20]   [12][11][10]  [02][01][00]      [00][01][02]   [10][11][12]   [20][21][22]
PENTAD

   [ 2 ]           [ 1 ]         [ 0 ]            [ 0 ]           [ 1 ]          [ 2 ]
TRIAD
```

Figure 6.   Theoretical ^{29}Si NMR sequence distribution.

3.0 RESEARCH INTRODUCTION

This study investigated the fundamental processes oc-
curring in the synthesis of functionally-terminated polydi-
methylsiloxane and polydimethyl-co-diphenylsiloxane
oligomers. The purpose of this study was not to develop
complicated and extensive rate laws for the mechanism of the
formation of these oligomers, but rather, to determine the
most efficient ways of preparing them.

The first task to accomplish was the determination of
suitable techniques for the study of these reactions. Re-
versed-phase high performance liquid chromatography was a
very useful technique in this area. The concentration of
both cyclic starting materials could be monitored fairly ea-
sily using this technique.

In order to monitor the concentration of the functional
siloxane, capillary gas chromatography proved to be the
technique of choice. In this study, oligomers with a tar-
geted molecular weight of 1200 g/mole were studied. At low
targeted molecular weights, of course, the molar amount of
aminopropyl disiloxane that is added is quite large and it
is most critical to incorporate as much of the disiloxane as
possible into the linear species in order to obtain a per-
fectly difunctional oligomer of controlled molecular weight.
If nearly all of the disiloxane, as well as the cyclics, is

not incorporated, neither the yield of linear species nor the desired functionality will be acceptable. Since only low molecular weight systems could be studied with this technique, and since the samples injected must be reasonably volatile, the dimethyl-co-diphenylsiloxane oligomers were not analyzed for disiloxane content.

The next parameter of importance in the polydimethyl-co-diphenylsiloxane systems is the number average sequence length of each type of siloxane unit. The nature of the distribution - blocky, statistical, or alternating - can play a major role, along with the composition and molecular weight, in determining some of the physical properties of the co-oligomer. For example, blocky co-oligomers, that is systems with long sequences of dimethylsiloxane and diphenylsiloxane units, would be expected to have two glass transition temperatures, one for each type of siloxane unit [11]. By studying the effect of reaction conditions on the sequence distributions in the co-oligomers it may be eventually possible to tailor make oligomers with specific sequence distributions and thus the desired properties.

^{29}Si nmr proved to be an invaluable technique in this regard. To date, there have been no experimental studies of the change in sequence distributions in polydimethyl-co-diphenylsiloxane oligomers as a function of reaction conditions and time. There have been reports of the ^{29}Si chemical shifts of various model compounds [92], and this was also the

initial work done in our laboratories [11, 98]. Once the chemical shifts for the various cyclic siloxanes, the disiloxane and the different types of <u>linear</u> siloxane units were established, the sequence distributions as a function of time at various reaction temperatures could be studied using both types of catalysts.

Contained in the second appendix are some preliminary investigations of the preparation of poly(butyleneterephthalate-co-dimethylsiloxane) copolymers. These polymers were initially prepared via a melt condensation technique taking advantage of the commercially important "ester interchange" process. It was hoped that the amide groups formed due to the aminopropyl-terminated polydimethylsiloxane oligomer would not participate in the ester interchange reaction, or at least would react more slowly than the ester linkages.

The polymers prepared in this fashion were highly crystalline materials and it was difficult to obtain high molecular weight polymers. Due to the high degree of crystallinity, thay were insoluble in many common solvents such as methylene chloride, chloroform, tetrahydrofuran, and n methyl pyrolidone. Characterization of these materials was largely limited to analysis by Fourier Transform infrared spectroscopy and wide angle x-ray patterns. For this reason, attempts were made to incorporate isophthalate linkages to disrupt the crystallinity. This was done via the melt con-

densation process, as well as by a solution technique. These oligomers could be analyzed by ^{1}H nmr for siloxane content as well as by FTIR, WAXS and intrinsic viscosity measurements. Even these oligomers possessed some crystallinity and so posed some insolubility problems. Vapor pressure osmometry, for example, could not be easilyperformed on all the products due to insolubility in the preferred toluene solvent.

4.0 EXPERIMENTAL

4.1 SYNTHESIS AND CHARACTERIZATION OF SILOXANOLATE CATALYSTS

4.1.1 POTASSIUM SILOXANOLATE CATALYST

The preparation of potassium siloxanolate catalyst was carried out in bulk. Potassium hydroxide pellets (certified, Fisher Chemical Company) were crushed and placed in the reaction vessel. Enough octamethylcyclotetrasiloxane was then added to produce a molar ratio of 10 moles D_4 to 1 mole potassium hydroxide. An argon stream was passed through the reaction mixture while stirring with an overhead mechanical stirrer as shown in Figure 7. The reaction mixture was heated to 120°C in a silicone oil bath for approximately 24 hours. After 24 hours the product, a transparent viscous material, was transferred into small vials which were then sealed and stored in a desiccator for later use.

An alternative method for the preparation of this catalyst was also briefly explored. In this method, enough toluene to make approximately a 50% wt/vol solution was added to the D_4/KOH mixture in order to function as an azeotroping agent. The catalyst was heated at 95°C for about 12 hours and then at 120°C for an additional 12 hours. After 24 hours,

OVERHEAD
STIRRER

CONDENSER

STIRRING ROD

DEAN STARK
TRAP

ARGON
INLET
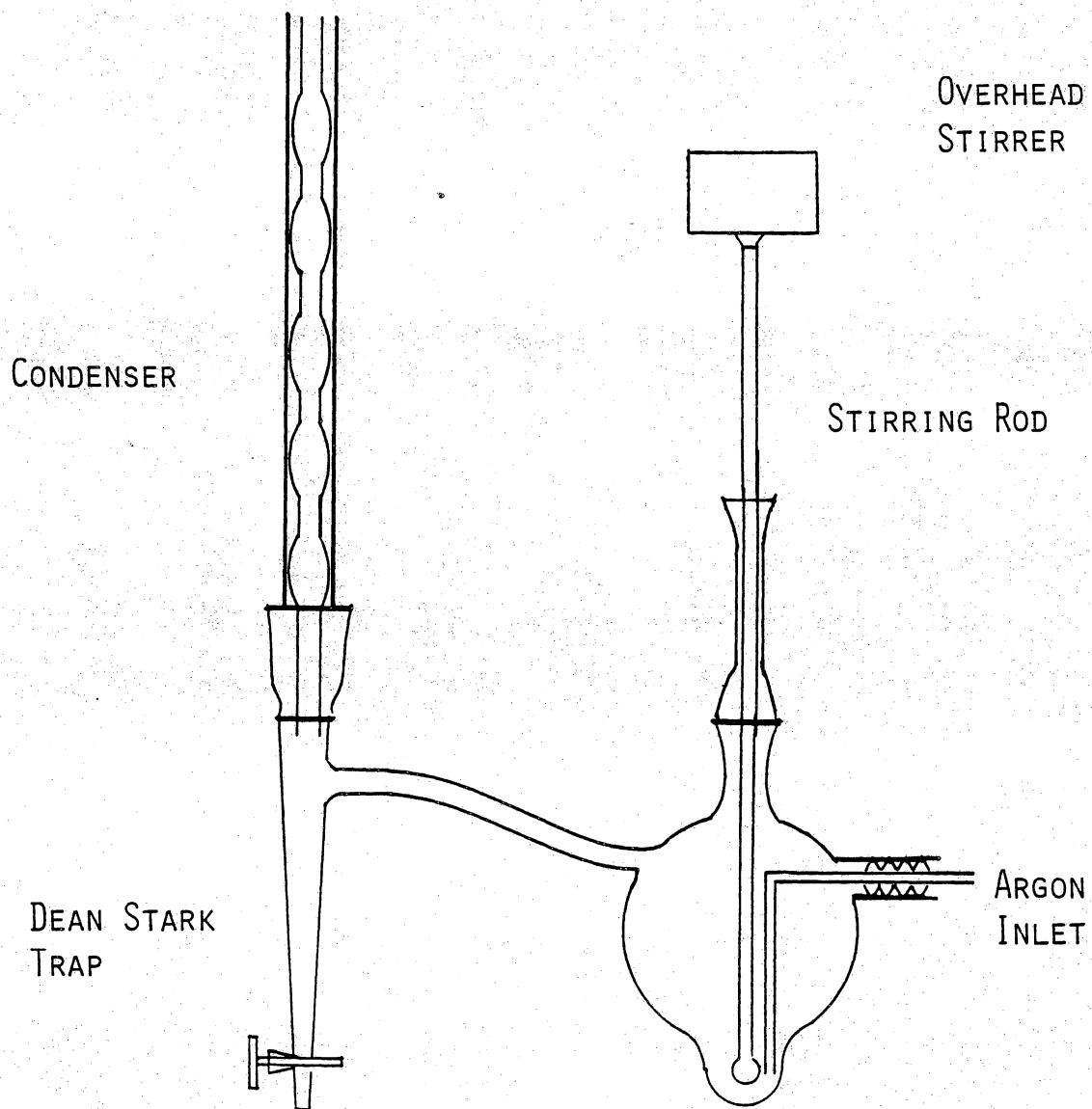
Figure 7. Apparatus for the preparation of potassium
siloxanolate catalyst.

Experimental

the product, transparent and viscous, was poured into vials, sealed and stored in a desiccator until use.

In order to determine the amount of potassium hydroxide (and thus the siloxanolate groups) present, the potassium siloxanolate catalyst was titrated with hydrochloric acid (0.0995 N in isopropanol, from Fisher Scientific) according to the following procedure: A known amount of catalyst (≈0.25 g.) was placed in a beaker with a magnetic stirring bar. Early work utilized a solvent system of 100 ml. iso-propanol (certified, Fisher Scientific) and 20 ml. distilled water with bromophenol blue as indicator (certified, 0.04 % solution from Fisher Scientific). The solution was allowed to stir for 30 minutes and was then titrated with a Fisher automatic titrator. Later work utilized a solvent system of 50 ml. isopropanol and 50 ml. tetrahydrofuran (certified, from Fisher Scientific) with bromophenol blue indicator. Each solvent system gave the same endpoint.

Proton NMR (^{1}H NMR) spectra were obtained on a Bruker 270 MHz instrument as described in section 4.2.5. No evidence for a silanol proton was observed. The absence of a silanol proton indicates the probability that this catalyst is a difunctional catalyst, ie. each oligomeric chain has a siloxanolate group at both ends.

4.1.2 TETRAMETHYLAMMONIUM SILOXANOLATE CATALYST

Tetramethylammonium siloxanolate catalyst was prepared in a similar manner to that described for the potassium catalyst. The reaction vessel is shown in Figure 8. In this case, tetramethylammonium hydroxide pentahydrate (TMAH) (97%, Aldrich Chemical Co.) was added to the flask and enough D_4 added to make a 10/1 molar ratio of D_4 to TMAH. The reaction mixture was heated in a silicone oil bath to approximately 80°C under a steady stream of argon with stirring by a magnetic stirring bar. The evolution of water from the system was indicated by the appearance of a pink color in the drierite (anhydrous $CaSO_4$ from Hammond). The material passed through an extremely viscous stage where the magnetic stirring bar was unable to stir the reaction mixture. Agitation was accomplished during this time period by the rapid stream of argon. After a period of usually several hours, the drierite began to regain its blue color, indicating reasonable dryness, and the stirring bar was again able to stir the reaction mixture. After 24 hours, the siloxanolate catalyst, a slightly viscous, but still cloudy material, was poured into vials, which were then sealed and stored in a dessicator until later use.

This catalyst was titrated with ethanolic hydrochloric acid (0.0995 N) in a solvent system of 50 ml. isopropanol and

DRYING TUBE

ARGON INLET

STIRRING BAR
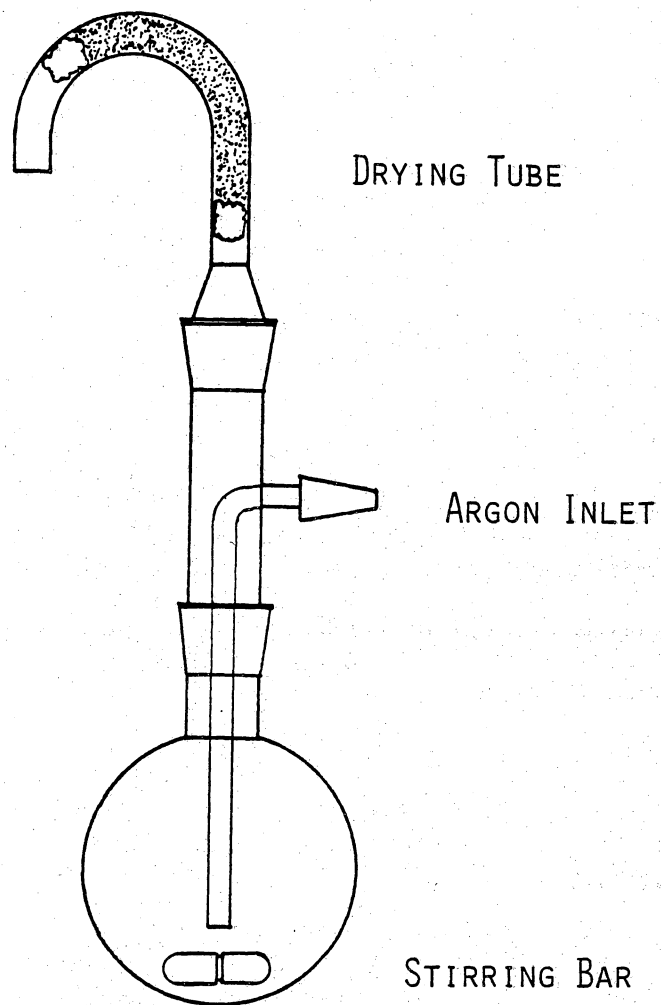
Figure 8.   Apparatus for the preparation of tetramethyl-
ammonium siloxanolate catalyst.

Experimental   40

50 ml. tetrahydrofuran, as described earlier for the potassium catalyst.

The ^{1}H nmr spectrum, run in deuterated chloroform as described in section 4.2.5, showed the presence of a a silanol proton, indicating that this catalyst could contain at least some monofunctionality. Limited thermal stability prevented the complete dimerization of the catalyst, unlike the potassium based system.

4.2 PREPARATION OF AMINOPROPYL-TERMINATED POLYDIMETHYL SILOXANE OLIGOMERS

4.2.1 PURITY OF STARTING MATERIALS

Octamethylcyclotetrasiloxane, D_4, was kindly provided by the General Electric Company and used as received. Bis(α,ω-aminopropyl)-1,3-tetramethyldisiloxane (referred to as the disiloxane) was obtained either from Silar or Petrarch and was also used as received. The D_4 starting material was analyzed by reversed-phase HPLC (conditions described in section 4.2.3) and found to contain a slight amount of decamethylcyclopentasiloxane ($\approx$1-2%), D_5, which will also participate in the equilibration process. The aminopropyl disiloxane was investigated by Capillary Gas Chromatography using a dimethylsiloxane stationary phase (conditions described in section 4.2.4), which showed a major peak and a

minor (<2%) peak with very similar retention times. Proton
nmr revealed the presence of two types of structures, shown
below in scheme 2.

$$CH_3 \qquad\qquad CH_3$$
$$| \qquad\qquad\quad |$$
$$H_2N(CH_2)_3Si \;-\; O \;-\; Si(CH_2)_3NH_2$$
$$| \qquad\qquad\quad |$$
$$CH_3 \qquad\qquad CH_3$$

$$CH_3CH_3 \qquad\qquad CH_3CH_3$$
$$|\;\;\; | \qquad\qquad\quad |\;\;\; |$$
$$H_2NCH_2C-Si \;-\; O \;-\; Si\text{-}CCH_2NH_2$$
$$|\;\;\; | \qquad\qquad\quad |\;\;\; |$$
$$H \;\; CH_3 \qquad\qquad CH_3 H$$
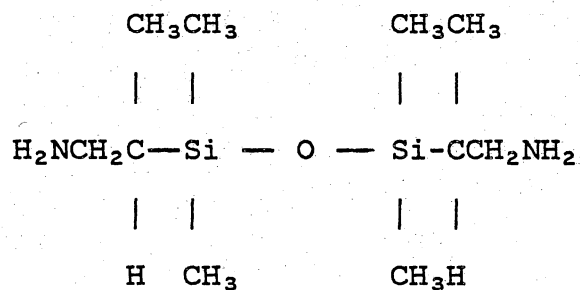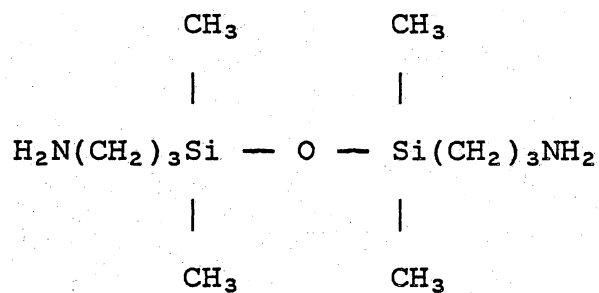
Scheme 2. Two structures present in commercial bis(α,ω-
aminopropyl)-1,3-tetramethyldisiloxane.

The ^{1}H nmr spectrum is shown in Figure 9. The amount of
isopropyl structure present in the backbone of a segmented
copolymer would play a role in the thermal stability of the

system. However, the presence of 1-2% of this structure, produced by abnormal hydrosilation, should not have too great of an effect on the equilibration reactions.

4.2.2 EQUILIBRATION REACTIONS

Polydimethylsiloxane oligomers were prepared by an equilibration process in bulk in order to minimize the extent to which backbiting occurred. D_4 and disiloxane were added to a three neck flask (Figure 10) equipped with a magnetic stirring bar, a gas inlet, a rubber sleeve septum and a re-flux condenser, in the correct ratio to make the desired molecular weight oligomer. For example, in order to prepare a 1200 Mn oligomer, 4 g. of D_4 (0.0135 moles) were used with 1 g. (0.004 moles) of disiloxane. Experiments were performed by adding the monomer, disiloxane and catalyst (by pipette) to the flask and then placing the flask into the silicone oil bath. The flask was then heated to the reaction temperature. Experiments were also performed in which the flask was heated to the reaction temperature before addition of the catalyst. Samples were removed at desired times by a syringe equipped with a stopcock. In the case of the control experiments in which only D_4 was reacted with the potassium catalyst, the increase in viscosity of the system determined the length of time over which samples could be removed. Reactions were
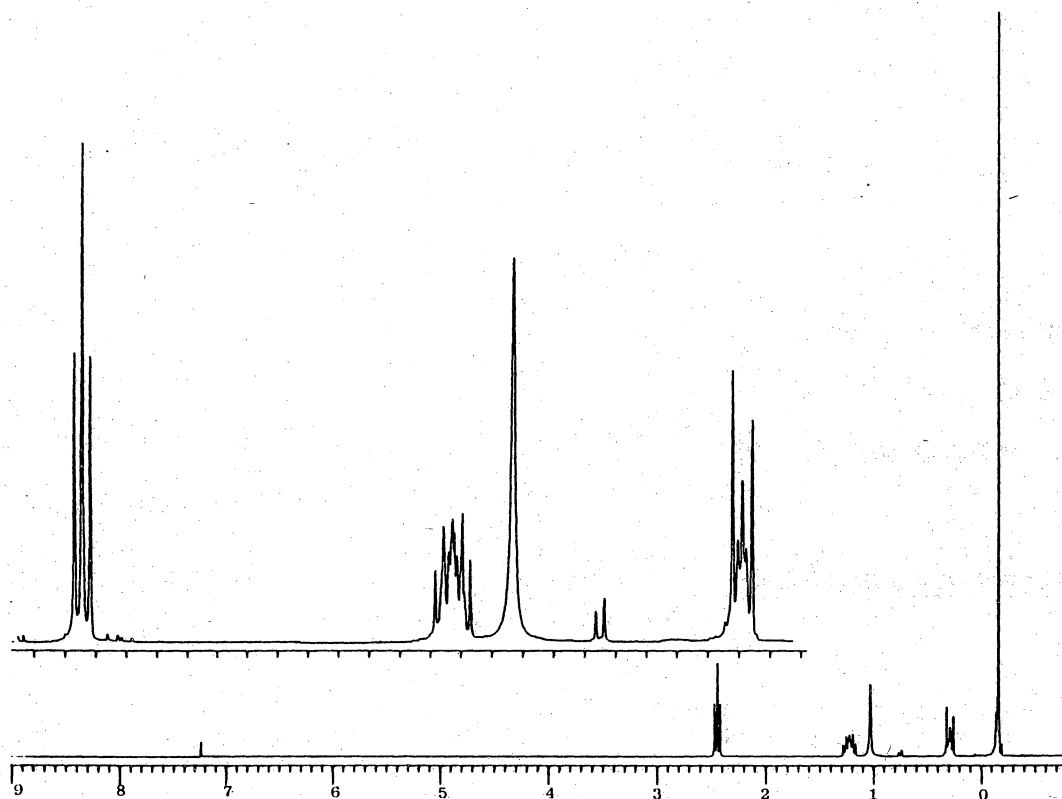
Figure 9. ^{1}H NMR spectrum of aminopropyldisiloxane.
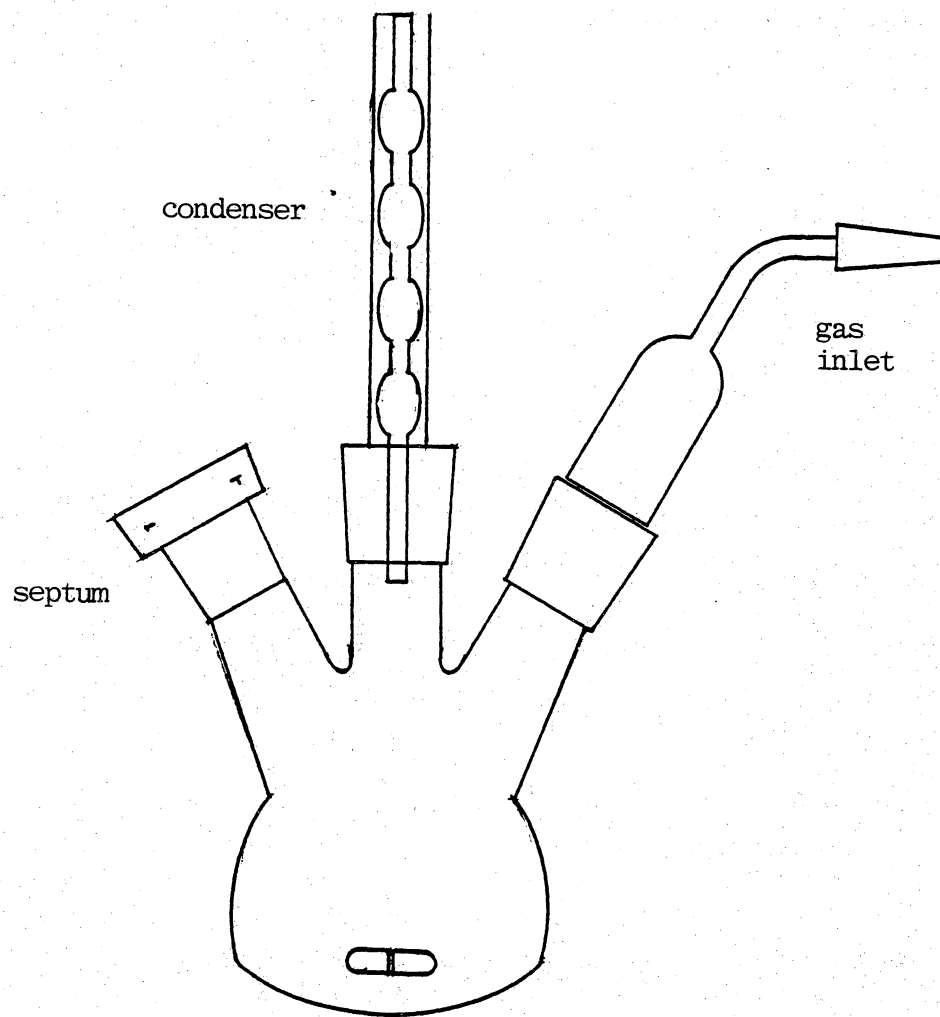
Figure 10.   Reaction setup for equilibration reactions.

conducted at temperatures ranging from 72°C to 140°C and for times ranging from 5 minutes to 24 hours.

4.2.3 REVERSED-PHASE HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

Analysis of the equilibration polymerization products was carried out initially on a Waters Model 450 Solvent Delivery System.   Later work utilized a Varian 5500 Liquid Chromatograph.   DuPont Zorbax ODS (C_{18}) columns were used in a variety of dimensions.   These packing materials are fully endcapped such that no free hydroxyl groups are present.   A typical separation was carried out on a 25 cm x 4.6 mm column using a mobile phase of 22/78 acetone/acetonitrile at a flow rate of 1.0 ml/min.   Adjustments were made to maintain chromatographic resolution due to changes in column pressure or column performance.   Toluene was used as the solvent, with a 10 microliter sample loop injector (Rheodyne).   A differential refractive index detector (Waters Model 401) was used initially.   Later, a Wilmad Infrared Detector at 12.45 microns (803 cm^{-1}) (Si-Me vibration) was found to be a more sensitive detector and was used exclusively.

Calibration curves for D_4 were obtained by plotting the peak height in mm for D_4, obtained by injecting known amounts of D_4 in toluene, vs micrograms injected.   It was necessary to actually plot the calibration curve when using the Waters system.   However, in the case of the Varian system this was

done internally by the Vista 402 data station according to the following formulae:

(8) Factor (i) = $\dfrac{\text{Amount (i) x Amt. Std. x 1000}}{\text{area (i)}}$

(9) Result (i) = $\dfrac{\text{Area (i) x factor (i) x Mltplr}}{\text{Divisor x 10000}}$

where the amount of standard is taken to be 1 if the same volume is injected during calibration and analysis runs, the divisor is the sample weight dissolved for the analysis runs, and the multiplier (mltplr) is 100 in order to give the answer in wt% D_4. The calibration factor (factor (i)) converts the measured area for a compound into the amount of that compound present. The factor is determined by injecting known amounts of the standard, and entering the Amount (i) into the data station method. The data station measures the area (or height, if desired) and calculates a factor for the internal standard. This is analogous to finding the slope of a plotted calibration curve. The 10000 functions as a scaling factor. Care was taken to assure the D_4 peak height in the chromatograms of equilibration samples fell within the

range of the calibration curve.   The results obtained were
accurate to $\simeq$ ±5%.

4.2.4 CAPILLARY GAS CHROMATOGRAPHY

Capillary Gas Chromatography was used to measure quan-
titatively the amount of
bis(α,ω-aminopropyl)-1,3-tetramethyldisiloxane in the equi-
libration samples.   Results were obtained using Perkin Elmer,
Hewlett-Packard, and Varian gas chromatographs.   In each
case, the conditions used were identical.   A dimethylsiloxane
stationary phase was used in a 12 m x 0.2 mm fused silica
column.   Either hydrogen or helium was used as the carrier
gas with a flow rate of 1.7 ml/min. at 80°C.   The temperature
program used was as follows: 100°C - 150°C at 5°C/min.,
150°C - 225°C at 30°C/min.   After 3 - 4 runs, the column was
held at 250°C for approximately 20 minutes to ensure that no
siloxane oligomer was being deposited on the column to elute
during a later run.   A flame ionization detector was used at
310°C and a split/splitless injector in the split mode at
275°C with a split ratio of 100/1 was employed.   The use of
the split injector requires that peak areas be used for
quantitative work, and an internal standard since exactly
reproducible sample sizes may not be placed on the column
with each injection [110].   Tetradecane (C_{14}) was used as the
internal standard to construct a calibration curve for the

Experimental   48

disiloxane. Solution concentrations in methylene chloride ranged from 0.5 - 3% wt/vol. and the injected sample size was 1 microliter. A calibration curve was obtained by plotting the disiloxane area/C_{14} area ratio vs the disiloxane wt/ C_{14} wt ratio. This type of calibration curve is thus valid for any, known, amount of internal standard used. The results obtained were valid to $\simeq \pm 5\%$.

4.2.5 PROTON NUCLEAR MAGNETIC RESONANCE (^{1}H NMR)

^{1}H NMR spectra were obtained on a Bruker 270 MHz intrument marketed by IBM Instruments. Solutions were run as 10% wt/vol. in deuterated chloroform (gold label, Aldrich) at room temperature using methylene chloride as the reference and a deuterium lock. Either 32 or 64 scans were accumulated for fourier transformation.

4.3 SYNTHESIS OF POLYDIMETHYL-CO-DIPHENYLSILOXANE OLIGOMERS

4.3.1 PURITY OF STARTING MATERIALS

The purity of octamethylcyclotetrasiloxane and bis(α,ω-aminopropyl)-1,3-tetramethyldisiloxane has already been discussed. Octaphenylcyclotetrasiloxane (D_4" or diphenyl tetramer) was kindly provided by the General Electric Company and was used as received. High Performance Liquid

Chromatography (section 4.3.3) indicated the presence of only one species.

4.3.2 EQUILIBRATION REACTIONS

Polydimethyl-co-diphenylsiloxane oligomers were also prepared in bulk in an equilibration process analogous to that described previously for the dimethyl siloxane system. Two different procedures were used for the preparation of these co-oligomers. In the first procedure, catalyst, D_4, and disiloxane were charged to a three neck flask equipped with an overhead stirrer, an argon inlet, and a glass stopper, and placed in a silicone oil bath. The reaction was allowed to proceed for approximately 6 hours before the D_4" was added. In the second procedure, all starting materials were added at once at the start of the reaction. The reaction mixture was heterogeneous at first because the D_4" starting material is a solid which is insoluble in D_4 or the disiloxane. In each case, samples were removed from the reaction vessel only after the reaction mixture became homogeneous. The time required for the reaction medium to become homogeneous depended on the composition of the co-oligomer as well as on the reaction temperature. In general, the higher the diphenyl content and the lower the reaction temperature, the longer it took for the reaction mixture to become homogeneous.

4.3.3 REVERSED-PHASE HPLC

These co-oligomers were analyzed by reversed-phase HPLC using a Varian 5500 liquid chromatograph. In this case, a DuPont Zorbax ODS (C_{18}) column, 25 cm x 9.6 mm was used. The mobile phase employed was a mixture of 10% methylene chloride and 90% acetonitrile at a flow rate of 1.0 ml/min. A Varian model UV 200 detector at 254 nm was used to observe the disappearance of the diphenyl tetramer. The IR detector, as described previously, was used to monitor the disappearance of the dimethyl tetramer. Equations (8) and (9) were used to calculate the amounts of D_4 and D_4" present.

4.3.4 ^{29}SI NUCLEAR MAGNETIC RESONANCE

^{29}Si nmr was used to determine the number-average sequence lengths of each type of siloxane unit in the co-oligomers as a function of time, reaction temperature, co-oligomer composition, catalyst type and concentration. Solutions were made up in deuterated chloroform (Aldrich, gold label) as 20% w/v with 0.01 g. (0.02 M) chromium triacetylacetonate (PCR Research Chemicals) as the shiftless relaxation agent. As the reference, 10 drops of tetramethylsilane (Aldrich, nmr grade) were added. Spectra were run on a Bruker 200 MHz instrument at a resonance frequency of 39.8 MHz at ambient temperatures. The pulse width

employed was 13 microseconds and a delay of 3 seconds between

pulses was used.   Broad band proton decoupling was used.

Between 2500 and 3000 scans were accumulated for each sample.

The automated sequence for the decoupling process is shown

in the second appendix.

5.0 RESULTS AND DISCUSSION

5.1 PREPARATION OF SILOXANOLATE CATALYSTS

The purpose of preparing the siloxanolate catalysts prior to use in the equilibration reactions is two-fold. First, by preparing the siloxanolate catalyst separately, a homogeneous system is obtained from the beginning of the equilibration reaction. Both potassium hydroxide and tetra-methylammonium hydroxide have limited solubility in the di-methyl tetramer and it takes some time for a homogeneous medium to result, especially at lower temperatures. In order to obtain reasonable kinetic data it is of course important to have a homogeneous system from the start of the equilib-ration process. Secondly, by preparing the catalysts sepa-rately, they can be dehydrated before use in the equilibration reactions. Water can have a damaging effect on these equilibration processes and certainly makes the si-tuation more complicated. Since at low catalyst concen-trations the degree of polymerization is inversely proportional to the catalyst concentration, the molecular weight of the polymer obtained can be greatly lowered by the presence of water, which can serve as a chain transfer agent. This is, of course, most important when a functional disi-

loxane is not used to regulate the molecular weight of the oligomer.

However, the presence of water can also alter the kinetic data obtained. For example, it has been reported [3] that D_4 is not polymerized by KOH in the presence of water at 100°C. However, a slightly faster polymerization rate at 150°C in the presence of water was found. This was attributed to the formation of stable complexes with the active polymerization center below 150°C.

It is therefore important to have reasonably dry siloxanolate catalysts for use in these equilibration reactions. In the preparation of the ammonium catalyst, the evolution of water was easily observed. It was just as easy to see, by the color change of the drierite, when the system was dehydrated. It was a more difficult situation with the potassium catalyst. Due to the need for an overhead mechanical stirrer, it was possible for some of the water present to escape through the stirrer sleeve, rather than being collected in the attached dean-stark trap as shown in Figure 7. The comparison between the bulk preparation of the potassium catalyst and the azeotroping method was done through control experiments where D_4 alone was reacted with the potassium catalyst. Detailed results of this are included in section 5.2.1 on equilibration reactions. Essentially no differences were found in catalyst efficiency when the same amounts of catalyst prepared by the two different methods were compared.

The titration of each catalyst with alcoholic HCl gave one major peak and one or two minor peaks, presumably due to the formation of different aggregates of the siloxanolate species in solution, or perhaps the presence of unreacted tetramethylammonium hydroxide or potassium hydroxide. Both catalysts are viscous materials, however the potassium catalyst is considerably more viscous than the tetramethyl-ammonium catalyst. There are at least two factors which could conceivably influence the viscosity of the catalysts. The first is the catalyst molecular weight. However, the molecular weight of the potassium catalyst is always on the order of 4-5000 g/mole and that of the ammonium catalyst is $\simeq$ 12000 g/mole. (For the potassium catalyst the molecular weight was calculated by assuming two siloxanolate species per chain, and using the titrated value for the base content to calculate the number of moles present. In the case of the ammonium catalyst, only one siloxanolate end group per chain was assumed, although teh true number is probably between one and two. Knowing the sample weight and the number of moles of chains present, the number-average molecular weight could be calculated.) These molecular weights would not be ex-pected to cause such viscous materials. Also, on the basis of the titrated molecular weights the ammonium catalyst would be expected to be the more viscous of the two catalysts, rather than the potassium catalyst.

The difunctionality observed for the potassium catalyst is probably due to the relatively high temperature at which this catalyst is prepared. Initially, it is probably a monofunctional system, with only one siloxanolate group per chain, and a silanol group at the other, as shown in Scheme 2. The silanol groups condense, to liberate water and produce siloxane chains of higher molecular weight.

$$D_4 \;+\; MOH \longrightarrow 2\; HO \sim\!\!\!\curvearrowright\!\!\!\sim O^{\ominus}\; M^{\oplus} \longrightarrow {}^{\ominus}O \sim\!\!\!\curvearrowright\!\!\!\sim O^{\ominus} \;+\; H_2O$$
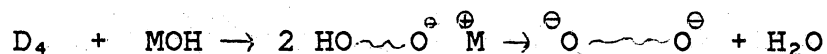
Scheme 3. Illustration of the formation of a difunctional catalyst.

The second factor that would influence the viscosity of the catalysts is association of the siloxanolate endgroups. Since the potassium catalyst is difunctional, the viscosity is even greater since each chain is potentially anchored at two points. The ammonium catalyst probably does not form as many highly associated species. Also, since the ammonium catalyst is prepared at a lower temperature than the potassium catalyst, it is possible that it is not a completely difunctional system, and so would not be expected to be as viscous a material.

5.2 EQUILIBRATION REACTIONS

5.2.1 REACTION OF D_4 WITH POTASSIUM CATALYST

The initial set of experiments performed was to check the accuracy of our technique of studying these reactions. Grubb and Osthoff [24] found that the reaction of D_4 with potassium hydroxide is first order in D_4 concentration. A series of experiments was therefore done using 0.02 wt% KOH (0.1 mole%) and at temperatures of 82°C, 111°C, 117°C, and 140°C. No disiloxane was added in these experiments to regulate the molecular weight of the polysiloxane formed. The viscosity of these systems determined the length of time during which samples could be removed. Thus, at higher reaction temperatures the viscosity, and hence the molecular weight, increased more rapidly. For example, at 82°C, the reaction mixture became too viscous to remove samples after 8.5 hours. However, at 140°C the viscosity of the system reached this point after only 15 minutes.

The molecular weight of the polysiloxane at the point the stirrer was unable to stir the reaction mixture was estimated by measuring the intrinsic viscosity of the product (chains plus cyclics) in chloroform at 25°C. After 10 minutes reaction time at 150°C, the intrinsic viscosity of the siloxane was 0.50 dl/g. Using the Mark-Houwink relationship, equation (10) [51], a viscosity-average molecular weight of

approximately 150,000 daltons was found. This number is no doubt somewhat higher than the true molecular weight. This could be due to the presence of the siloxanolate end groups which could associate, causing an increase in the viscosity of the system and therefore an apparent increase in the molecular weight of the siloxane. Alternatively, residual cyclics could act as a diluent and lower the apparent viscosity average molecular weight.

(10) $[\eta] = k \, Mv(exp \, -a)$

A plot of $\ln[D_4]$ vs. reaction time for the different temperatures studied is shown in Figure 11 on page 60. As expected, each plot is linear, indicating the first order behavior in D_4 concentration. The slope of each straight line provides an apparent or "global" rate constant at that temperature. The rate constants obtained at the different temperatures are shown in Table 4. Also included here are rate constants obtained from reactions that employed potassium catalyst prepared by the "azeotroping" method. An Arrhenius plot of these data is shown in Figure 12. A very good straight line is obtained; rate constants obtained from experiments using both the bulk catalyst and the azeotroped catalyst fall on the same line. The activation energy can be calculated from

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(11) $k(T) = \beta \exp(-Ea/RT)$

where k(T) is the rate constant at temperature T in °K, R is the ideal gas constant, and β is a constant of integration. The value of the activation energy calculated from the slope of the graph in Figure 12 is 18.6 kcal/mole, which agrees well with previous work done in this field [3].

The fact that the rate constants obtained using both types of potassium catalysts (bulk vs. azeotroped) fell on the same line in the Arrhenius plot indicates that the two methods of preparation have comparable effectiveness in dehydrating the system. The good agreement of the activation energy found from Figure 12 with values found in the literature indicates that our technique for studying this equilibration reaction is an appropriate method.
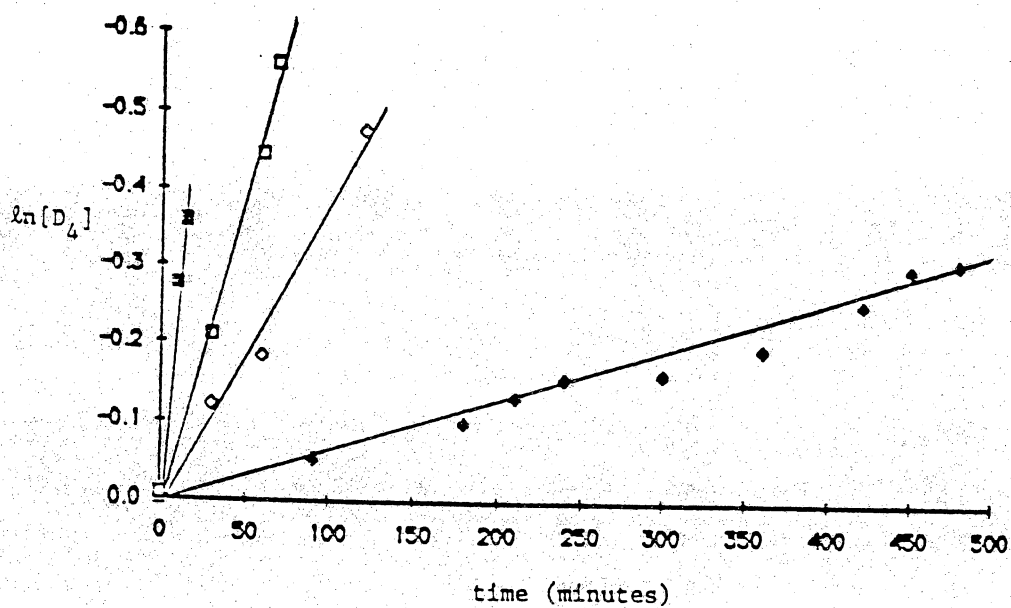
Figure 11. First order plots for the reaction of D_4 with potassium catalyst: $\ln[D_4]$ vs reaction time in minutes at temperatures of 82°C (♦), 111°C (◇), 117°C (□), 140°C (▪) with 0.1 mole% KOH.

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Table 4.   Rate constants from $\ln[D_4]$ vs t plot.

Temperature (°C)	Rate Constant k (min^1) x 10^3	Method of Catalyst Preparation
82	0.6	Bulk
111	3.5	Bulk
117	7.9	Azeotroped
139	24.0	Bulk
139	24.0	Azeotroped
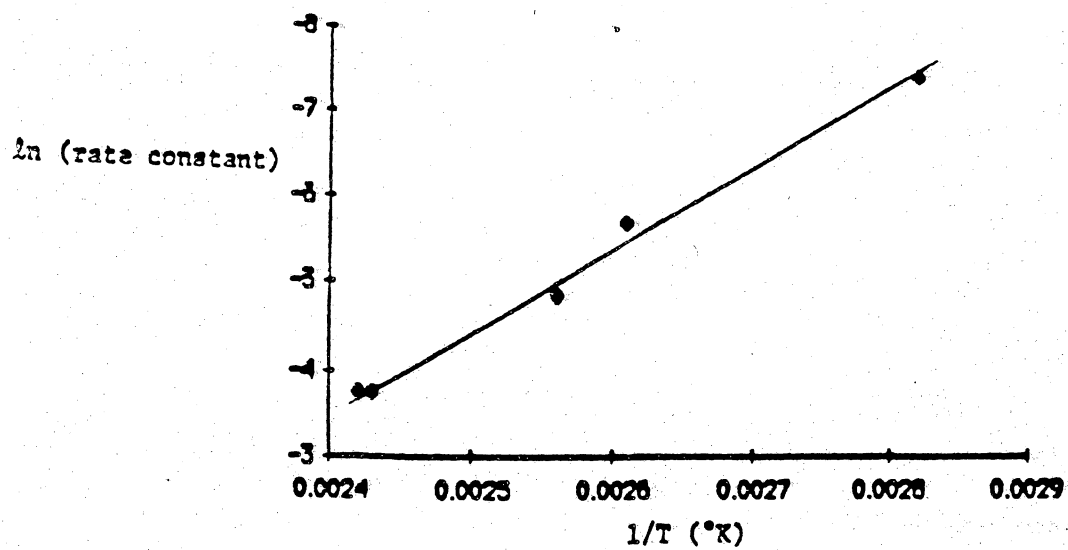
Figure 12. Arrhenius plot for the reaction of D_4 with potassium catalyst.

5.2.2 PREPARATION OF AMINOPROPYL-TERMINATED POLYDIMETHYLSILOXANE OLIGOMERS.

The polymerization of D_4 in the presence of the disiloxane under a wide variety of reaction conditions was investigated. The results obtained are shown in Figure 13 through Figure 24.

The first major observation is that the reaction of D_4 with the potassium catalyst is apparently much faster in the presence of the disiloxane than in the absence of the disiloxane. Shown in Figure 13 to illustrate this is a plot of wt fraction D_4 vs reaction time at 110°C with 0.12 wt% (0.6 mole%) KOH in the presence and absence of disiloxane. The targeted molecular weight for the reaction run in the presence of the disiloxane was 1000 g/mole.

The dramatic difference between the rate of reaction of D_4 in the presence and absence of the disiloxane is clearly indicated. After 15 minutes in the presence of the disiloxane, the amount of D_4 present has decreased to less than 10 wt% while in the absence of the disiloxane it is still on the order of 75 wt%. Further examples of this are shown in Figure 14 and Figure 15. In every case, there is a very large difference in the rate of reaction of D_4 in the presence and absence of disiloxane.

The accelerated rate of reaction of D_4 in the presence of the disiloxane is probably due to the fact that the bulk

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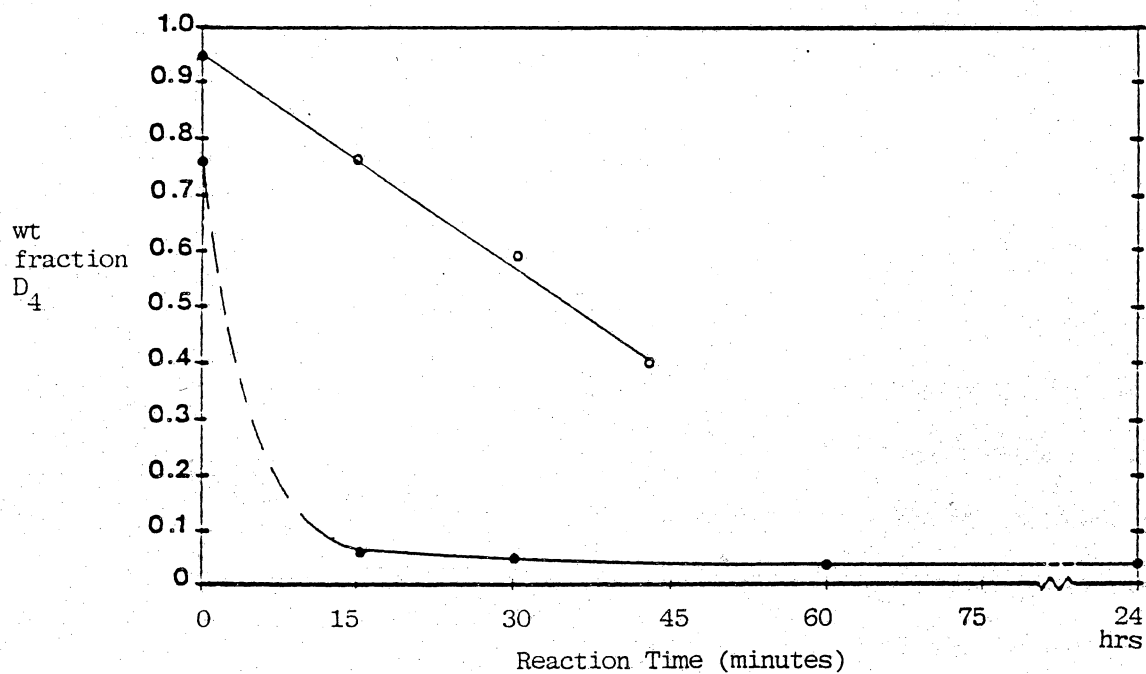
Figure 13. Disappearance of D_4 in the presence and absence of disiloxane at $110^\circ C$ with 0.6 mole% potassium hydroxide: Targeted molecular weight for reaction done in the presence of the disiloxane (●) was 1000 g/mole. (O) = reaction done without disiloxane.

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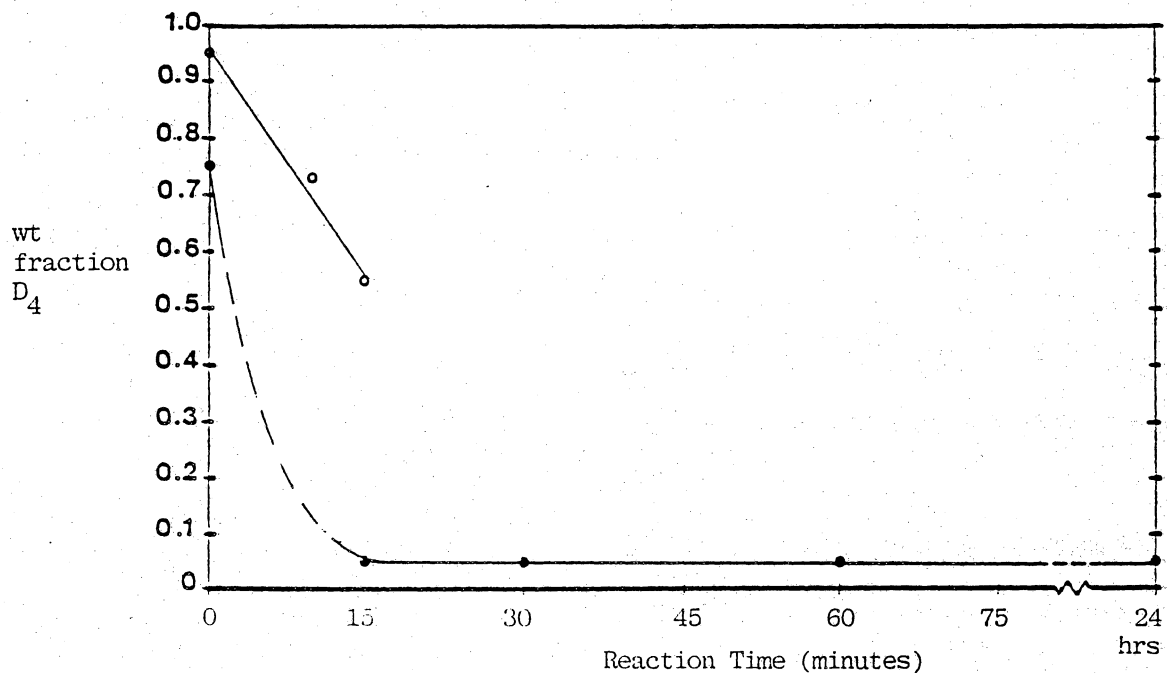
Figure 14. Disappearance of D_4 in the presence and absence of disiloxane at $132°C$ with 0.6 mole% potassium hydroxide: Targeted molecular weight in the presence of the disiloxane (●) was 1000 g/mole. (O) = reaction done without disiloxane.
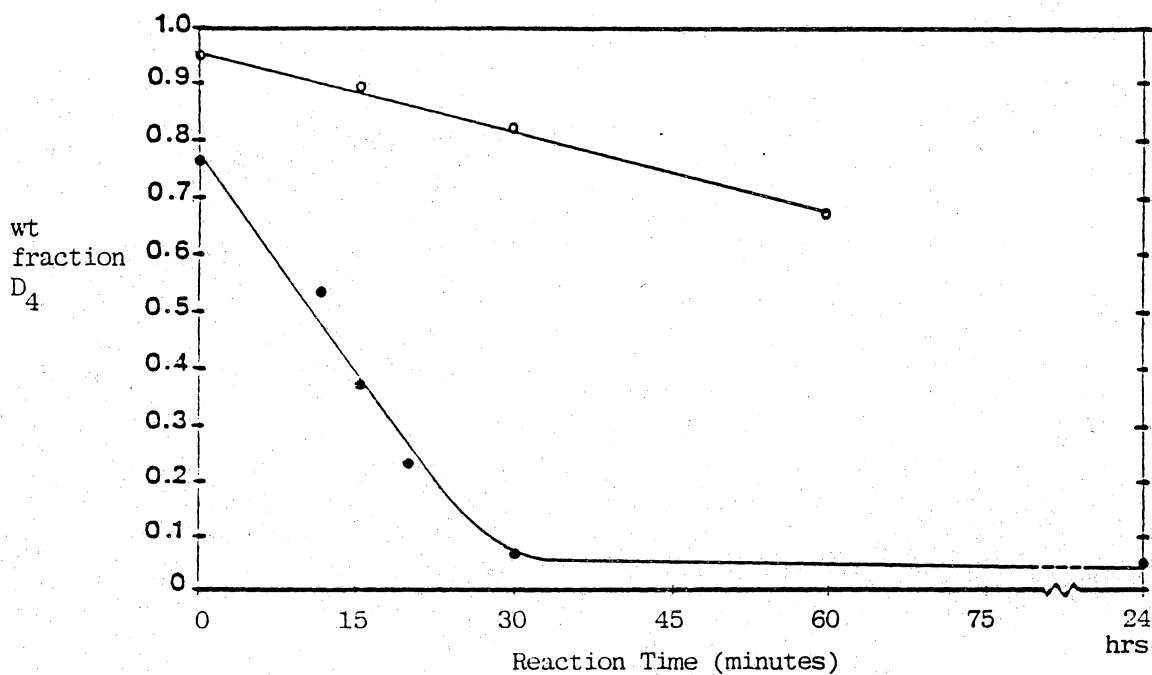
Figure 15. Disappearance of D_4 in the presence and absence of disiloxane at 90°C with 0.6 mole% potassium hydroxide: Targeted molecular weight in the presence of the disiloxane (●) was 1000 g/mole. (O) = reaction done without disiloxane.
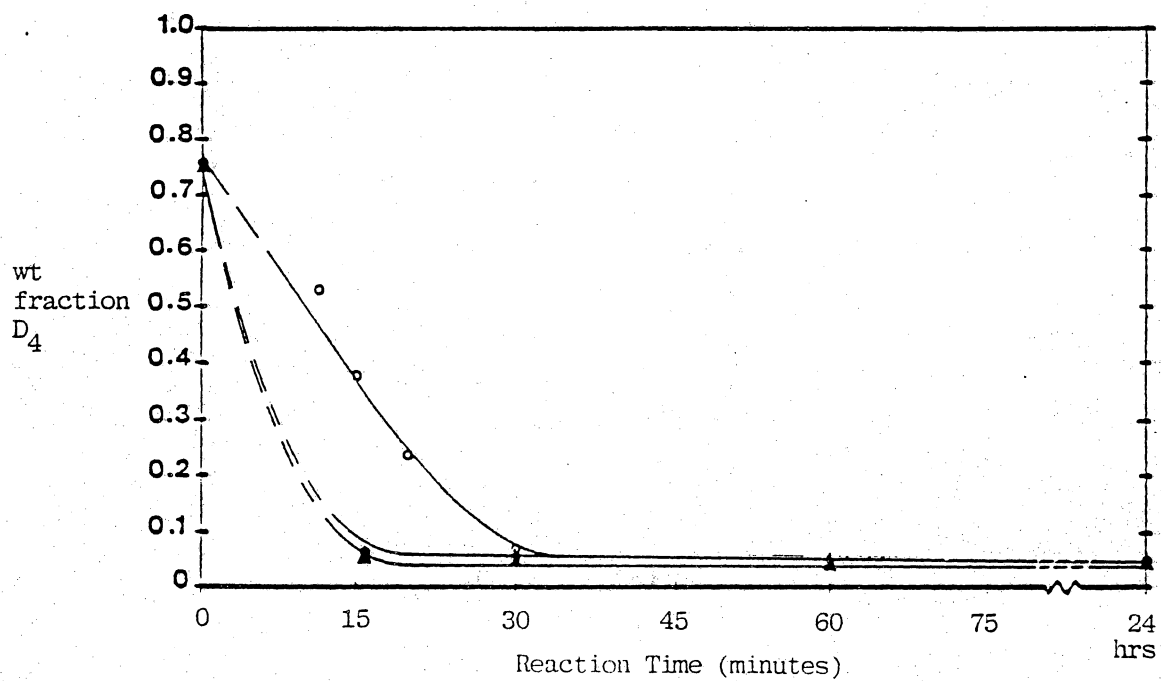
Figure 16. Disappearance of D_4 in a targeted 1000 Mn oligomer with 0.6 mole% potassium hydroxide: at 90°C (O), 110°C (●), 132°C (▲).
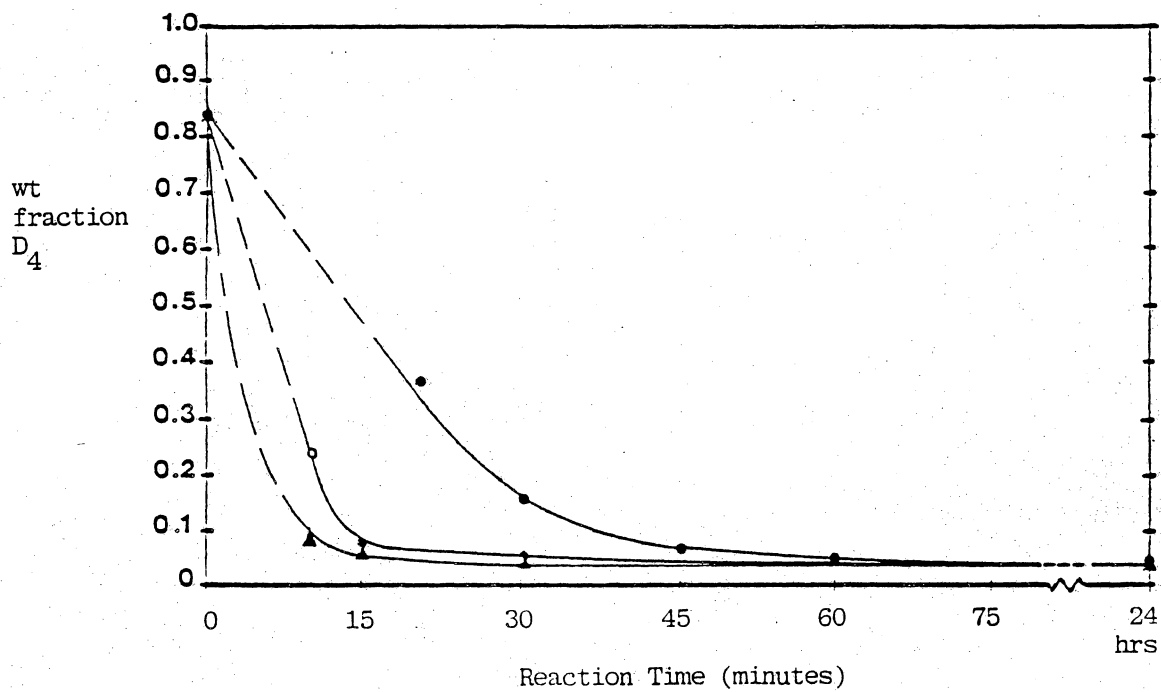
Figure 17. Disappearance of D_4 in a targeted 2000 Mn oligomer with 0.6 mole% potassium hydroxide: at 91°C (●), 114°C (o), 130°C (▲).
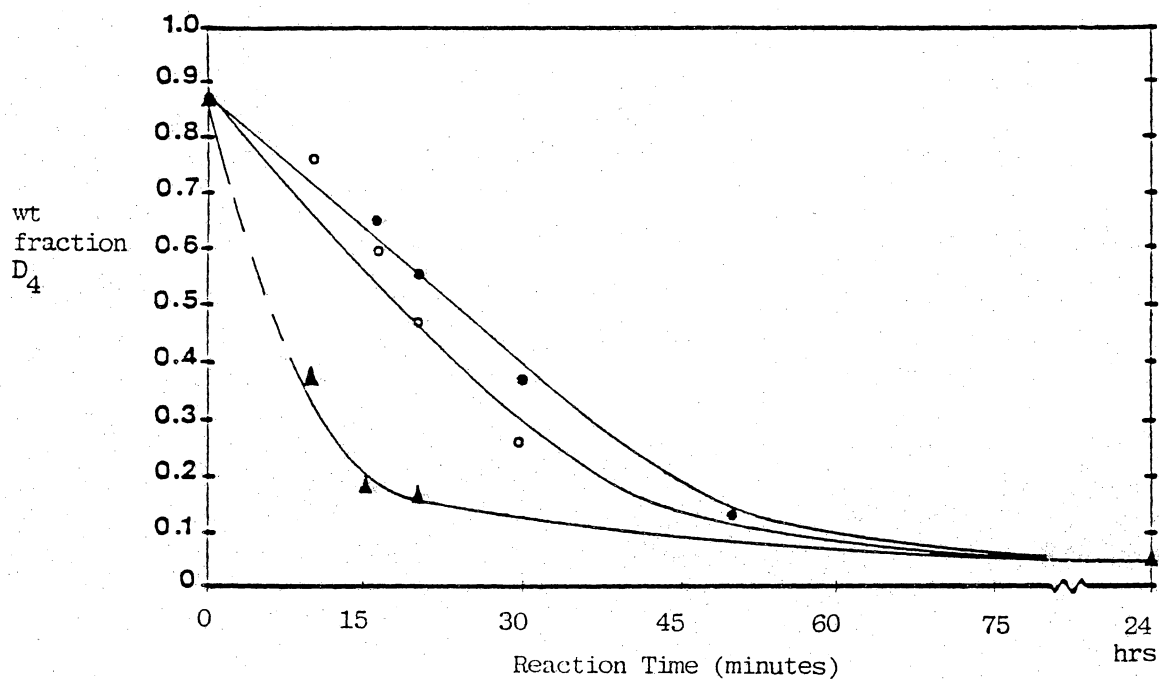
Figure 18. Disappearance of D_4 in a targeted 3000 Mn oligomer with 0.6 mole% potassium hydroxide: at 95°C (●), 103°C (○), 127°C (▲).
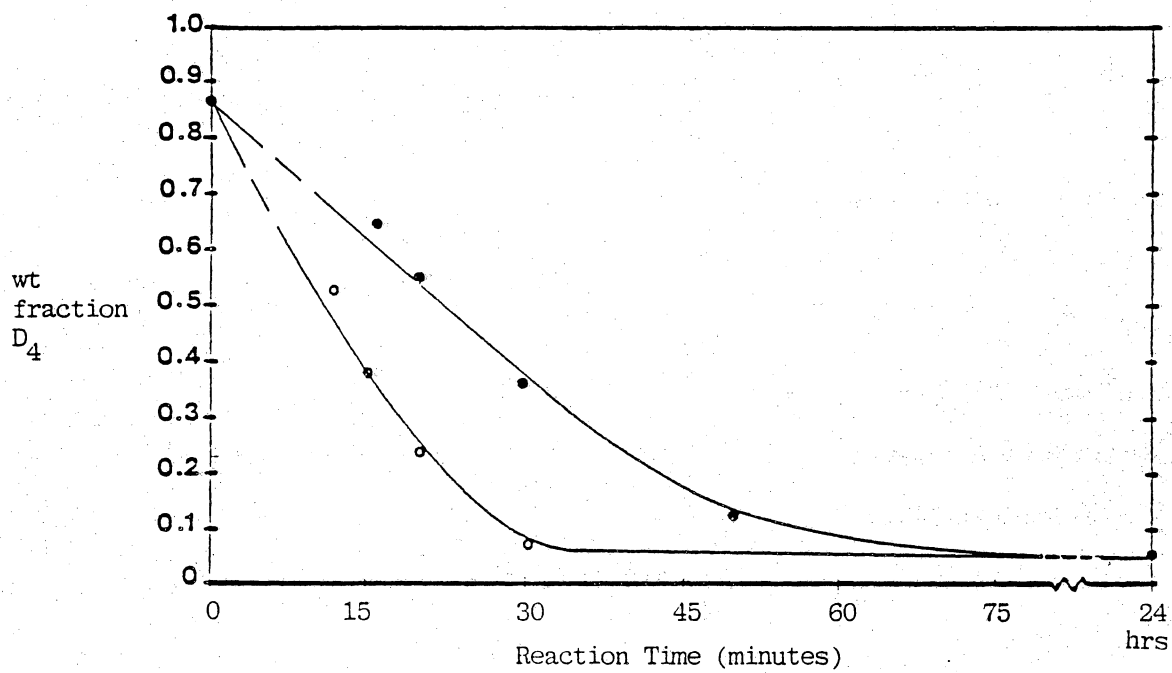
Figure 19. Example of the effect of molecular weight on
the rate of reaction of D_4 with 0.6 mole%
potassium hydroxide: Reaction of D_4 in an
oligomer targeted at 1000 g/mole at 90°C (o)
and in a 3000 Mn oligomer at 95°C (●).

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reaction mixture is considerably less viscous in the presence of the disiloxane than in its absence. This is because the disiloxane functions analogously to a chain transfer agent, acting to limit the molecular weight and therefore the viscosity of the system. Since this is, at least in part, a diffusion-controlled process, the reaction is allowed to proceed more rapidly in a less viscous medium. A further illustration of this viscosity effect can be observed by increasing the targeted molecular weight (and therefore the viscosity of the system). As can be seen in Figure 16 through Figure 19, higher molecular weights correlate with a slower rate of reaction of D_4. This is most clearly illustrated by Figure 19. A reaction conducted at a slightly lower (5°C) temperature and a lower targeted molecular weight (1000 g/mole) still proceeded at a much faster rate than the reaction run at a higher targeted molecular weight (3000 g/mole).

The trends just discussed for the reaction of D_4 with the potassium catalyst also hold true for the reaction with the ammonium catalyst. The results of the experiments with the ammonium catalyst are shown in Figure 20 through Figure 23. The reaction of D_4 with the ammonium catalyst proceeds quite rapidly in the presence of the disiloxane. Even at a catalyst concentration of 0.2 mole% TMAH in a targeted molecular weight oligomer of 2000 g/mole at 85°C, the amount of D_4 after only 25 minutes is under 10 wt%.

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Figure 20 and Figure 21 show only a slight molecular weight effect. Figure 22 shows the expected increase in the rate of reaction of D_4 with an increase in catalyst concentration

It can also be seen, in Figure 23, that D_4 reacts more rapidly with the ammonium catalyst than with the potassium catalyst. The same weight per cent of each catalyst was used. However, this corresponds on a molar basis to almost twice as much potassium siloxanolate as tetramethylammonium siloxanolate (0.6% vs 0.4%). There is, in addition, a slight temperature difference favoring the potassium catalyst. However, the reaction with the potassium catalyst is still significantly slower than the reaction with the ammonium catalyst.

The reason for this is probably related to the formation of aggregates of the siloxanolate species in solution, which was discussed earlier. The siloxanolate, it is believed [3], must be "free" and not bound up in a "complex" with other end groups, in order to attack the Si-O bond in the D_4 molecule. Since it is believed that the bulkier tetramethylammonium counter-ion forms these complexes less easily, it follows that there should be more of the "free", or at least less associated siloxanolate present in that case. Usually, a faster rate of reaction is observed in the case of the less associated anion.

It must be mentioned at this point that these particular experiments were performed by placing all starting materials
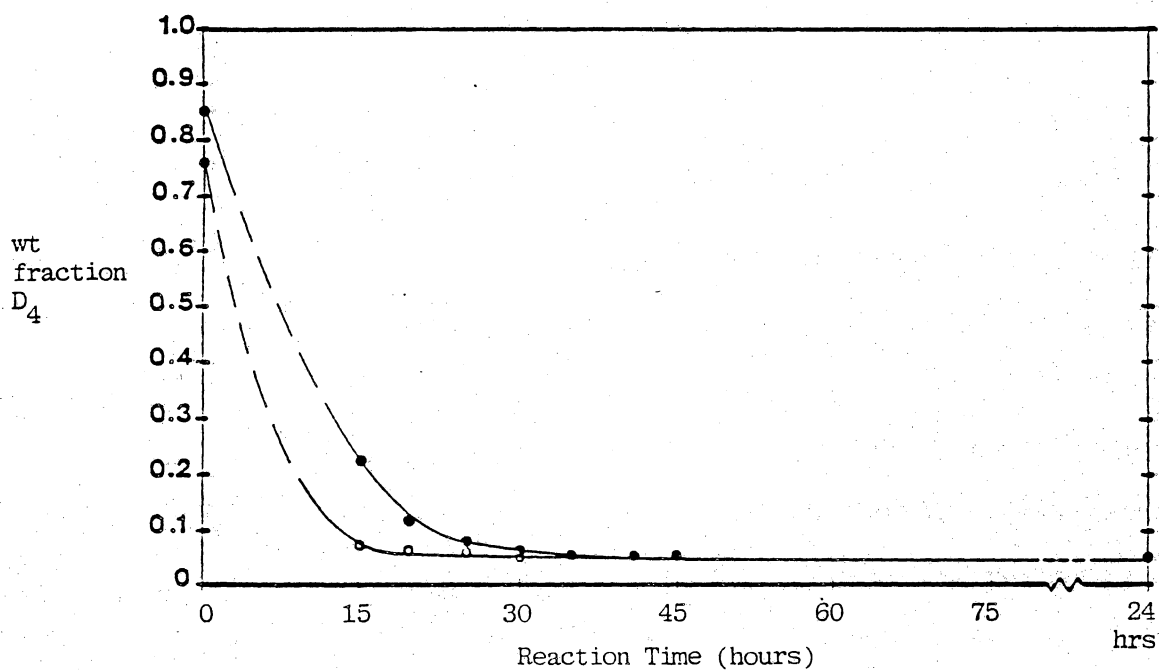
Figure 20. Molecular weight effect on the reaction of D_4 with 0.2 mole% tetramethylammonium hydroxide: at 85°C and targeted molecular weights of 2000 (●) and 1200 (o).
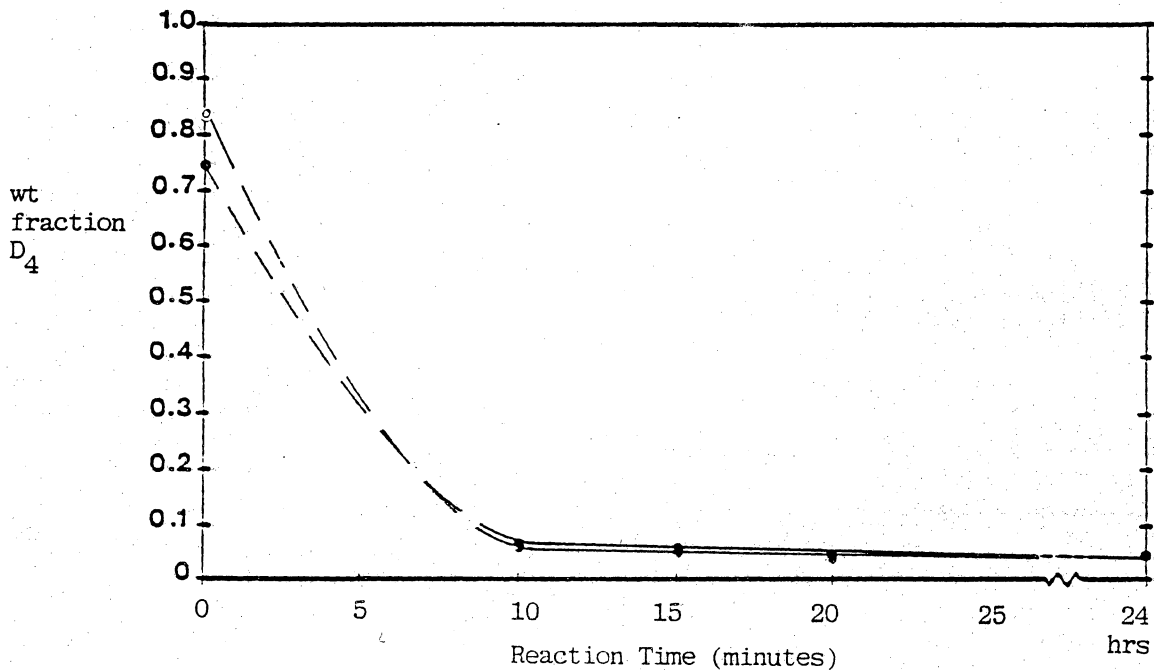
Figure 21. Reaction of D_4 with 0.4 mole% tetramethyl-
ammonium hydroxide at different targeted mo-
lecular weights: 1200 Mn (●) at 102°C and
2000 Mn (o) at 99°C.
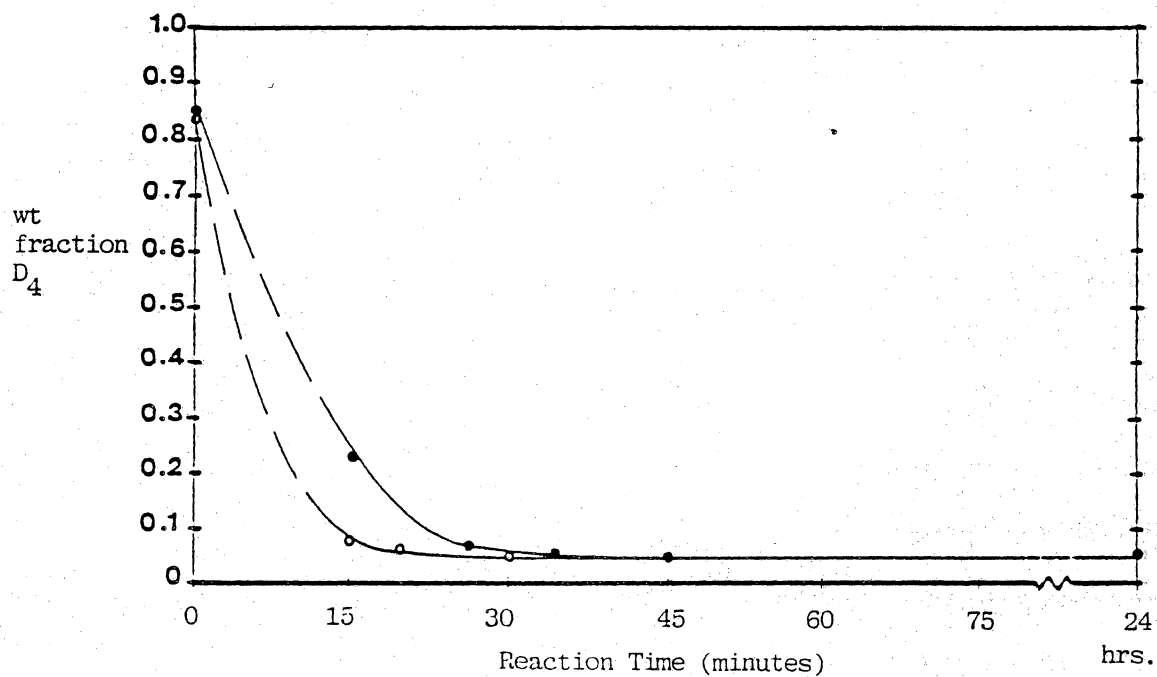
Figure 22. Effect of catalyst concentration in the re-
action of D_4 with tetramethylammonium cata-
lyst: at 83°C and 0.4 mole % (.12 wt% TMAH)
(o), and at 85°C and 0.2 mole % (0.06 wt%)
TMAH (●), at a targeted molecular weight of
2000 g/mole.

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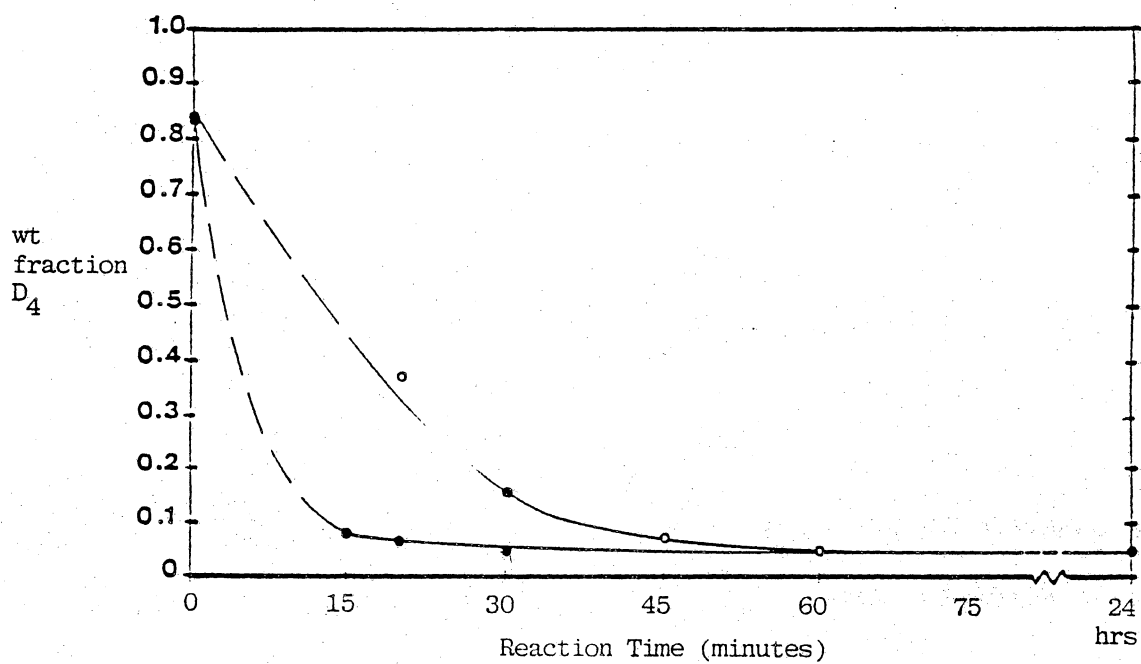
Figure 23. Comparison of the rate of reaction of D_4 with each catalyst: in a 2000 Mn targeted oligomer at 83°C with 0.12 wt% (0.4 mole%) TMAH (●) and at 91°C with 0.12 wt% KOH (0.6 mole%) (○).

including the appropriate catalyst in the reaction vessel and then in the oil bath. During approximately the first 5 minutes of reaction, the temperature of the starting materials was changing. In order to determine what effect this had on the results obtained, an experiment was done where the catalyst was added after the D_4 and disiloxane had been brought to temperature in the reaction vessel. Shown in Figure 24 are the results obtained at 89°C, using 0.06 wt% KOH (0.4 mole%) for an oligomer targeted at 1200 Mn, compared with an equilibration done by the previous method. Clearly, the initial reaction rate is higher, as one might expect, when the catalyst is added after the reaction flask is brought up to the reaction temperature. However, after about 20 minutes, the two curves are in quite good agreement and both indicate the same trend: within 1 hour, the amount of D_4 remaining is approximately 10 wt%.

The final point remaining to be considered in this section is that of the equilibrium amount of D_4 remaining. As discussed earlier, these reactions do not proceed to completion. There is always a distribution of linear species in equilibrium with a distribution of cyclic species. At equilibrium, the amount of D_4 remaining is always about 5-6 wt%. This is true regardless of the reaction conditions employed. By varying the reaction temperature, catalyst type, and concentration, we only change the _rate_ at which the D_4 is consumed, not the amount remaining at equilibrium. This
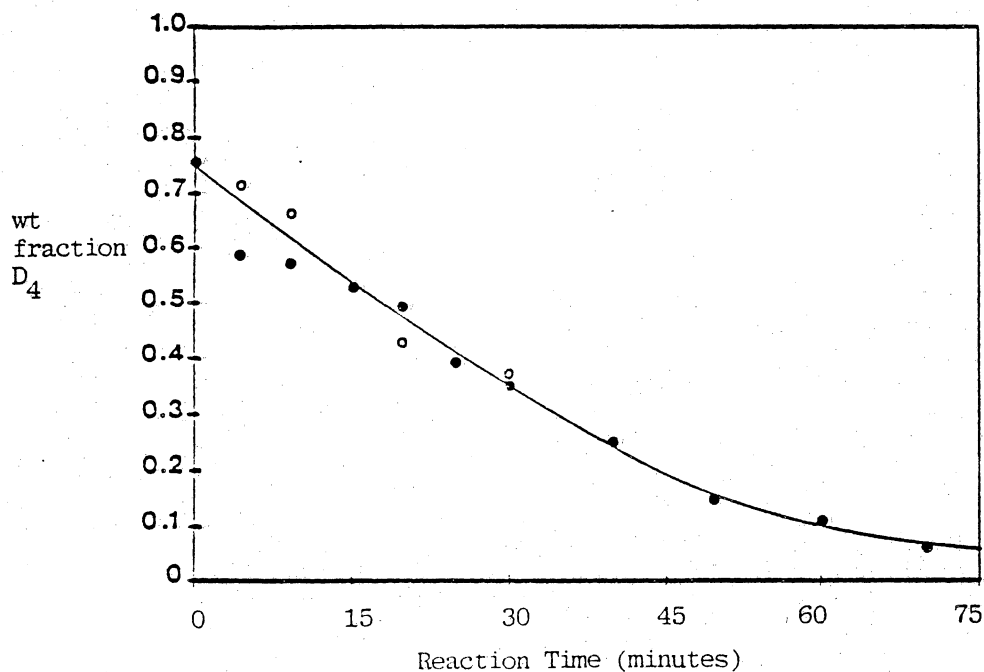
Figure 24.   Comparison of the two methods of catalyst
             addition: at 89°C, 0.3 mole% potassium hy-
             droxide and 1200 targeted Mn; catalyst added
             with other starting materials (o), and cat-
             alyst added after other starting materials
             were brought up to temperature (●).

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does not mean, of course, that after approximately 2 hours when the D_4 has reached its equilibrium concentration, that the reaction is over. This can be considered in some ways to be analogous to a so-called "living" polymerization. The siloxanolate anion may still attack D_4 molecules present, as well as any other rings present, as well as any linear species present. Additional D_4 may be formed through the back-biting process discussed previously, and then consumed.

The next point to be addressed is the rate of disappearance of the disiloxane and the amount remaining at equilibrium. Capillary GC proved to be the technique of choice for quantitative analysis of the disiloxane remaining as a function of time. Reversed-phase HPLC was not as useful here due to inadequate resolution of the disiloxane peak from a peak due to the catalyst.

Since capillary GC was employed, only fairly low molecular weight oligomers could be studied. This still yielded valuable information since at lower molecular weights more moles of disiloxane are added to the system and must be totally incorporated into the system to produce the desired monomodal difunctional oligomers of predictable molecular weight.

At first, there was concern that the high temperatures necessary for gas chromatographic analysis would generate additional cyclic species or cause additional consumption of the disiloxane, thus distorting the results obtained. The

initial experiments done, therefore, served the purpose of checking the validity of the GC method. Once a method was found that gave satisfactory separation between peaks produced by the disiloxane, catalyst, and equilibration samples, the calibration curve for the disiloxane was checked by injecting known amounts of the disiloxane mixed with the potassium catalyst. Good agreement was found between the actual amount injected and the amound calculated from the calibration curve. In addition, the use of each of the 2 disiloxane peaks was investigated. Table 5 summarizes the results obtained for the disappearance of disiloxane in a 1200 Mn oligomer using 0.6 mole% KOH at 128°C, using calibration curves prepared using the first, smaller disiloxane peak, the second, larger disiloxane peak, and the sum of the two peaks. Both peaks disappear at approximately the same rate, indicating that each type of structure has very nearly the same reactivity. However, there is very slightly better agreement between the use of the second peak and the sum of the two peaks, particularly at the lower disiloxane concentrations. Since the smaller the peak area, the more error involved, and the larger peak could be used to lower disiloxane concentrations, subsequent work utilized the area of the second peak for the calibration curves and the determination of the amount of disiloxane in the equilibration samples.

Table 5.   Comparison of the WT% Disiloxane Found by us-
            ing Different Peaks in the Gas Chromatogram.

wt% disiloxane using 1st Peak	wt% disiloxane using 2nd Peak	wt% disiloxane using the sum of Peaks 1 & 2
15.5%	16.0%	16.0%
10.7%	12.4%	12.4%
8.5%	9.5%	9.9%
3.2%	4.0%	4.0%

A variety of experiments were performed to investigate the effects of temperature, catalyst type and concentration on the rate of disappearance of the disiloxane. The first important observation is that the disiloxane reacts with either the potassium or the tetramethylammonium catalyst more slowly than D_4. One example of this is shown in Figure 25 for a reaction using 0.6 mole% KOH and a 1200 targeted molecular weight. The results of further experiments are illustrated in Figure 26 through Figure 28. In each case, although a direct comparison is not made here for every experiment, the reaction of the disiloxane with the siloxanolate catalyst used is slower than the reaction of the D_4.

This difference in the rates of reaction of D_4 and disiloxane might be expected on the basis of electronegativity differences during an anionic polymerization. The more electropositive the silicon atom, the more readily is the silicon - oxygen bond under attack broken. A silicon atom bound directly to two oxygen atoms is certainly more electropositive than a silicon atom bound to one oxygen atom and an alkyl group, all other things being equal. This means that a silicon atom in a D_4 ring, or in a linear siloxane, should be more rapidly attacked than in the disiloxane.

The difference in reactivity between D_4 and the disiloxane is not as pronounced when the ammonium catalyst is used. One example of this is shown in Figure 26. D_4 still reacts more quickly than the disiloxane, however, although

it is just a slight difference. This effect, of the relative rates of reaction of the the disiloxane and D_4 becoming more similar, is probably due to the greater efficiency of the ammonium catalyst as compared with the potassium catalyst. The large difference in the efficiency of each catalyst towards the disiloxane is very clearly illustrated by Figure 27. The disiloxane is about 80-90% consumed by the ammonium catalyst before it is even half gone in the reaction with the potassium catalyst.

Since the reaction of the disiloxane with the potassium catalyst was so slow, no attempt was made to study lower catalyst concentrations than 0.6 mole% potassium hydroxide. Shown in Figure 28 is a summary of the experiments done with the potassium catalyst, showing the expected increase in reaction rate with an increase in temperature. It is important to note that, at the higher temperatures after 24 hours there is on the order of 2 wt% disiloxane remaining. However, at the lower temperatures after 24 hours there is a significant amount of disiloxane remaining. For example, at 91°C after 24 hours there is $\approx$ 7% remaining. Since it is critical to incorporate as much of the disiloxane as possible in a reasonable amount of time, a low temperature equilibration done with potassium catalyst would not seem to be a viable way of attaining this goal.

Since the disiloxane reacted with the ammonium catalyst in a reasonable amount of time, two catalyst concentrations
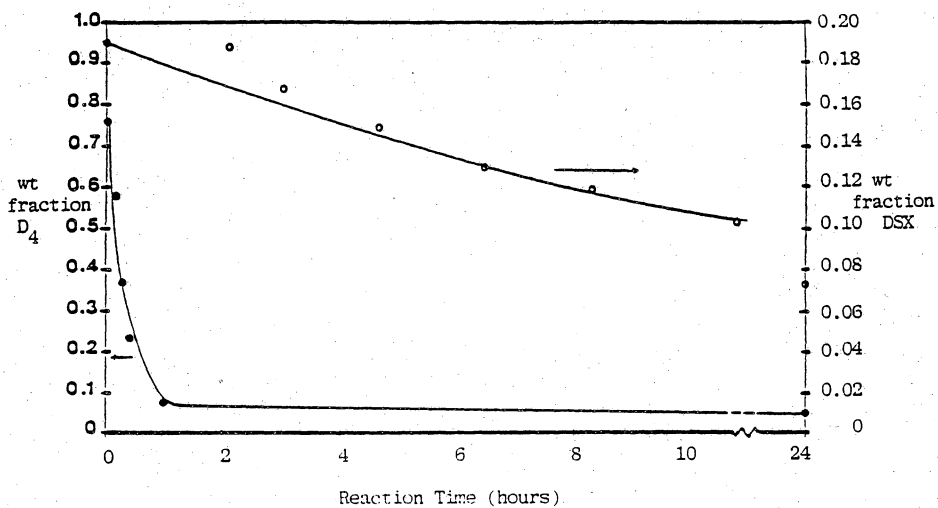
Figure 25. Comparison of the rates of reaction of D_4 and disiloxane using potassium catalyst: at a targeted molecular weight of 1200 g/mole and 90°C (D_4) (●) and 91°C (disiloxane) (o), 0.6 mole% potassium hydroxide.

Results and Discussion
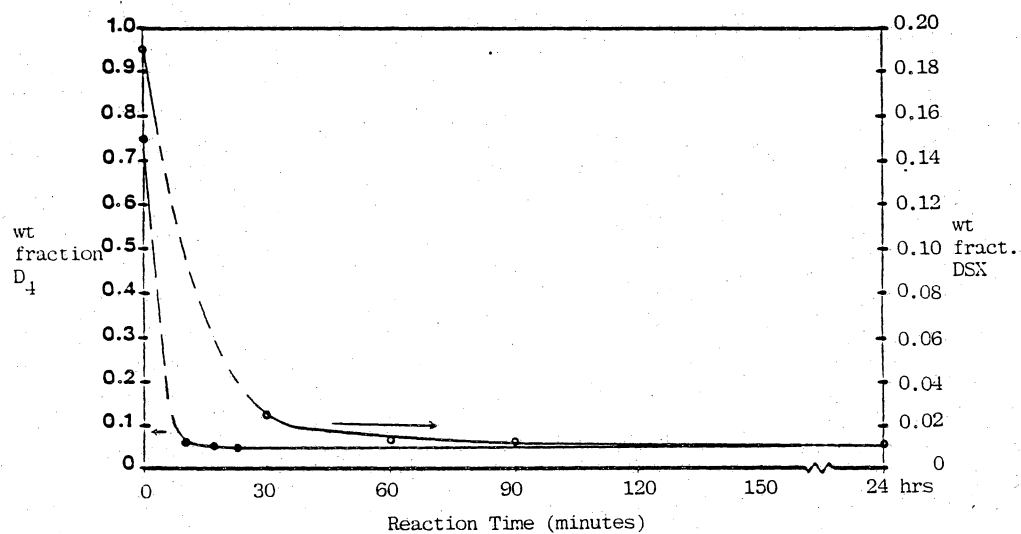
Figure 26. Comparison of the rates of reaction of D_4 and disiloxane using ammonium catalyst: at a targeted molecular weight of 1200 g/mole and 102°C (D_4) (●) and 101°C (disiloxane) (○), 0.12 wt% TMAH.

Results and Discussion
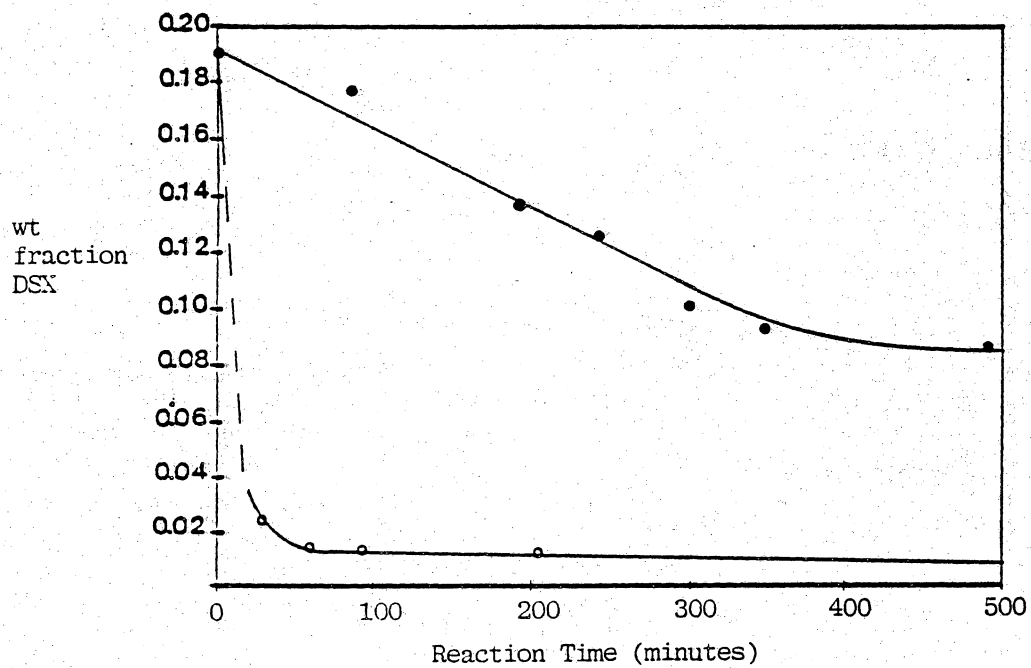
Figure 27. Comparison of the rate of reaction of disiloxane with each catalyst: at 100°C with 0.6 mole% potassium hydroxide (●), 0.4 mole% tetramethylammonium hydroxide (o).
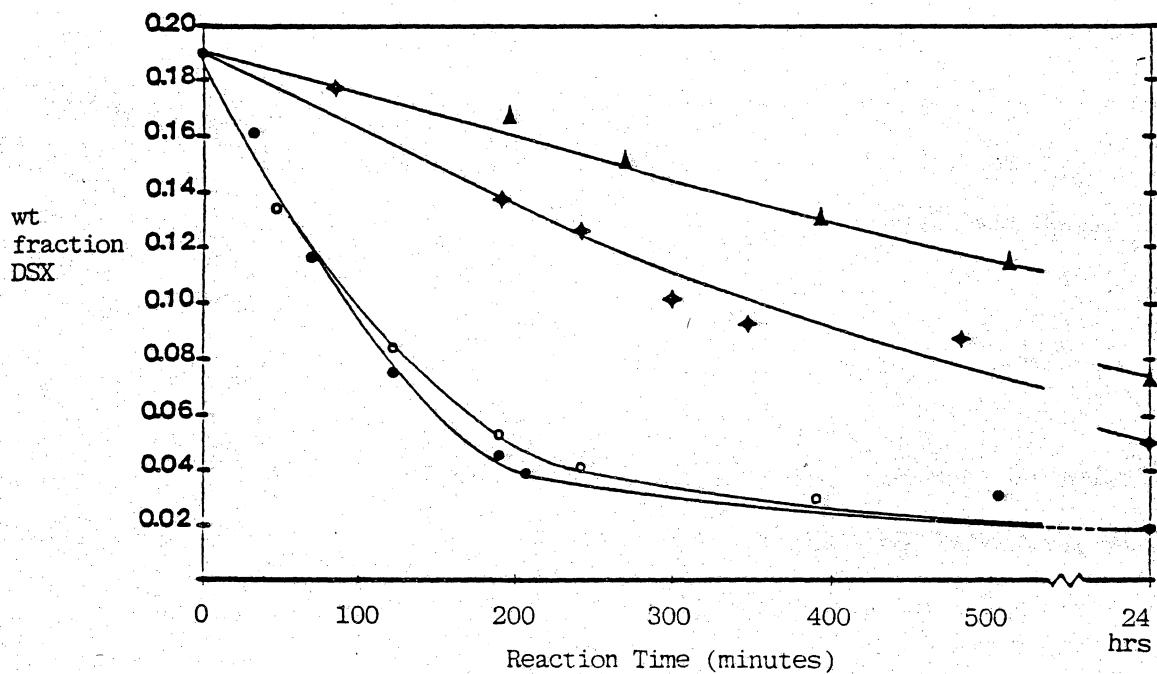
Figure 28. Reaction of disiloxane with potassium cata-
lyst: in a 1200 Mn oligomer at temperatures
of 91°C (▲), 105° C (◆), 129°C (o), 140°C
(●) with 0.6 mole% potassium hydroxide.

were studied: 0.4 mole% and 0.2 mole% tetramethylammonium

hydroxide. The results of experiments done with the ammonium

catalyst are shown in Figure 29 through Figure 32. The in-

crease in reaction rate caused by increasing the temperature

at a constant catalyst concentration is shown in Figure 29

and Figure 30 for 0.2 mole% and 0.4 mole% tetramethylammonium

hydroxide respectively. Each catalyst concentration gives

reasonable reaction times even at the lowest temperature.

The expected effect of catalyst concentration is illustrated

in Figure 31 and Figure 32: increasing the catalyst concen-

tration causes a (slight) increase in the rate of reaction

of the disiloxane.

5.2.2.1 SUMMARY

The polymerization of octamethylcyclotetrasiloxane in

the presence of

bis(α,ω-aminopropyl)-1,3-tetramethyldisiloxane with potas-

sium siloxanolate and tetramethylammonium siloxanolate cata-

lysts has been investigated. As would be predicted on the

basis of electronegativity differences, D_4 was found to react

with each catalyst more rapidly than the disiloxane did. The

silicon atom in a D_4 ring is more electropositive than the

silicon atom in a disiloxane molecule, and so that silicon -

oxygen bond is more rapidly attacked by a basic catalyst.

Although not studied here, the reverse situation is observed
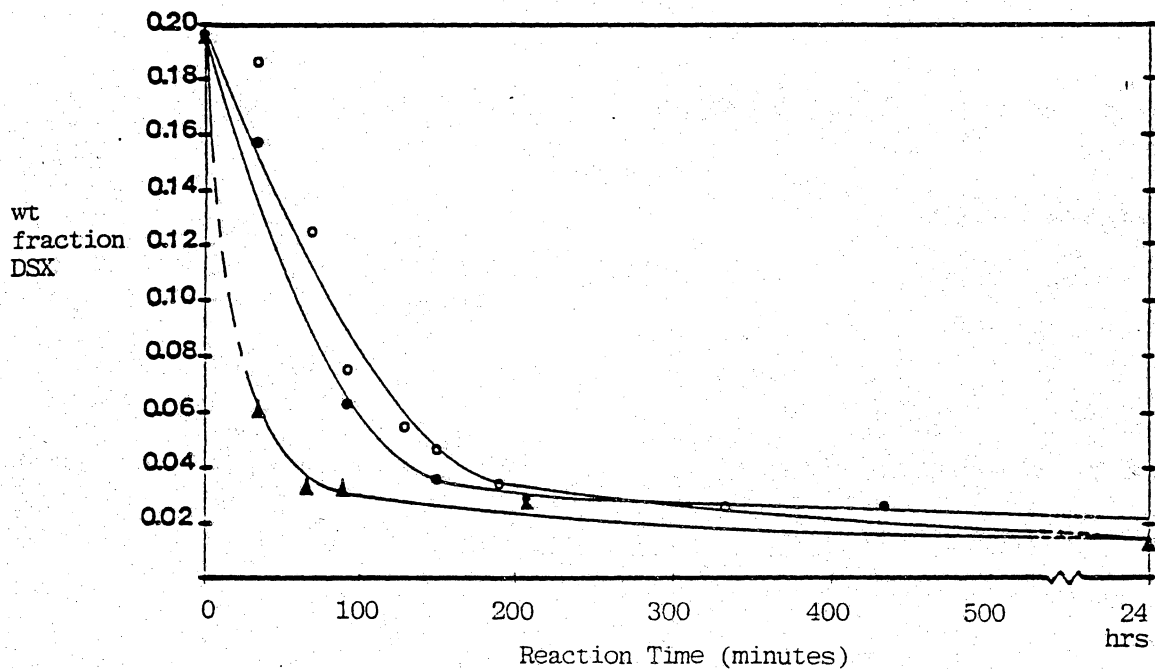
Figure 29. Reaction of disiloxane with 0.2 mole% tetra-
methylammonium hydroxide: in a 1200 Mn ol-
igomer at temperatures of 72°C (o), 91°C
(●)and 103°C (▲).
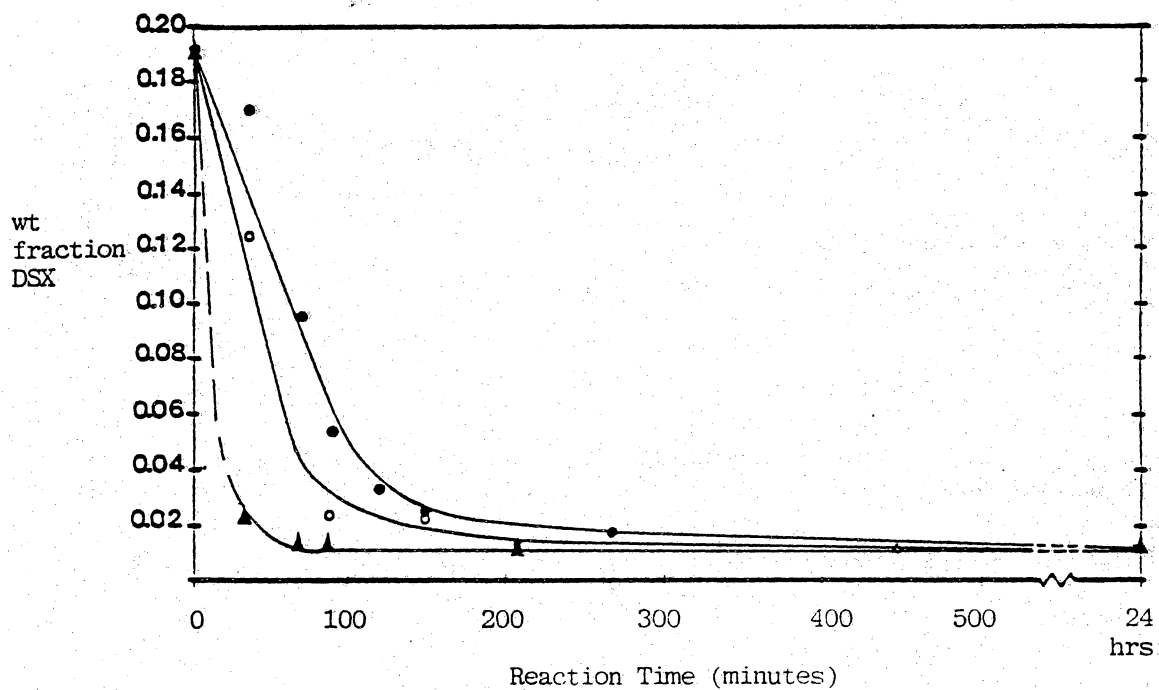
Figure 30. Reaction of disiloxane with 0.4 mole% tetra-
methylammonium hydroxide: in a 1200 Mn ol-
igomer at temperatures of 73°C (●), 87°C
(○), and 101°C (▲).
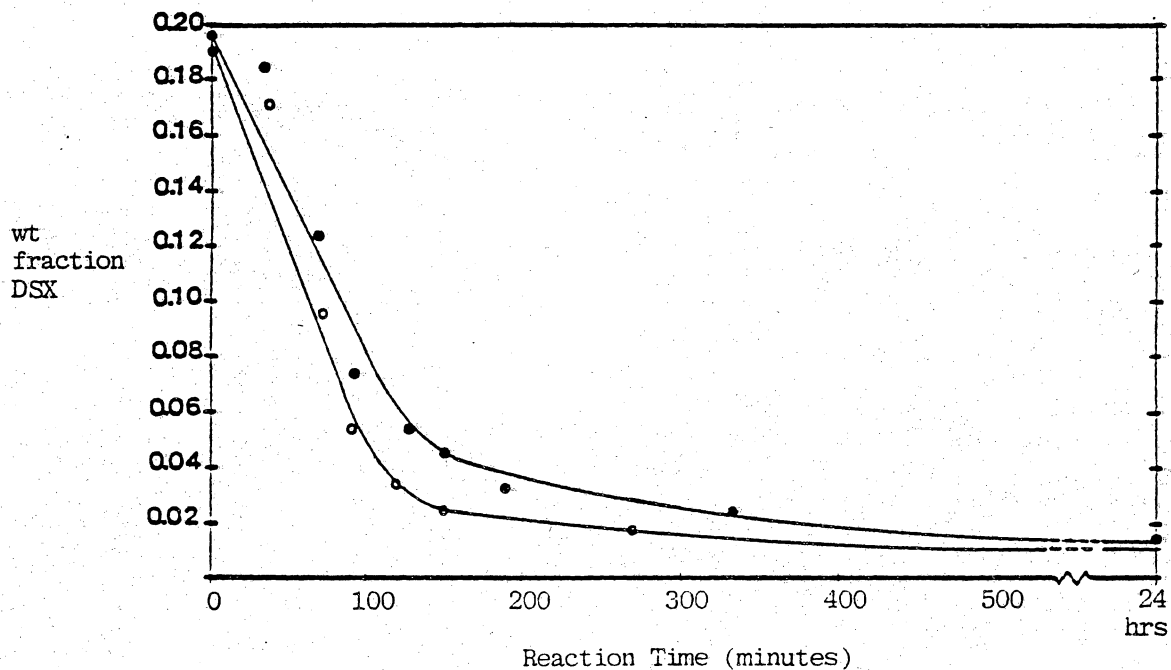
Figure 31. Illustration of the effect of catalyst con-
centration on the reaction of disiloxane with
tetramethylammonium catalyst: in a 1200 Mn
oligomer with 0.2 mole% tetramethylammonium
hydroxide at 72°C (●) and 0.4 mole% tetra-
methylammonium hydroxide at 73°C (O).
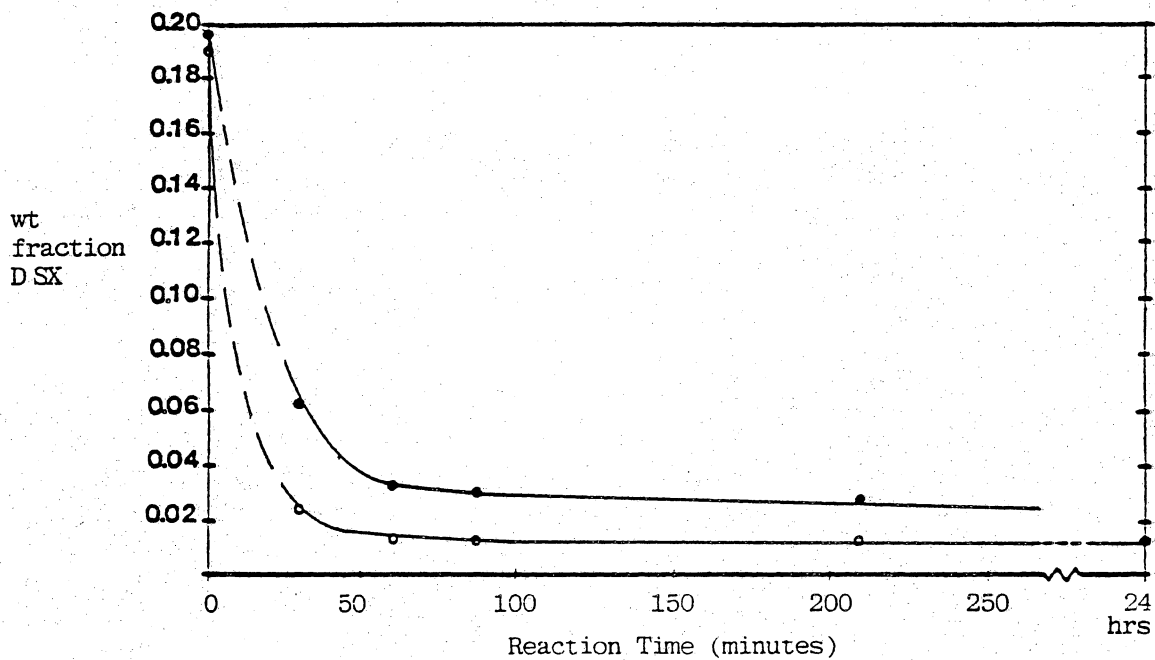
Figure 32.   Effect of catalyst concentration on the re-
action of disiloxane with tetramethyl-
ammonium catalyst: in a 1200 Mn Oligomer
with 0.2 mole% tetramethylammonium hydroxide
at 103°C (●) and 0.4 mole% tetramethyl-
ammonium hydroxide at 101°C (○).

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when an acidic catalyst is used. An acidic catalyst, how-
ever, is not feasible in this particular system due to the
possibility of reaction with the functional end groups.

Since the "limiting step" in these polymerizations seems
to be the consumption of the disiloxane, a convenient way of
preparing aminopropyl-terminated polydimethylsiloxane oli-
gomers would be to first prepare a low molecular weight oli-
gomer ($\approx$ 1000 g/mole for example). As it became necessary
to have siloxane oligomers of higher molecular weight, this
$\approx$ 1000 Mn oligomer could be used in the equilibration re-
actions, instead of the disiloxane, along with an appropriate
amount of D_4 in order to get the desired molecular weight
oligomer. Indeed, this is, in fact, the procedure that is
followed in the preparation of silylamine-terminated siloxane
oligomers [11]. A silylamine oligomer of $\approx$ 900 g/mole is
equilibrated with D_4 to produce higher molecular weight oli-
gomers. Preparing the oligomers in this fashion would elim-
inate the need for long reaction times, to incorporate the
disiloxane, in the preparation of every oligomer. Long re-
action times would only be required for the starting $\approx$ 1000
Mn oligomer. However, one would still have to demonstrate
equilibrium had been reached.

The use of the ammonium catalyst gave faster reaction
rates than the potassium catalyst at the same temperature,
probably due to the formation of aggregates of the potassium
siloxanolate end groups. However, by increasing the temper-

ature in the potassium-catalyzed equilibrations, we can achieve comparable reaction times as with the ammonium catalyst at lower temperatures. The use of the ammonium catalyst is perhaps slightly more appealing, because at the end of the reaction the reaction mixture can simply be heated above 130°C for several hours to decompose the catalyst. A thermally stable polymer is therefore obtained very easily, although it is difficult to remove all traces of the odorous triethylamine which is produced in the decomposition of the catalyst.

In contrast, the potassium catalyst must be neutralized in order to produce a thermally stable polymer. One way of doing this would be to dissolve the siloxane oligomer in methylene chloride and then wash with dilute aqueous HCl. The aqueous layer can be removed; the methylene chloride layer containing the siloxane can be dried and then the methylene chloride removed by flash distillation. This is, of course, a more involved procedure than is needed for the removal of the ammonium catalyst, but a thermally stable polymer is still the result with no disagreeable odor as is produced by the triethylamine from the ammonium catalyst. Alternatively, there may be ion-exchange column procedures for effective neutralization.

5.2.3 POLYDIMETHYL-CO-DIPHENYLSILOXANE OLIGOMERS

5.2.3.1 RATE OF REACTION OF CYCLIC STARTING MATERIALS

The first synthetic technique investigated involved the preparation of an aminopropyl-terminated polydimethylsiloxane oligomer as the first step. After 5-6 hours of reaction, the diphenyl tetramer was added to the reaction vessel; no attempt was made to characterize the polydimethylsiloxane oligomer before the addition of the D_4". It has been suggested [47, 49, 50] that D_4 is the slower reacting of the two cyclics. The D_4" ring is believed to open more rapidly because the silicon atom in the ring is more electropositive than the silicon atom in the D_4 ring. As discussed previously, however, we know that the reaction of D_4 in the presence of the aminopropyl disiloxane is quite rapid. By preparing the dimethyl oligomer first, we hoped to enhance the rate of preparation of these aminopropyl-terminated polydimethyl-co-diphenylsiloxane oligomers. Since the D_4 is at its equilibrium concentration, the only ring present to be attacked by the catalyst, at least initially, are the D_4" rings. Of course, the silicon-oxygen bonds present in the linear chains are of approximately equal reactivity with the D_4 silicon-oxygen bonds and will also participate in the equilibration process. This will result in the incorporation of diphenylsiloxane units into existing chains.

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There were some experimental difficulties involved in following the above procedure. The major problem was transferring the required amount of D_4" into the reaction vessel so that it would stir without becoming caked on the inside walls of the flask, since we do not have the option of rinsing the D_4" in with a solvent. The actual amount of D_4" incorporated into the system is probably slightly less than the charged amount.

The second problem encountered was due to the fact that the D_4" is a solid which is not soluble in either the D_4 or disiloxane. The reaction mixture is therefore heterogeneous initially and no samples could be removed during this time for analysis by HPLC. The reaction mixture becomes homogeneous only when the D_4" content is under ≈ 10 wt% ($< \approx 5$ mole%).

The initial set of experiments was done in a temperature range of 80-90°C, at a targeted molecular weight of 2500 g/mole and 25 wt% (13 mole%) diphenyl content using both the tetramethylammonium and potassium siloxanolate catalyst. Under these conditions it took 2-3 hours for the reaction mixture to become homogeneous. When this occurred and samples could be removed, LC analysis showed on the order of 1 wt% (<1 mole%) D_4 remaining. The "homogenization" of the reaction mixture occurs, in other words, not due to dissolution of the D_4", but rather due to its reaction. Shown in Figure 33 and Figure 34 are the results for the rate of disappearance of D_4", where TMAH represents the tetramethyl-

ammonium siloxanolate catalyst and KOH represents the potassium siloxanolate catalyst. These oligomers were not analyzed for D_4 content. It was assumed that the D_4 was largely consumed by the time of addition of D_4'' since the D_4 was allowed to react before the addition of the D_4''.

Since the next objective was to study the sequence distribution as a function of reaction conditions, it was desireable to prepare higher diphenyl content oligomers. A co-oligomer with 25 wt% diphenylsiloxane units has only about 13% diphenyl units on a molar basis. A more interesting system for the NMR studies would be an ≈50 mole% diphenyl co-oligomer. However, since this latter case is close to a 75 wt% diphenyl oligomer, it would be difficult to prepare an oligomer of only 2500 g/mole with reasonably complete incorporation of the D_4''. This is due to the difference in the molecular weight of the starting materials. The diphenylsiloxane repeat unit molecular weight is 792 g/mole, while that of the dimethylsiloxane repeat unit is 296 g/mole. The molecular weight of the disiloxane is 248.5 g/mole. Thus, synthesis of a higher molecular weight oligomer, 5000 g/mole, for example, was necessary. Also, due to the reaction size and the amount of D_4'' it was necessary to add to achieve a 75 wt% diphenyl oligomer, it was impractical to add the diphenyl tetramer after the dimethyl oligomer had been prepared. A typical recipe for a 5000 Mn oligomer with 75 wt% (51 mole%) diphenyl content is as follows:

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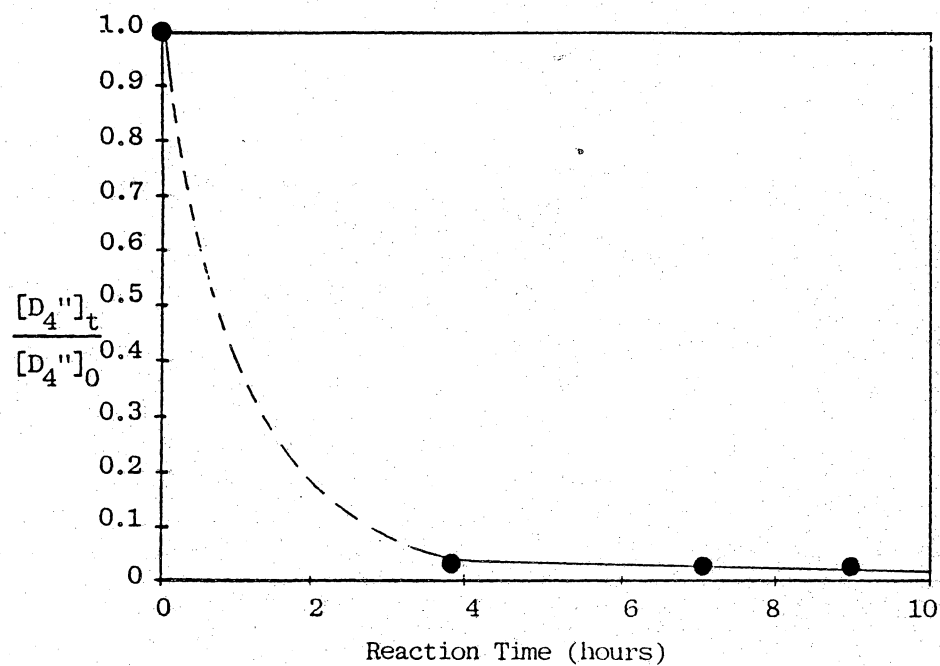
Figure 33. Reaction of $D_4"$ with 0.06 wt% (0.2 mole%)
TMAH: at 91°C in a 2500 targeted Mn oli-
gomer at 25 wt% (13 mole%) $D_4"$, dimethyl ol-
igomer prepared first.
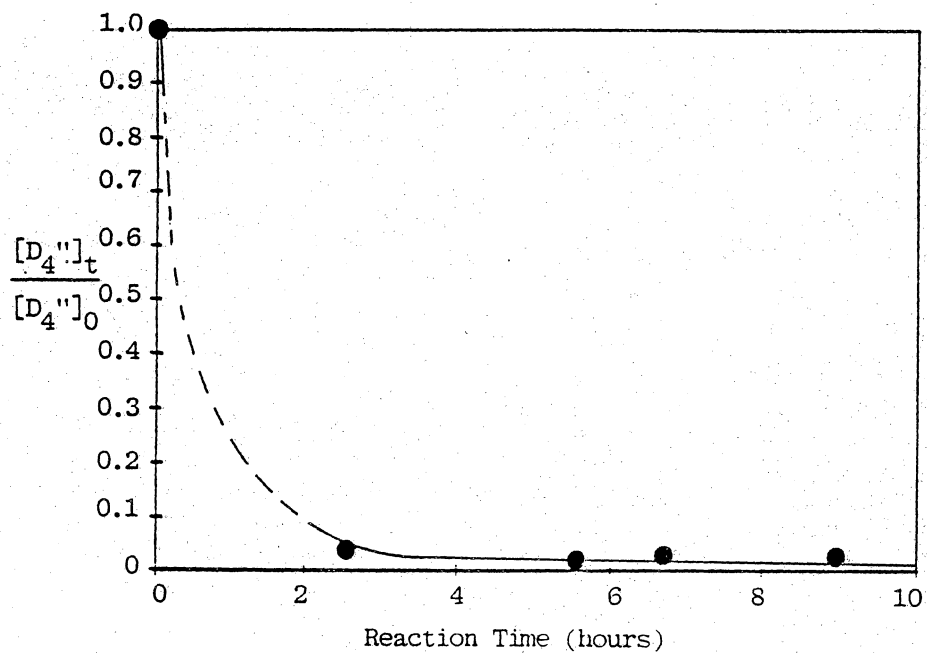
Figure 34.   Reaction of D_4'' with 0.06 wt% (0.4 mole%)
KOH: at 92°C in a 2500 targeted Mn oligomer
at 25 wt% (13 mole%) D_4'', dimethyl oligomer
prepared first.

- 1 g. disiloxane (0.004 moles)

- 4.03 g. D_4 (0.014 moles)

- 15.09 g. D_4" (0.019 moles)

- + appropriate catalyst

For these reasons, the technique of adding the D_4" after the D_4 and disiloxane had been allowed to equilibrate for a period of time was abandoned in favor of adding all starting materials together at the start of the reaction.

The latter method of preparation of polydimethyl-co-diphenylsiloxane oligomers proved to be more versatile. Since all the starting materials are charged to the reaction flask at the beginning of the reaction, there was no difficulty in transferring the correct amount of the diphenyl tetramer into the reaction vessel at the high diphenylsiloxane content systems.

Reversed-phase HPLC allowed the concentrations of the diphenyl tetramer and the dimethyl tetramer to be easily monitored. The use of two different detectors made it possible to distinguish between the two cyclic starting materials. The UV detector, which was used to monitor the D_4" concentration, did not observe the D_4, since polydimethylsiloxane oligomers are UV-transparent materials [2]. The IR

detector was operated at a frequency of 12.45μ (≈ 800 cm^1).
Since this corresponds to a Si-CH$_3$ vibration, and there is
no absorption by D$_4$" in that range, the IR detector could
measure only the D$_4$ concentration. This was fortunate since
there was some overlap between the D$_4$ and D$_4$" peaks in the
chromatograms. However, due to the selectivity of the two
detectors, this was not a problem.

The first major observation was that D$_4$" generally re-
acted more quickly D$_4$, as shown in Figure 35 through
Figure 42. However, when the tetramethylammonium catalyst
is used, particularly at high D$_4$" concentrations, the re-
action rate of D$_4$ occasionally briefly surpasses that of D$_4$".
This could possibly be due to the bulky tetramethylammonium
counter-ion. While this may inhibit the aggregation of the
siloxanolate end groups, it may also sterically hinder the
attack on the D$_4$" ring. In these figures, the amounts of D$_4$
and D$_4$" have been expressed in moles rather than weight
fractions, due to the large difference in the molecular
weights of D$_4$ and D$_4$". Also, since they are reacting simul-
taneously, in order to clearly compare the rates of reaction,
the moles of each cyclic at time t, divided by the initial
moles of each, is the quantity that is compared and plotted.
Catalyst concentrations are given in both mole% and weight%.
Slight differences in the mole% catalyst concentration at a
constant wt% are a result of the changing co-oligomer compo-
sition. (These difficulties in clarifying the process were

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not a factor in the all dimethyl system since the molecular weights of D_4 and the disiloxane are similar and since the rates of reaction of the two were so clearly different.) At temperatures of $\approx 90°C$, as the diphenyl content was increased, the time needed to begin to approach the equilibrium concentration of the D_4 and $D_4"$ increased as compared to the time it took for D_4 to reach its equilibrium concentration in the absence of $D_4"$. (Recall that in the reaction of D_4 and the aminopropyl disiloxane to prepare a 3000 Mn oligomer, it took <2 hours for the D_4 concentration to decrease to less 10 wt%.) For example, in the preparation of a 5000 Mn co-oligomer at 88°C using 0.06 wt% (0.4 mole%) potassium hydroxide with 50 wt% (27 mole%) diphenyl content, it took over 6 hours for both the cyclic starting materials to begin to level off into their equilibrium concentrations, as shown in Figure 36.

Now, since these reaction mixtures are initially heterogeneous due to the insolubility of the $D_4"$ in either the D_4 or the disiloxane, these figures show dashed lines for the initial stages of the polymerization. Any attempts to homogenize the reaction medium, such as adding a solvent, would change the position of the ring-chain equilibrium. There is, in fact, a critical concentration below which only cyclic structures are present [13]. This concentration effect applies not only to the addition of a solvent but also to the type of substituents on the silicon atom. There thus appears
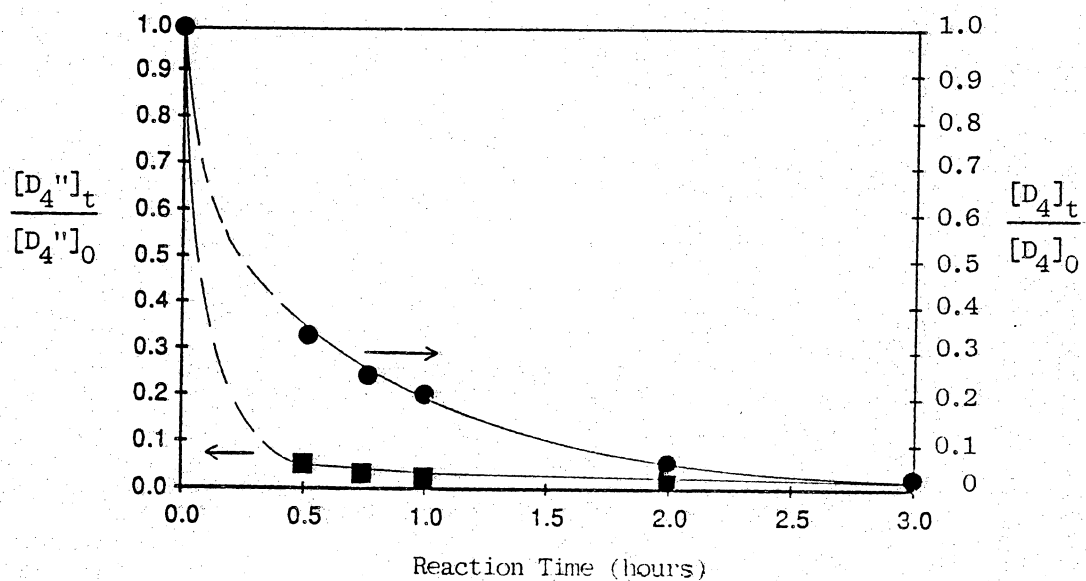
Figure 35.   Disappearance of D_4 and D_4'' with 0.12 wt% (0.8 mole%) KOH at 50 wt% (27 mole%) D_4'' content: in a 5000 Mn oligomer at 131°C.
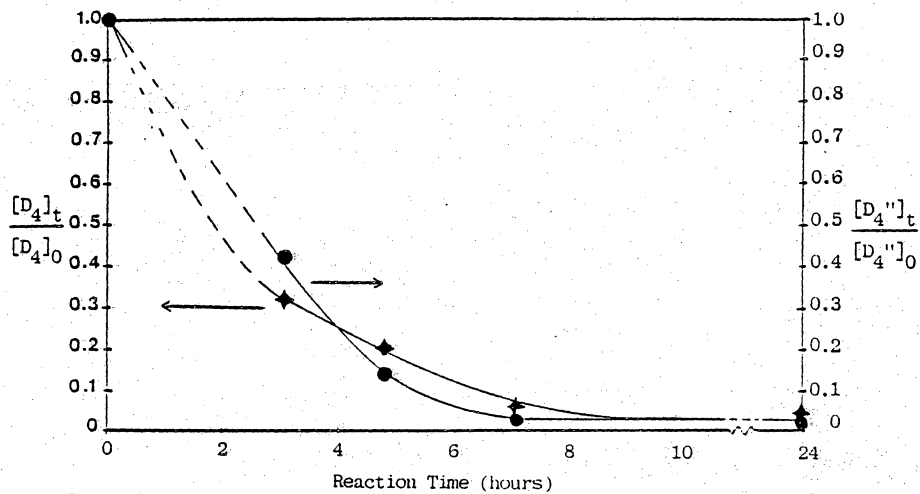
Figure 36. Disappearance of D_4 and D_4'' with 0.06 wt%
(0.4 mole%) KOH at 25 wt% (13 mole%) D_4''
content: in a 5000 Mn oligomer at 89°C.
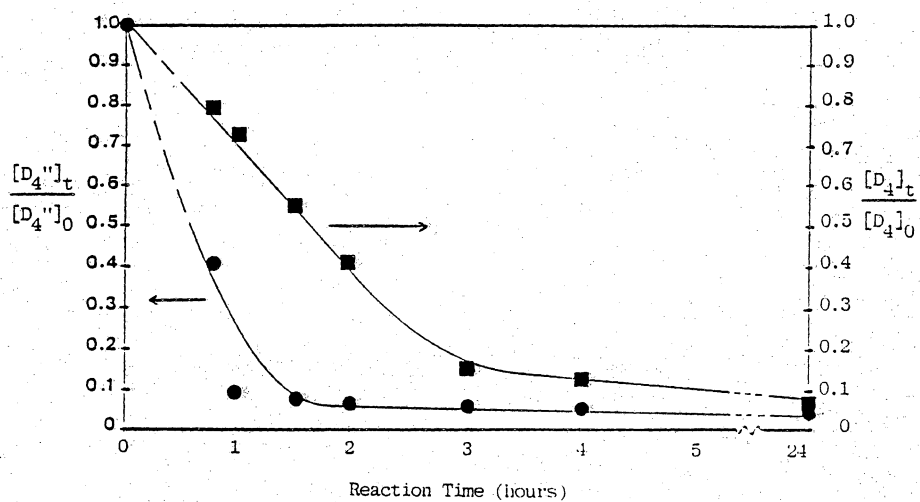
Figure 37. Disappearance of D_4 and D_4'' with 0.06 wt% (0.4 mole%) KOH at 50 wt% (27 mole%) D_4'' content: in a 5000 Mn oligomer at 128°C.
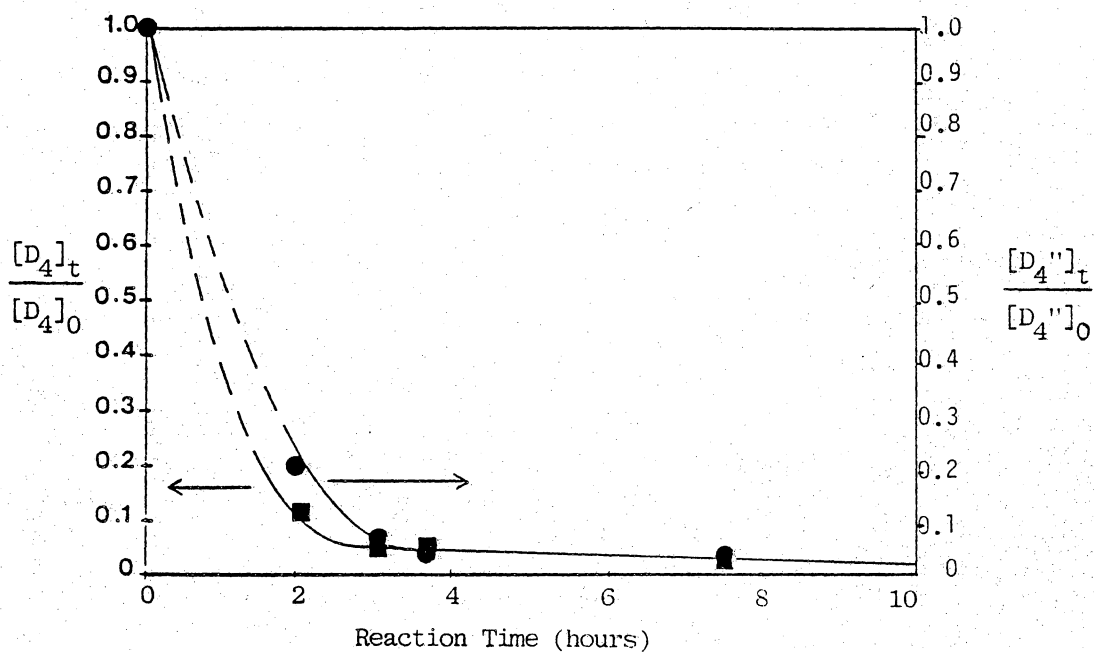
Figure 38.   Disappearance of D_4 and D_4'' with 0.12 wt%
(0.4 mole%) TMAH at 25 wt% (13 mole%) D_4''
content: in a 5000 Mn oligomer at 89°C.
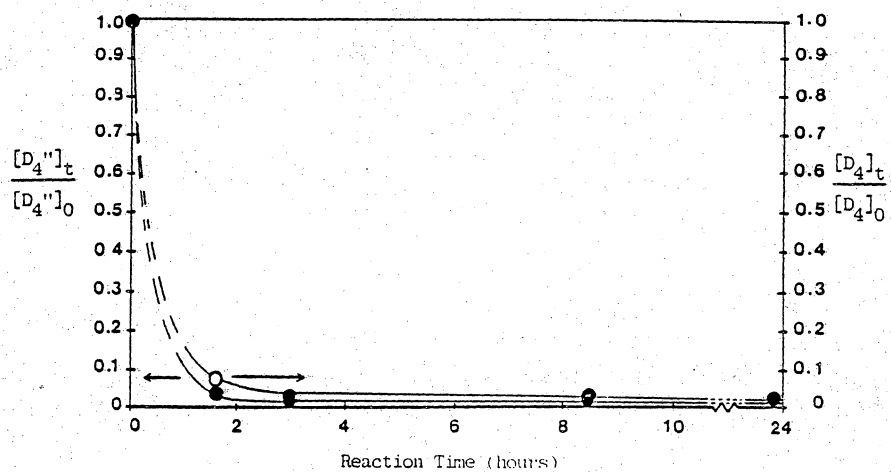
Figure 39. Disappearance of D_4 and D_4'' with 0.12 wt% (0.6 mole%) TMAH at 50 wt% (27 mole%) D_4'' content: in a 5000 Mn oligomer at 88°C.

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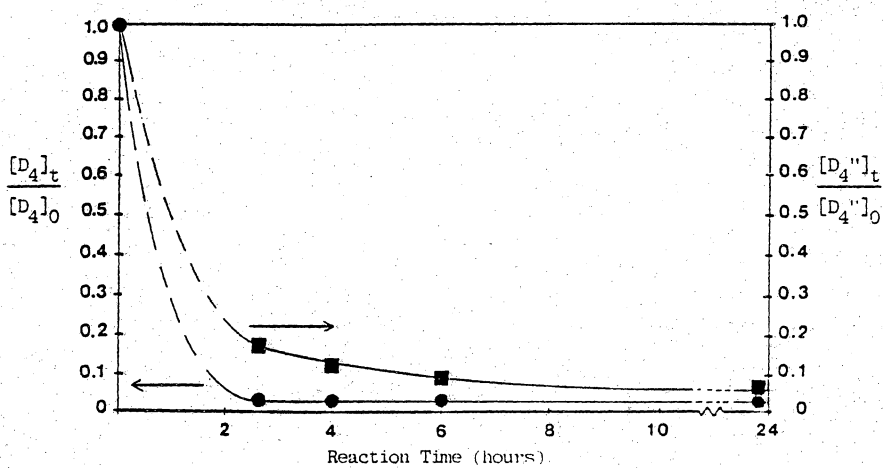
Figure 40. Disappearance of D_4 and $D_4{''}$ with 0.12 wt% (0.7 mole%) TMAH at 75 wt% (51 mole%) $D_4{''}$ content: in a 5000 Mn oligomer at 89°C.
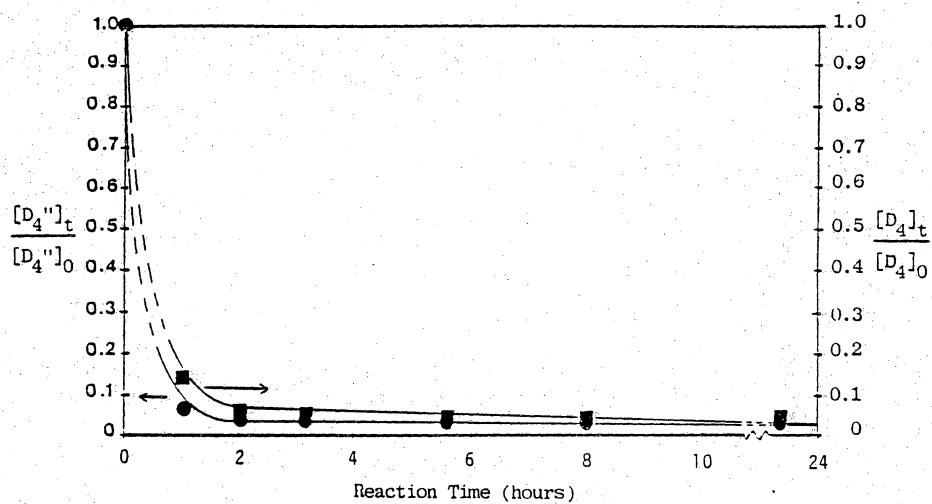
Figure 41.   Disappearance of D_4 and D_4'' with 0.06 wt% (0.2 mole%) TMAH at 25 wt% (13 mole%) D_4'' content: in a 5000 Mn oligomer at 88°C.

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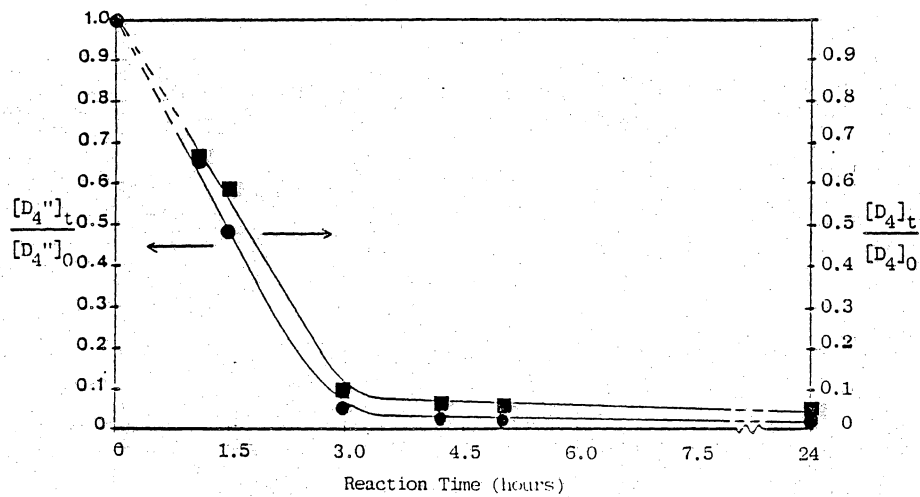
Figure 42. Disappearance of D_4 and D_4'' with 0.06 wt% (0.2 mole%) TMAH at 50 wt% D_4'' (27 mole%) content: in a 5000 Mn oligomer at 88°C.

to be no practical way of obtaining a homogeneous system right from the start of the polymerization that would not significantly alter the polymerization process.

The next observation was that the tetramethylammonium catalyst again reacted much more rapidly than the potassium catalyst. This is seen in Figure 43 through Figure 48. This is in accordance with the previous results obtained for the all dimethyl systems. The faster rate of reaction of the tetramethylammonium catalyst is still presumably due to less aggregation of the end groups in this case into unreactive complexes.

The expected temperature effect on the rate of reaction of D_4 and D_4'' is illustrated in Figure 49 through Figure 54: increasing the temperature increases the rate of reaction. In addition, in performing the equilibration at high temperatures ($\approx 132°C$) with the potassium catalyst, a homogeneous system was obtained very quickly, in less than 2 hours. However, there was still a measureable amount (≈ 6 wt%, ≈ 3 mole%) of D_4'' left in the system at this point. At these higher reaction temperatures, therefore, the system becomes homogeneous not only because of reaction of the D_4'', but also because the D_4'' does have some limited solubility in the oligomer at elevated temperatures. Reactions done at the higher temperatures, therefore, potentially give more information on the reaction rates since samples can be removed earlier in the equilibration process. This is feasible only
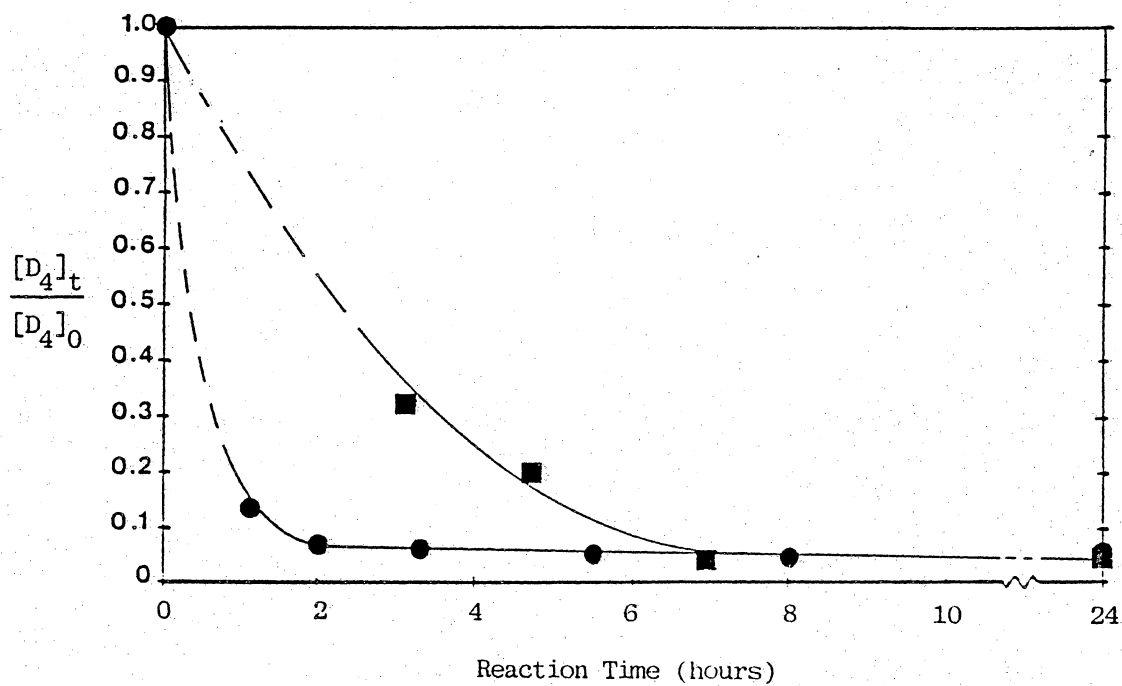
Figure 43. Comparison of the rate of reaction of D_4 with each catalyst at 25 wt% (13 mole%) D_4" content: in a 5000 Mn oligomer with 0.06 wt% (0.4 mole%) KOH (■) and 0.06 wt% TMAH (0.2 mole%) (●).

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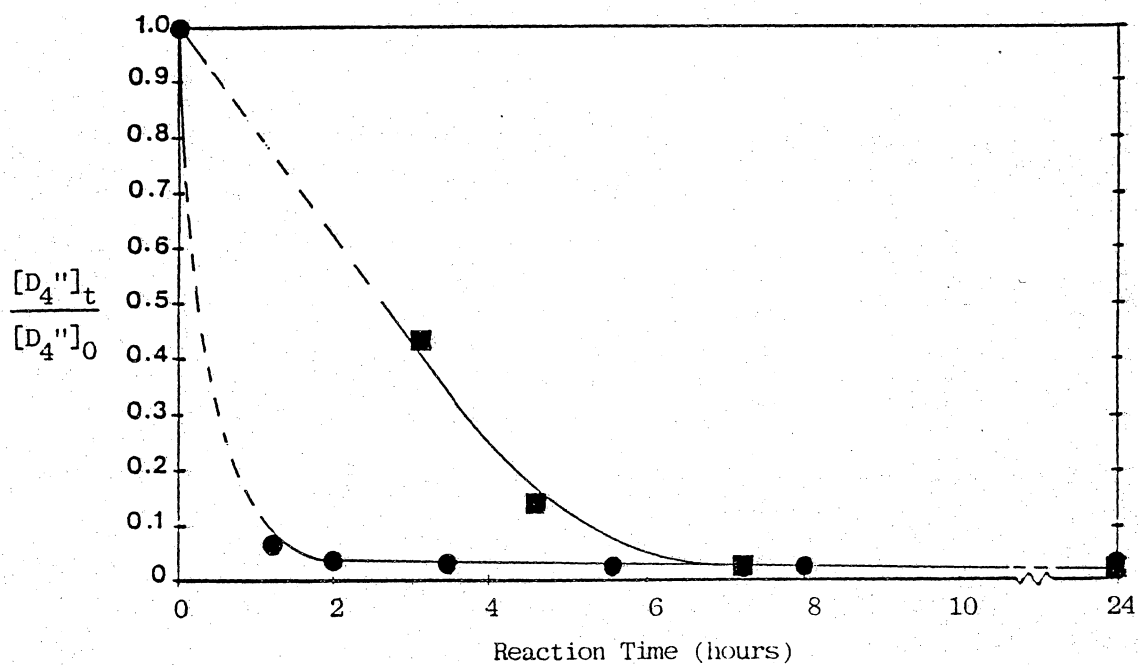
Figure 44. Comparison of the rate of reaction of D_4'' with each catalyst at 25 wt% D_4'' (13 mole%) content: in a 5000 Mn oligomer with 0.06 wt% (0.4 mole%) KOH (■) and 0.06 wt% TMAH (0.2 mole%) (●) at 88°C.
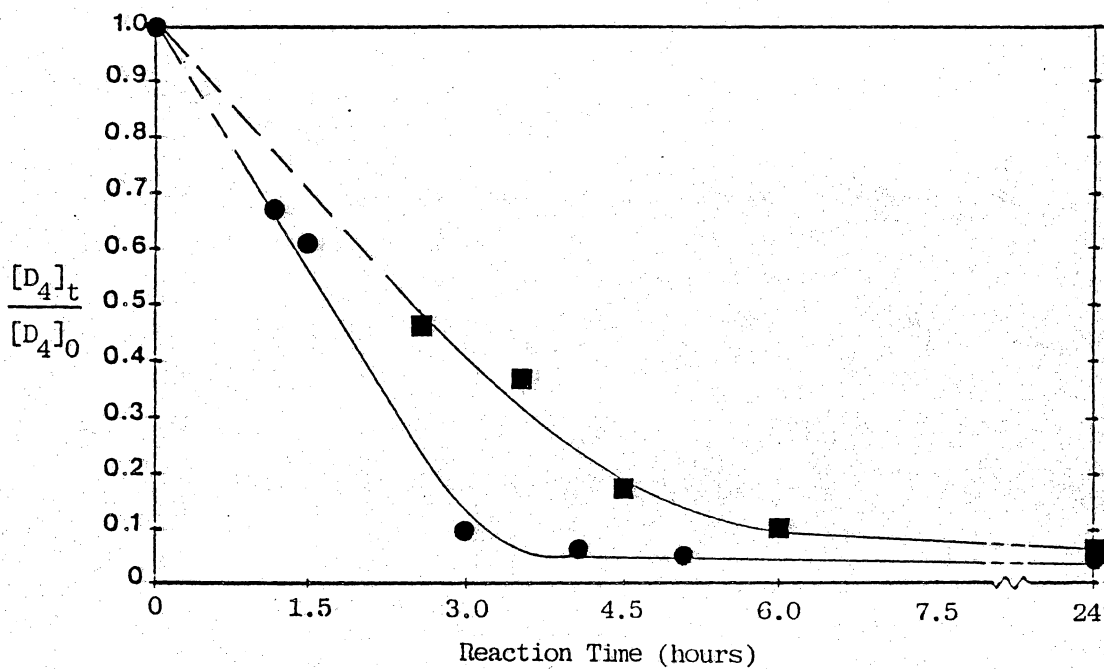
Figure 45. Comparison of the rate of reaction of D_4 with each catalyst at 50 wt% D_4" (27 mole%) content: in a 5000 Mn oligomer with 0.06 wt% (0.4 mole%) KOH (■) and 0.06 wt% TMAH (0.2 mole%) (●) at 88°C.

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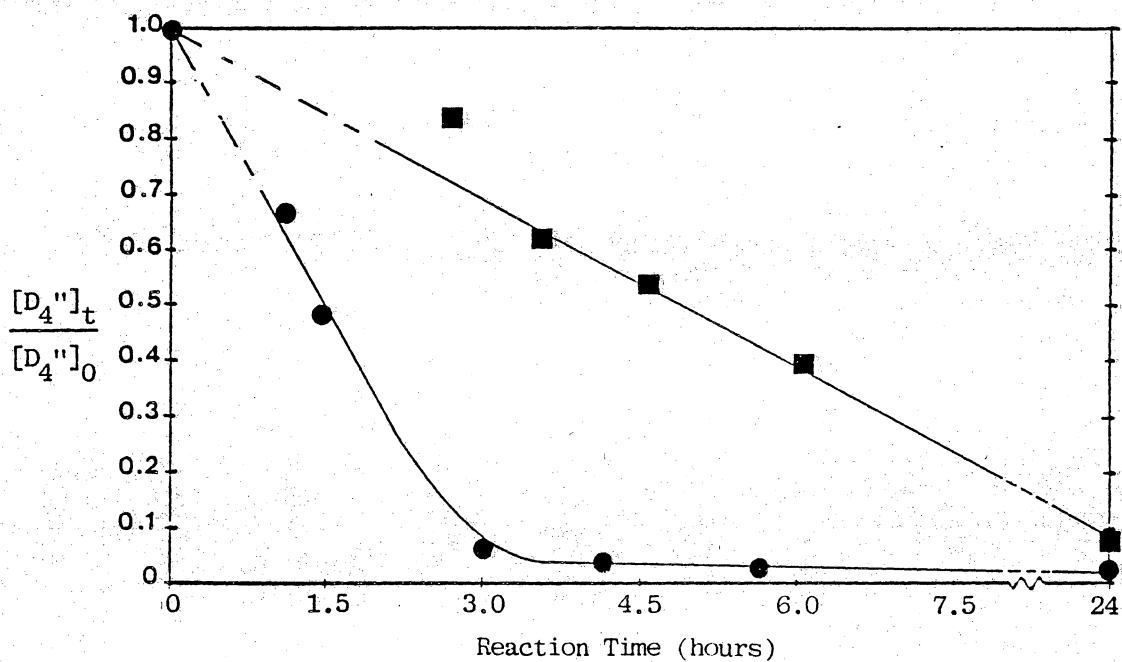
Figure 46. Comparison of the rate of reaction of D_4'' with each catalyst at 50 wt% (27 mole%) D_4'' content: in a 5000 Mn oligomer with 0.06 wt% (0.4 mole%) KOH (■) and 0.06 wt% TMAH (0.2 mole%) (●) at 88°C.
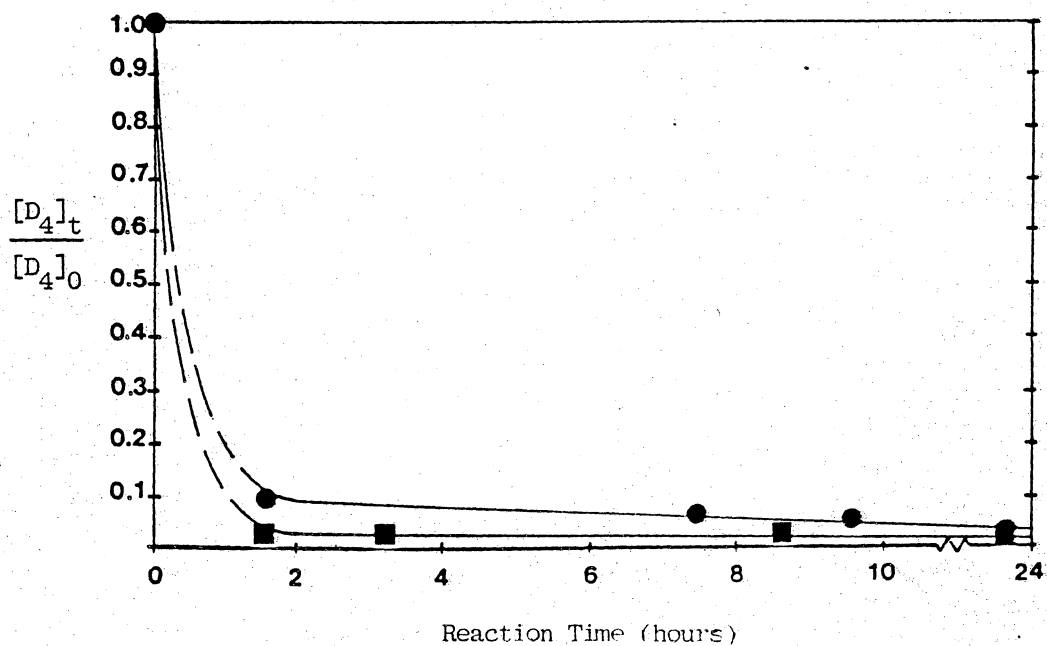
Figure 47. Comparison of the rate of reaction of D_4 with each catalyst at 50 wt% (27 mole%) D_4" content: in a 5000 Mn oligomer with 0.12 wt% (0.8 mole%) KOH (●) and 0.12 wt% TMAH (0.6 mole%) (■) at 88°C.
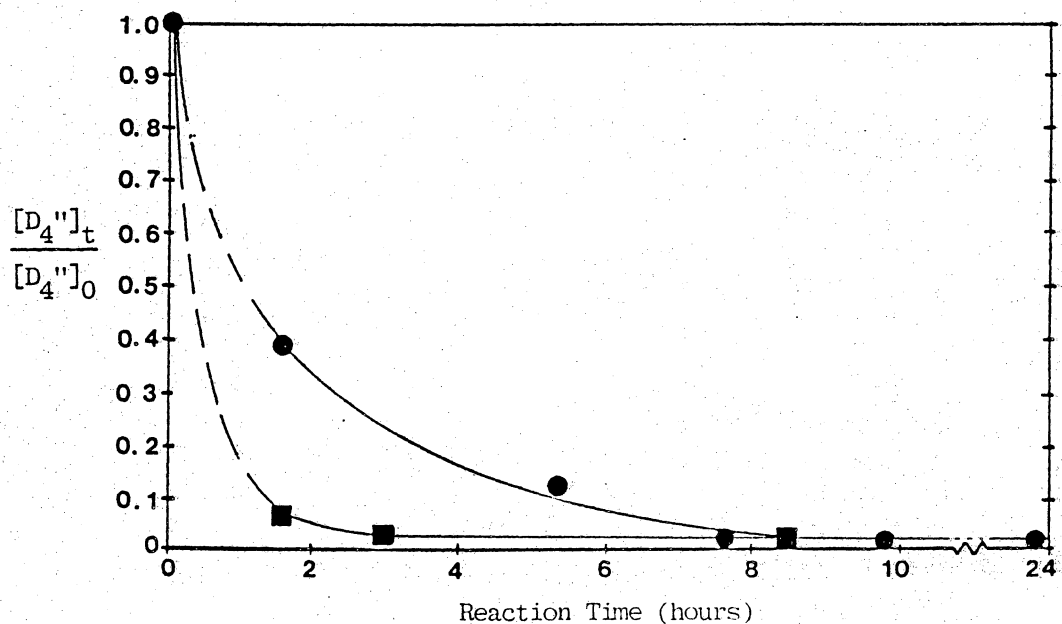
Figure 48. Comparison of the rate of reaction of D_4'' with each catalyst at 50 wt% (27 mole%) D_4'' content: in a 5000 Mn oligomer with 0.12 wt% (0.8 mole%) KOH (●) and 0.12 wt% TMAH (0.6 mole%) (■) at 88°C.

with the potassium catalyst, however, since the tetramethyl-ammonium catalyst is not stable at the necessary temper-atures. Therefore the temperature effect on the rate of reaction with the tetramethylammonium catalyst was not stu-died in detail.

The next point to be addressed is the question of the equilibrium amounts of D_4 and D_4'' remaining. This is much more complicated than in the case of the all dimethyl system. Here there is not only the possibility of D_4 and D_4'' rings being present at equilibrium, but also of rings with both dimethyl-substituted and diphenyl-substituted silicon atoms in the ring. This occurs due to backbiting. One can envision the formation of so-called "mixed cyclics" by processes sim-ilar to that outlined in scheme 3. The types of mixed cyclics formed and the number of different types of mixed cyclics, will depend on the sequence distribution of the two types of siloxane units near the end of the chain. This point will be discussed in more detail in the section on ^{29}Si nmr, but the concept must be kept in mind for this discussion of the equilibrium amounts of the cyclic starting materials.

Looking first at the D_4 equilibrium concentration in Table 6 and Table 7 at various temperatures with each cata-lyst, it is clear that the equilibrium concentration is very low in every case. (Recall that the D_4 equilibrium concen-tration in the all dimethyl system was on the order of 5 wt%.) One possible explanation is that the presence of mixed cy-
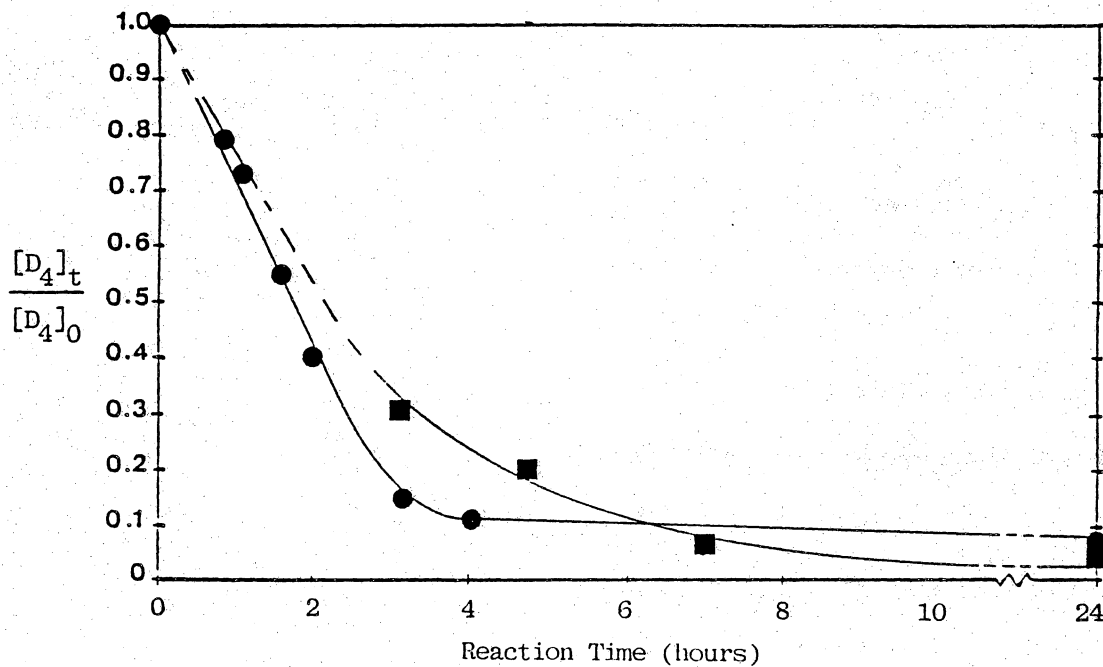
Figure 49. Effect of temperature on the reaction of D_4 at 25 wt% (13 mole%) D_4" content and 0.06 wt% (0.4 mole%) KOH: 89°C (■), 128°C (●).
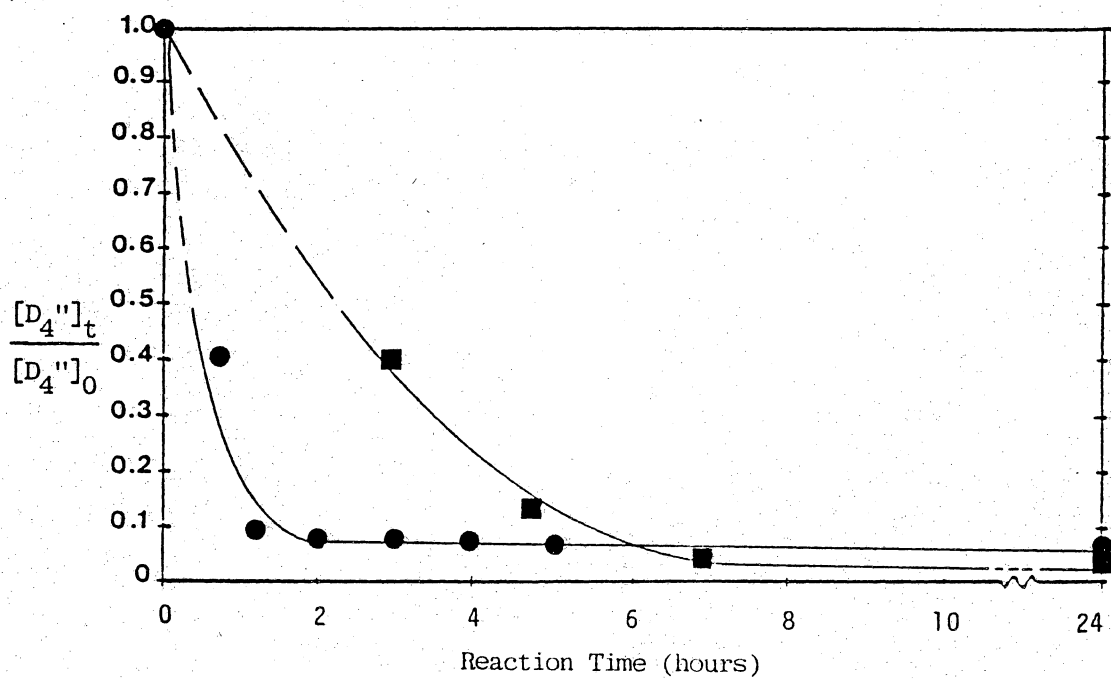
Figure 50. Effect of temperature on the reaction of D_4''
at 25 wt% (13 mole%) D_4'' content and 0.06 wt%
(0.4 mole%) KOH: 89°C (■), 128°C (●).
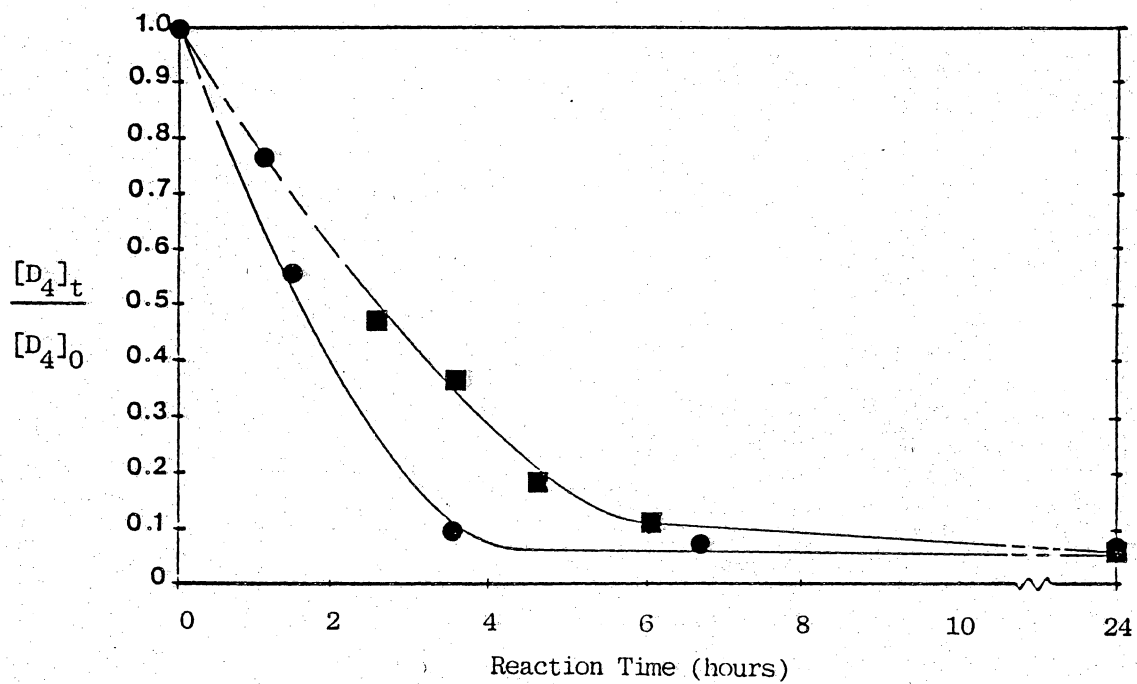
Figure 51.   Effect of temperature on the reaction of D_4 at 50 wt% (27 mole%) D_4'' content and 0.06 wt% (0.4 mole%) KOH: 89°C (■), 131°C (●).
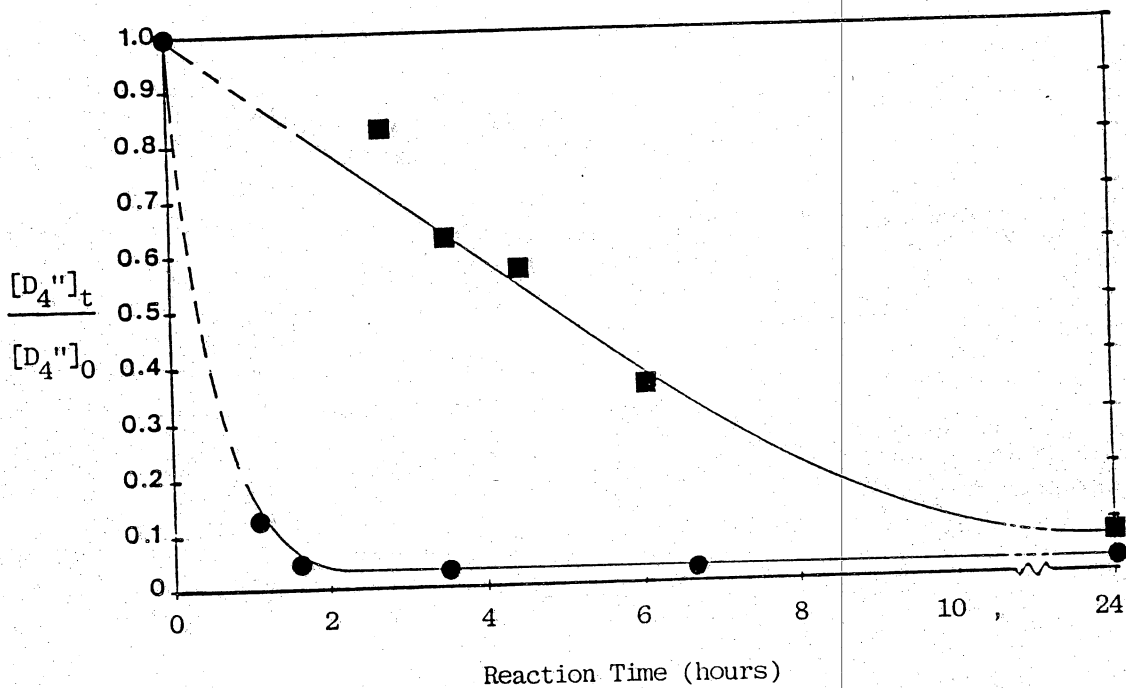
Figure 52. Effect of temperature on the reaction of D_4'' at 50 wt% (27 mole%) D_4'' content and 0.06 wt% (0.4 mole%) KOH: 89°C (■), 131°C (●).

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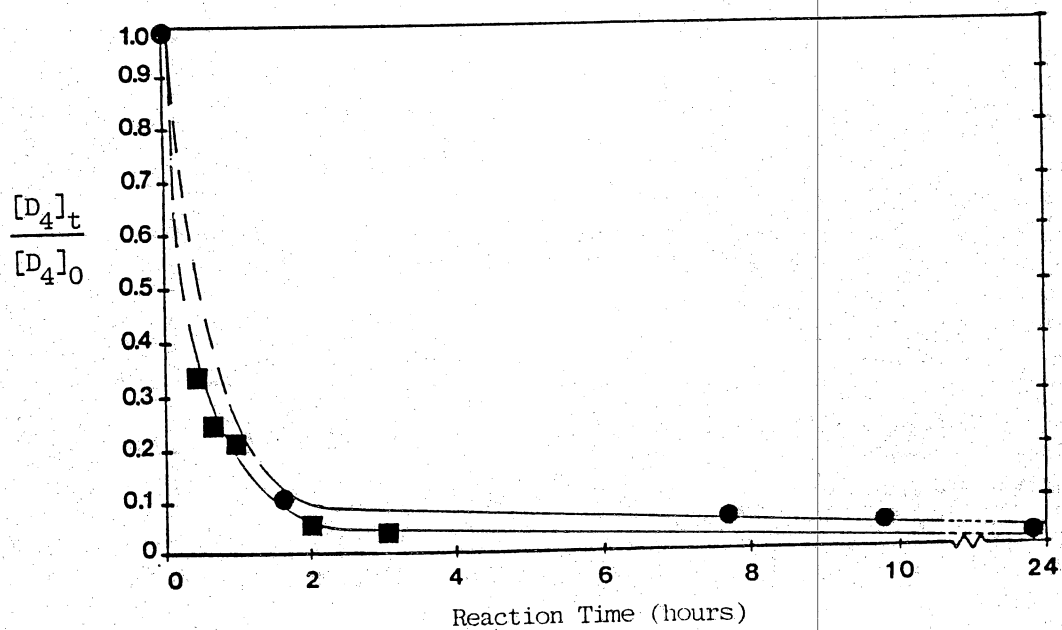
Figure 53. Effect of temperature on the reaction of D_4 at 50 wt% (27 mole%) D_4" content and 0.12 wt% (0.8 mole%) KOH: 88°C (●), 131°C (■).
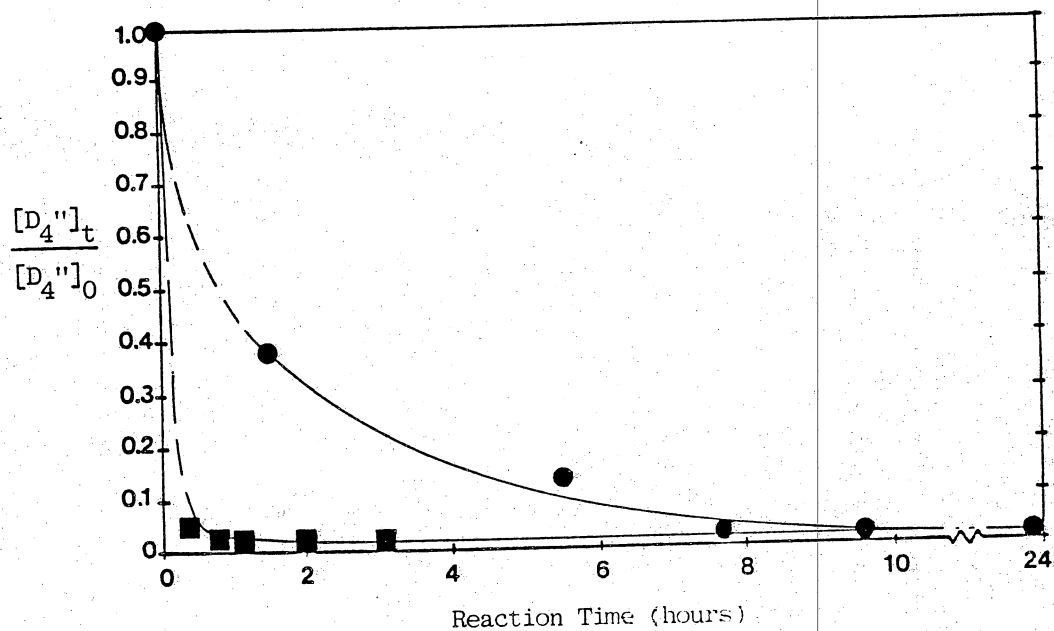
Figure 54. Effect of temperature on the reaction of D_4"
at 50 wt% (27 mole%) D_4" content and 0.12 wt%
(0.8 mole%) KOH: 88°C (●), 131°C (■).

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clics detracts from the formation of D_4 by backbiting. That is, it is not that the amount of backbiting has decreased, but that there are a greater variety of structures that can be formed, particularly if the sequence distribution consists of very short runs of each type of unit. The sequence distribution is clearly a critical parameter in determining the types of mixed cyclics that are formed.
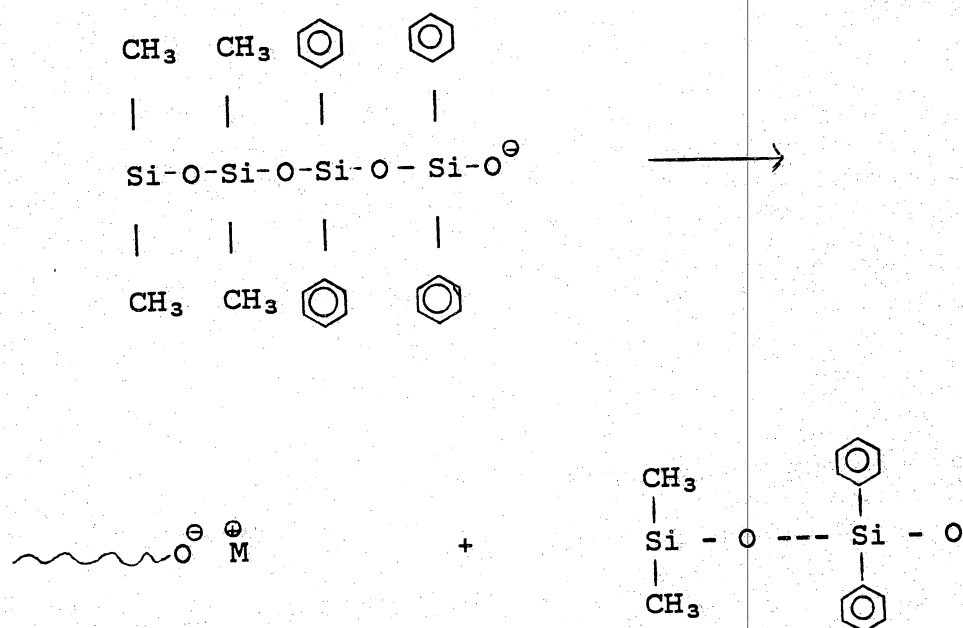
Scheme 3. Process by which mixed cyclics may be formed in an equilibration reaction.

The equilibrium amount of D_4'' seemed to depend in part on the amount of D_4'' that was originally charged to the reaction vessel. Shown in Table 8 and Table 9 are the equilibrium concentration of D_4'' under various reaction

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conditions. Generally, the higher the initial D_4'' concentration, the more D_4'' remaining after reaction times of $\simeq$ 24 hours. It is possible that still longer reaction times would be useful for greater incorporation of D_4'' into the co-oligomer. Even at higher reaction temperatures, a lower incorporation of D_4'' is observed at high initial D_4'' concentrations. These observations are probably a result of the low basicity of the diphenylsiloxanolate anion: once formed this is the slower reacting anion. The more D_4'' that is charged to the reaction, the more siloxanolate anions which are stabilized by the phenyl substituents are formed, and the slower is the reaction. After 24 hours, the reaction is probably still slowly proceeding in favor of the linear species.

There is an additional factor affecting the rate of reaction of D_4'': the co-oligomer composition. As shown in Figure 55 and Figure 56, the more diphenyl tetramer charged to the reaction flask at a given temperature and catalyst concentration, the slower the rate of reaction. The slower rate of reaction means that it takes a longer time for the reaction mixture to become homogeneous. The greatest effect is seen at lower reaction temperatures. At high temperatures ($\simeq 130^\circ$C) the rate of reaction has been observed to be quite rapid over the range of compositions studied. In the 75 wt% diphenyl content systems, for example, at 88-90°C, even after 24 hours the reaction mixture is not totally transparent.

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Longer reaction times are required [11], and even then when the reaction mixture cools to room temperature some material precipitates out of the liquid product, presumably D_4".
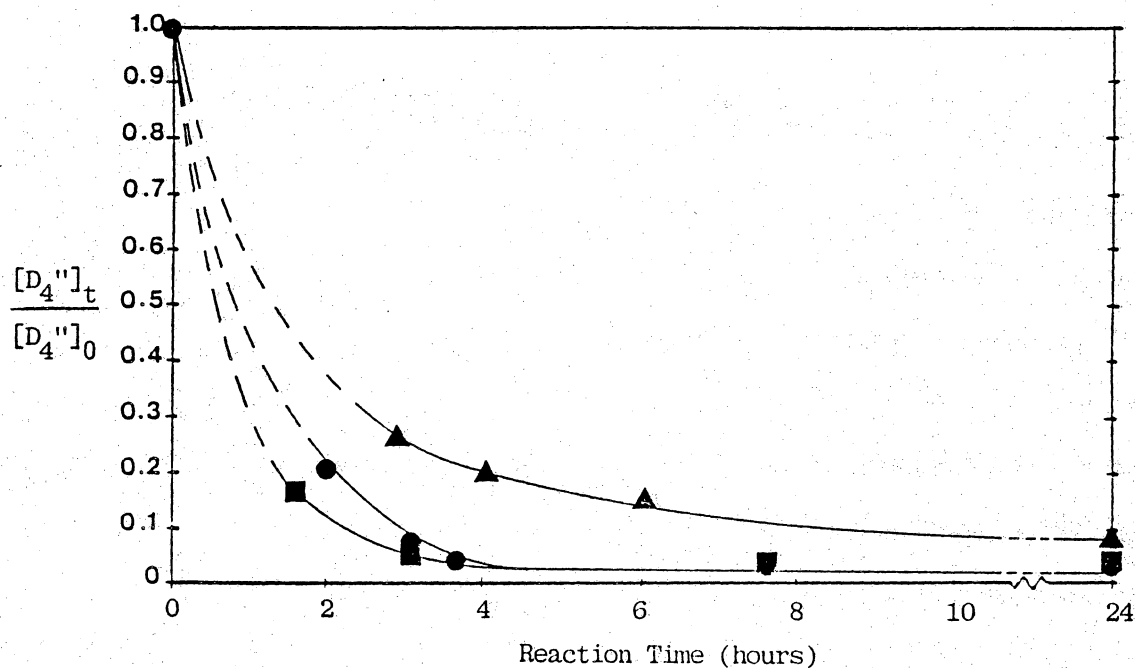
Figure 55. Illustration of the effect of increasing the $D_4"$ concentration on the rate of reaction of $D_4"$ with TMAH: in a 5000 Mn oligomer at 25 wt% (13 mole%) $D_4"$, 0.12 wt% (0.4 mole%) TMAH (●), 50 wt% $D_4"$ (27 mole%), 0.12 wt% TMAH (0.6 mole%) (■), and 75 wt% $D_4"$ (51 mole%), 0.12 wt% TMAH (0.7 mole%) (▲).
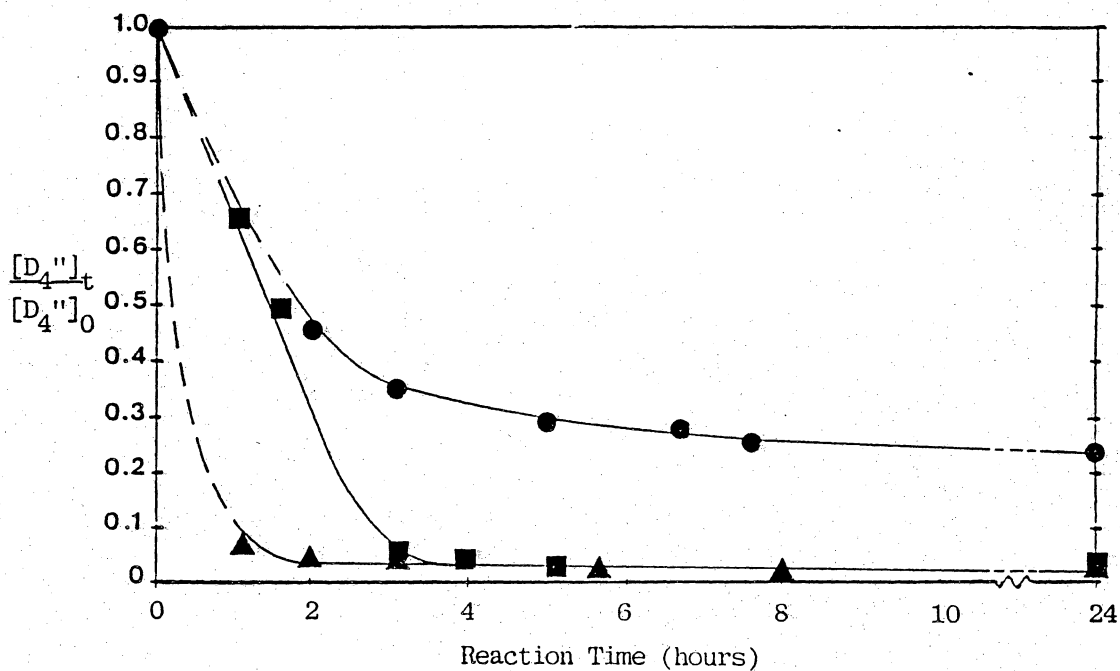
Figure 56. Illustration of the effect of increasing the D_4'' concentration on the rate of reaction of D_4'' with TMAH: in a 5000 Mn oligomer at 25 wt% (13 mole%) D_4'', 0.06 wt% TMAH (0.2 mole%) (▲), 50 wt% D_4'' (27 mole%), 0.06 wt% TMAH (0.2 mole%) (■), and 75 wt% (51 mole%) D_4'', 0.06 wt% TMAH (0.3 mole%) (●)

Table 6. "Equilibrium" Amount of D_4 at 24 hrs with Potassium Catalyst.

T (°C)	wt% D_4	fraction of initial conc. (moles)	Catalyst conc. (mole%)	mole% D_4" charged
132	2.8	0.009	1.0	58
131	3.1	0.07	0.8	30
131	3.0	0.045	0.8	15
88	2.2	0.049	0.8	30
131	3.3	0.075	0.4	30
131	2.0	0.108	0.5	58
128	2.0	0.083	0.4	15
89	3.0	0.043	0.4	15
89	2.9	0.068	0.4	30

Table 7.   "Equilibrium" Amount of D_4 at 24 hrs with Tetramethylammonium Catalyst.

T (°C)	wt% D_4	fraction of initial conc. (moles)	Catalyst conc. (mole%)	mole% D_4" charged
88	2.0	0.048	0.6	30
89	4.2	0.014	0.4	15
89	1.9	0.092	0.7	58
88	2.4	0.054	0.2	30
88	3.5	0.052	0.2	15
89	1.0	0.015	0.3	58

Table 8.   "Equilibrium" Amount of D_4" at 24 hrs with
Potassium Catalyst.

T (°C)	wt% D_4"	fraction of initial conc. (moles)	Catalyst conc. (mole%)	mole% D_4" charged
132	5.8	0.079	1.0	58
131	0.2	0.003	0.8	30
131	1.0	0.001	0.8	15
88	1.0	0.017	0.8	30
131	1.0	0.016	0.4	30
131	5.1	0.065	0.5	58
128	2.0	0.097	0.4	15
89	3.1	0.010	0.4	15
89	4.4	0.068	0.4	30

Table 9.   "Equilibrium" Amount of D_4" at 24 hrs with Tetramethylammonium Catalyst.

T (°C)	wt% D_4"	fraction of initial conc. (moles)	Catalyst conc. (mole%)	mole% D_4" charged
88	1.2	0.033	0.6	30
89	1.0	0.030	0.4	15
89	7.2	0.099	0.7	58
88	1.0	0.016	0.2	30
88	1.0	0.032	0.2	15

5.2.3.2 SUMMARY

In agreement with previous work in the field, D_4'' was found to be a faster reacting material than D_4, in reactions performed with the potassium catalyst. However, at high charged amounts of D_4'' when the tetramethylammonium catalyst was used, the rate of reaction of D_4 is slightly faster than that of D_4''. In this case, the bulky tetramethylammonium counter-ion and the presence of diphenyl-substituted siloxanolate anions cause the steric effects to dominate, rather than electronic which is the case with the potassium catalyst. Increasing the reaction temperature, using the potassium catalyst, greatly speeded up the rate of reaction of both cyclics. Although D_4'' reacted more quickly than D_4, once formed that siloxanolate was more stable and slower reacting. This was evidenced by the slower reaction rates at high D_4'' concentrations. More information could have been obtained at earlier reaction times. However, the experimental techniques are limited due to the need for a homogeneous reaction medium for the removal of representative samples from the reaction. Nevertheless, quantitative information was obtained on both cyclic starting materials.

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The distribution of dimethylsiloxane and diphenyl-
siloxane units in the chains was also of interest, in addi-
tion to the rate at which each cyclic starting material was
consumed. The number average sequence lengths of each type
of unit could be assessed by ^{29}Si NMR. The formation of mixed
cyclic siloxanes can also be easily observed since the reso-
nances of silicon nuclei in rings are well separated from
those of silicon nuclei in linear molecules. A sample ^{29}Si
NMR spectrum is shown in Figure 57 of a solution containing
the starting materials in these polymerizations, (end
blocker, $D_4"$, D_4) as well as other cyclic siloxanes poten-
tially present in the system ($D_3"$, D_3). Figure 58 shows a
sample NMR obtained for a sample removed by pipette from a
reaction mixture (conditions shown in the figure). One con-
cludes that adequate resolution between the triad peaks for
quantitative analysis of the sequence distribution of como-
nomer units has been achieved.

In the quantitative analysis of ^{29}Si NMR spectra, the
question of the influence of the chromium triacetylacetonate,
$Cr(acac)_3$, on the relaxation times of the different types of
silicon nuclei must be considered. As long as the delay be-
tween pulses is sufficient to allow for complete relaxation,
the quantitative results should not be affected. A compar-
ison was made between the results obtained using different

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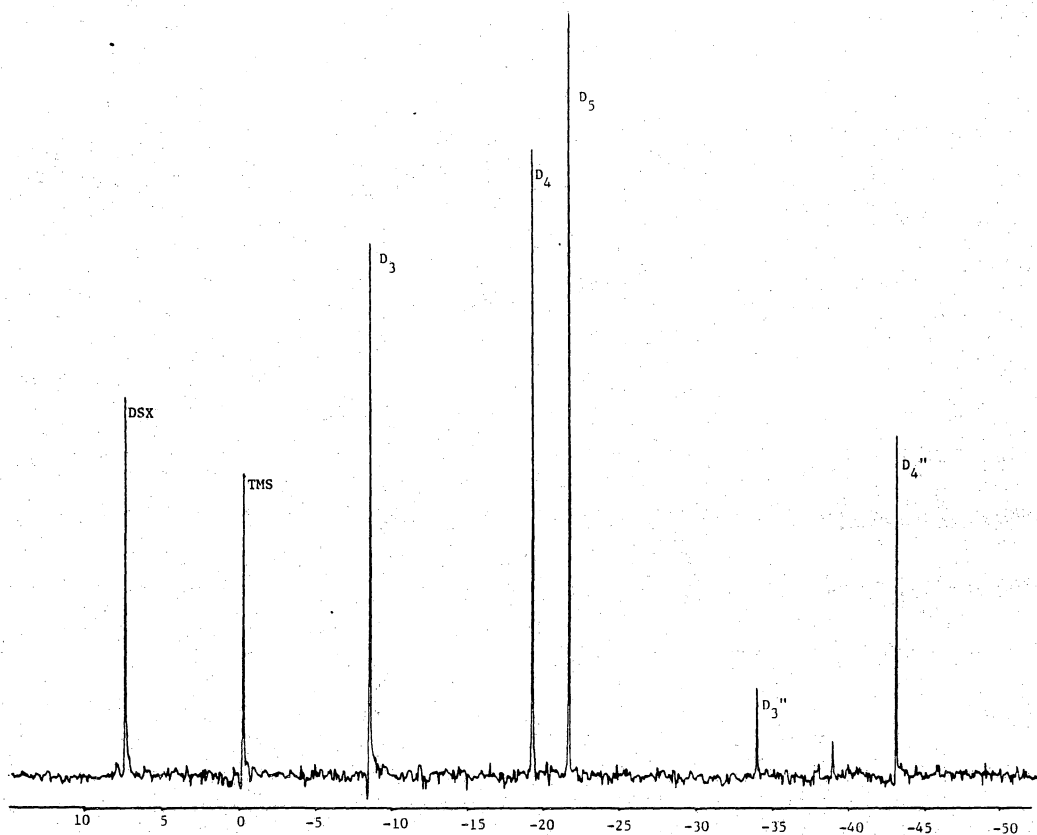
Figure 57. ^{29}Si NMR spectrum of aminopropyl disiloxane and cyclic siloxanes.

4 hrs. reaction, 58 mole% D_4", 86°C, 0.2 mole% TMAH
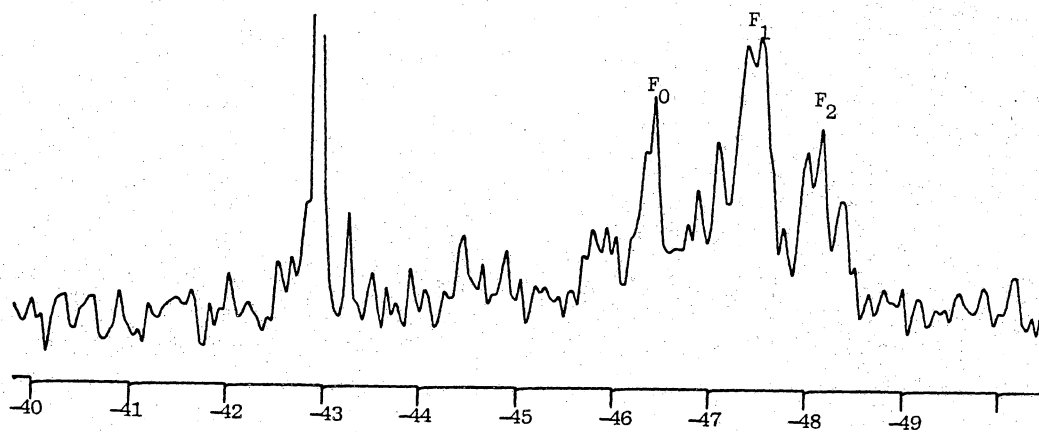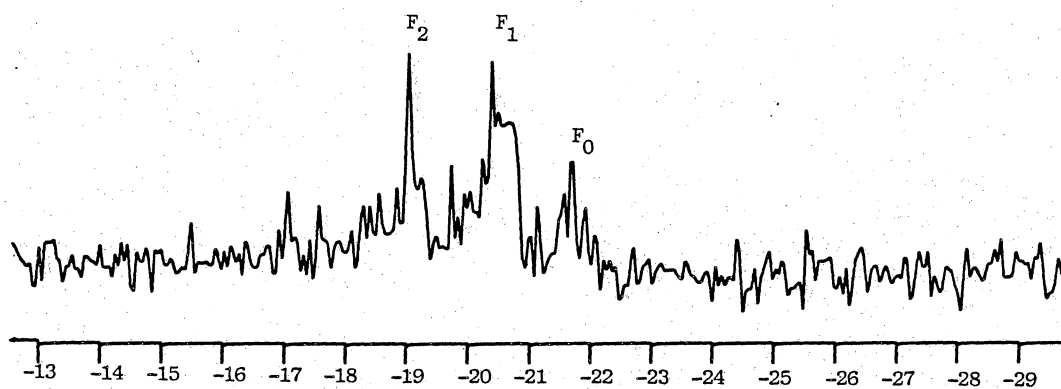
Figure 58. ^{29}Si NMR spectrum of an equilibration sample of a 5000 Mn targeted oligomer.

amounts of Cr(acac)$_3$, as well as in the absence of Cr(acac)$_3$. The reults obtained are shown in Table 10.

Entries 1 through 4 contain the results of experiments performed on 4 different solutions of the same equilibration sample. Entry 5 represents another experiment done on the same solution as #4; the computer memory was simply cleared and accumulation of the FID begun again. The results obtained for the sequence distributions in entries 1 through 5 indicate that the amount of Cr(acac)$_3$ does not appreciably affect the quantitative analysis of the triad distributions. The sequence distributions calculated agree with one another within the experimental error of the instrument.

A different equilibration sample was used to prepare solutions for entries 6 and 7. In this case, spectra were run with (#6) and without (#7) the addition of Cr(acac)$_3$. In the absence of Cr(acac)$_3$ a 30 second delay was used between pulses. Good agreement in the calculation of the sequence distributions between these 2 solutions is observed, indicating that a delay of 3 seconds between pulses with the use of Cr(acac)$_3$ is sufficient.

The use of NMR to determine sequence distributions in copolymers is well established [107-109]. It is first necessary to define the nomenclature used. Recalling the triad and pentad distributions given in chapter 2, the number average sequence lengths for "0" type units and "1" type units are given by equations (12) and (12) [109].

Table 10. Effect of the amount of $Cr(acac)_3$ on sequence distribution calculations.

Sample Number	Amount of $Cr(acac)_3$ (g)	$\langle n \rangle_0$	$\langle n \rangle_1$
1	0.010	1.4	1.6
2	0.015	1.4	1.4
3	0.0064	1.5	1.5
4	0.015	1.4	1.6
5	0.015	1.4	1.3
6	0.01	2.0	1.7
7	0	1.9	1.8
$\langle n \rangle_0$ = dimethyl sequences $\langle n \rangle_1$ = diphenyl sequences			
Numbers 6 and 7 are samples from a different reaction than 1 through 5.			

(12)　$<n_0> = \dfrac{000 + 001 + 101}{1/2(001) + 101}$

(13)　$<n_1> = \dfrac{111 + 110 + 010}{1/2(110) + 010}$

Each triad (000, 001, etc.) is normalized, and the intensities can be measured from the ^{29}Si NMR spectrum obtained. The average sequence length is determined in each case from three experimental observations. Alternatively, the "run number" concept developed by Harwood et al. [107] may be used to determine whether a given copolymer has a statistical, blocky, or alternating distribution. Jancke et al. developed equations relating the triad distributions, average sequence length, and run number [95]:

(14)　$[0] = \dfrac{100 \; k_0}{k_0 + k_1}$　;　$[1] = 100 - [0]$

(15)　$Rexp = k_0 \times [0] = k_1 \times [1]$

(16)　$ki = 4F_2/(2F_2 + F_1)$

　　　　$= 2F_1/(F_1 + 2F_0)$

(17)　$<n_0> = 2[0]/Rexp$　;　$<n_1> = 2[1]/Rexp$

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where [0] and [1] are the mole% of "0" and "1" type units respectively. (Recall that F_0 is the 000 or 111 triad, F_1 is the 001 or 110 triad, and F_2 is the 010 or 101 triad). A run number, Rrand, corresponding to a random distribution can also be calculated:

(18) $Rrand = [0] \times [1]/50$

A comparison of Rrand and the value of Rexp obtained from equation (15) indicates the type of distribution. If Rrand = Rexp, the distribution tends to be statistical. When Rexp > Rrand there is a tendency towards alternation in the copolymer and when Rexp < Rrand, this indicates a blocky type of arrangement of the monomer units in the copolymer [107].

In these ^{29}Si NMR studies, the mole% of $D_4"$ relative to the mole% of D_4 is of importance. The intensity of the ^{29}Si chemical shift of an end group silicon nucleus does not enter into the sequence distribution or run number calculations. The charged mole% $D_4"$ at a given wt% $D_4"$ is therefore slightly higher in these calculations than in the HPLC calculations. Table 11 through Table 16 give results for the number average sequence lengths of diphenylsiloxane and dimethylsiloxane repeat units, calculated by both methods explained above, and experimental run numbers compared with the run number corresponding to the random distribution. Good agreement between the two sets of calculations of sequence

lengths is generally observed. The sequence distribution

calculation from equations (12) and (13) is slightly more

appealing since all three experimental observations are used

simultaneously.

The main conclusion that can be drawn from these results

is that, at these reaction times and conditions, the type of

distribution obtained depends primarily on the co-oligomer

composition. An oligomer with 75 wt% D_4'' (58 mole%) ini-

tially charged has close to an alternating distribution of

comonomer units. When 50 wt% D_4'' (30 mole%) is charged, the

distribution tends to be blocky over the range of temper-

atures and conditions studied. However, it is probably at

the shorter reaction times that the greatest changes in the

sequence distributions are observed, due to the relative re-

action rates of D_4 and D_4''. For example, after 90 minutes

reaction at 132°C with 0.12 wt% (1.0 mole%) potassium hy-

droxide, 58 mole% D_4'' charged, the distribution is observed

to be blocky, with slightly longer blocks of diphenylsiloxane

units than dimethylsiloxane units, rather than alternating.

There was a temperature effect on the equilibration

process, as one might expect. In the 75 wt% (57 mole%) D_4''

co-oligomers, reactions run at high temperatures ($\simeq$132°C and

158°C) produced a greater number of mixed cyclic peaks than

those run at lower temperatures. Figure 59 shows an example

of such a spectrum. Comparison with Figure 58 shows a number

of additional peaks. In the diphenylsiloxane region of the

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spectrum ($\simeq$-30 to -49 ppm) the additional peaks must be due
to mixed cyclics since the linear region is from $\simeq$-45 to -49
ppm. The chemical shift of D_3'' is $\simeq$-38 ppm and the addition
of dimethylsiloxane units would shift the resonance of a di-
phenyl-substituted silicon nucleus to lower frequency. In
the dimethyl region of the spectrum, the addition of diphe-
nylsiloxane units to dimethyl rings results in a shift to
higher frequency. It is important to realize that _each_ ad-
ditional peak does not indicate the presence of a mixed cy-
clic. For each mixed cyclic peak in the dimethyl region,
there is a corresponding peak in the diphenyl region. Each
mixed cyclic will give rise to at least two peaks: one in
the dimethylsiloxane region and one in the diphenyl region.
This can be more clearly illustrated by considering the
structures shown below. Structures 1 and 2 will each give
rise to one peak in the dimethyl and one peak in the diphenyl
region. However, structure 3 will give rise to two peaks in
the dimethyl region and 1 peak in the diphenyl region, prod-
cuing potentially complex spectra.

CH₃

```
    CH3        CH3         ⬡              CH3         ⬡
    |          |           |              |           |
 ─ Si - O - Si - O - Si - O - Si - O - Si - O ─
    |          |           |              |           |
    CH3        CH3         ⬡              CH3         ⬡
```
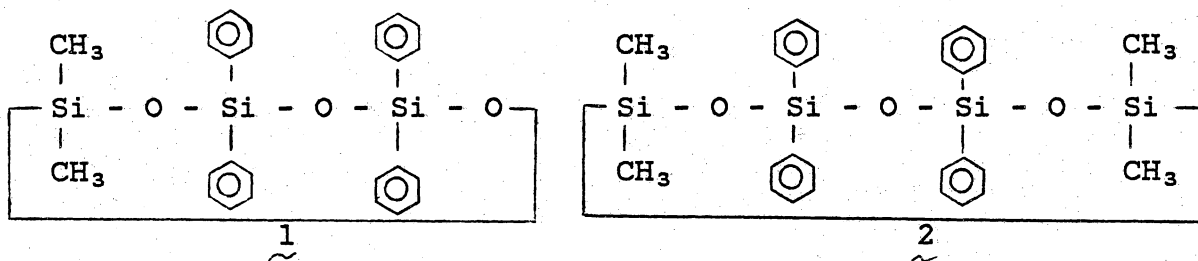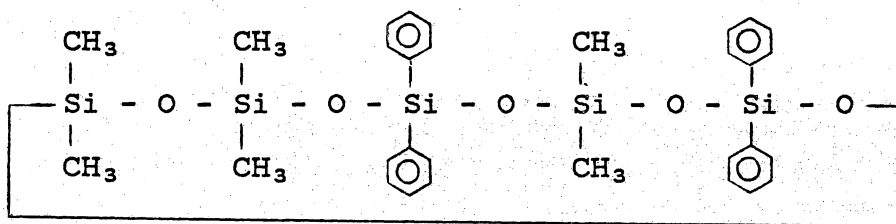
3

The relatively large number of peaks due to the forma-
tion of mixed cyclics is only observed when there are close
to equimolar amounts of diphenyl- and dimethylsiloxane units
in the oligomer, corresponding to nearly an alternating dis-
tribution. Depending on the exact distribution of comonomer
units near the end of the chain, backbiting can produce cy-
clic siloxanes with differing amounts of diphenylsiloxane and
dimethylsiloxane units present in the same ring. If there
is also, besides a greater number of types of mixed cyclics,
a greater total amount of cyclics at equilibrium, the use of
high reaction temperatures, 131°C for example, for 24 hours
or less may not be an efficient technique for achieving
equilibrium. Neither HPLC nor the ^{29}Si NMR analysis is able
at this time to determine the total amount (wt% or mole%) of
cyclics at equilibrium. The determination of the total
amount of cyclics remaining at equilibrium by HPLC would re-
quire extensive model compound work. ^{29}Si NMR also requires
extensive model compound work to identify which cyclic peaks
observed in the spectrum correspond to silicon nuclei in the

same rings. GPC is a technique which potentially could determine the amount of cyclics present, but is not viable with 1° amine-terminated polymers. Alternatively, one may be able to take advantage of solubility differences between the cyclics and polymer to achieve separation, and therefore a quantitative measure of the equilibrium cyclics concentration.

^{29}Si NMR SPECTRUM OF EQUILIBRATION SAMPLE AT
131°C, 52 mole% Ø, 0.4 mole % KOH
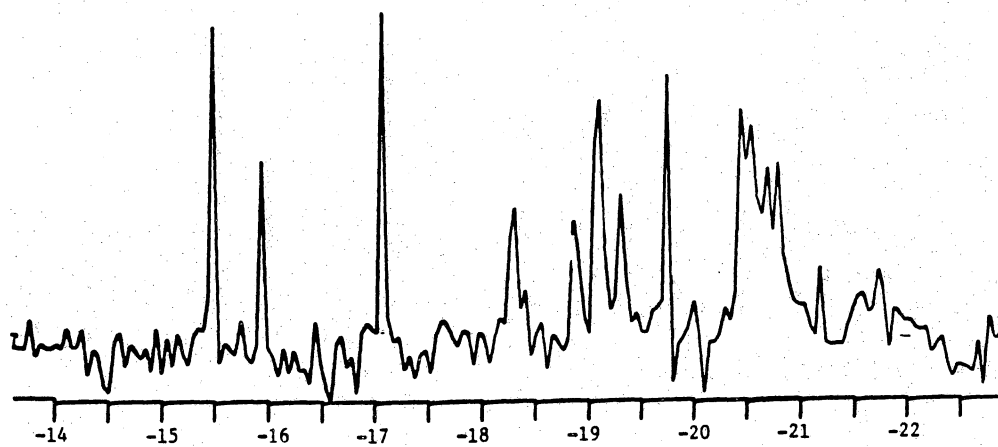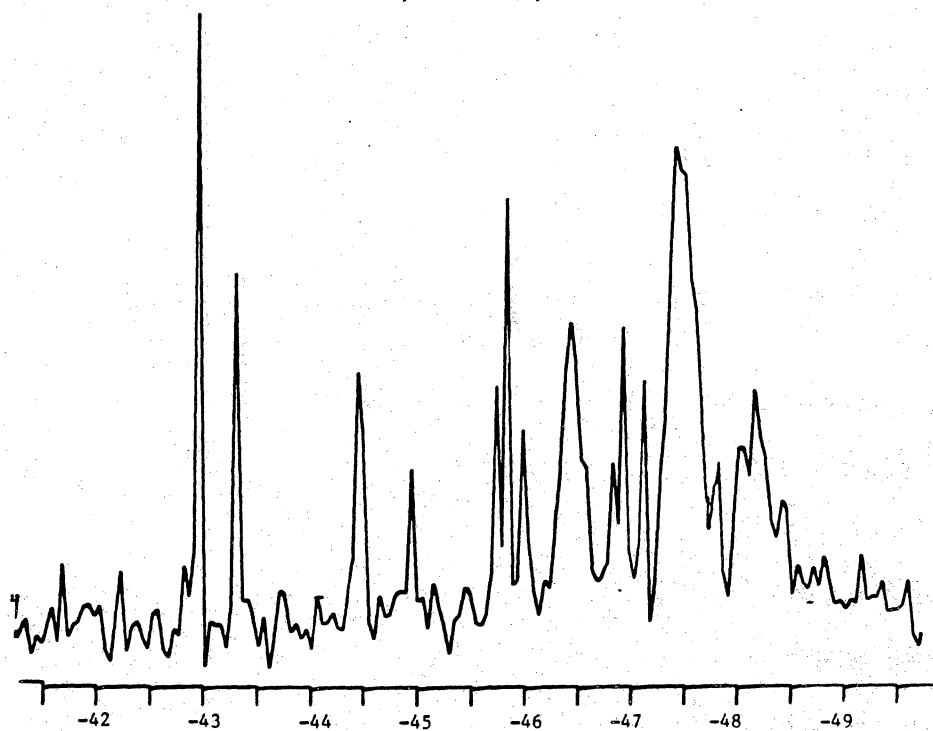
Figure 59. ^{29}Si NMR spectrum of a sample from an equi-
libration run at 131°C.

Table 11.   Influence of Reaction Time on Sequence Lengths
            in Polymerizations Conducted with 0.2 Mole%
            TMAH, 58 Mole% D_4" Charged.

Rxn Temp. (°C)	$\langle n \rangle_0$		$\langle n \rangle_1$		R (exp)	R (rand)	Rxn Time (hours)
	I	II	I	II			
86	2.7	2.6	1.7	1.7	46.8	47.1	7.5
	1.9	1.9	1.7	1.7	56.2	49.6	20.0
	1.9	2.0	1.8	1.7	56.5	50.0	24.0
	2.0	2.0	1.9	1.9	51.5	50.0	30.0
	2.0	2.0	1.7	1.8	55.5	50.0	32.0
86	2.6	2.7	2.0	2.0	43.2	48.9	3.0
	2.0	2.1	1.7	1.8	51.4	48.4	20.5
	2.1	2.2	2.1	2.2	50.0	46.6	28.75
89	1.9	2.0	1.8	1.9	53.6	50.0	20.0

I = from Randall [109] II = Jancke method [95], $\langle n \rangle_0$ = dimethyl sequence lengths, $\langle n \rangle_1$ = diphenyl sequence lengths

Table 12. Influence of Reaction Time on Sequence Lengths at 88°C with 0.2 Mole% TMAH and 30 Mole% D_4" Charged.

$\langle n \rangle_0$		$\langle n \rangle_1$		R (exp)	R (rand)	Time (hrs)
I	II	I	II			
5.7	4.7	1.5	1.8	32.0	37.9	1.5
3.6	3.5	1.4	1.4	40.8	41.4	4.0
3.3	3.3	1.3	1.3	31.5	44.2	6.0
3.4	3.3	1.4	1.4	41.5	43.1	8.0
3.4	3.3	1.4	1.3	40.4	45.4	9.5
3.6	3.9	1.4	1.4	37.8	40.0	22.5
I = from Randall [109], II = Jancke method [95], $\langle n \rangle_0$ = dimethyl sequence lengths, $\langle n \rangle_1$ = diphenyl sequence lengths						

Table 13. Influence of Reaction Time on Polymerizations Conducted at 132°C with KOH, 58 mole% D_4" Charged.

Mole% KOH	$\langle n\rangle_0$		$\langle n\rangle_1$		R (exp)	R (rand)	Rxn Time (hrs)
	I	II	I	II			
1.0	1.7	1.7	2.3	2.3	48.6	51.3	1.5
1.0	1.6	2.0	1.9	1.9	51.1	50.0	4.5
1.0	1.7	1.6	1.9	1.9	56.2	49.2	9.0
1.0	1.4	1.7	2.0	2.0	55.3	49.4	22.0
0.5	1.7	1.7	1.8	1.9	56.7	47.7	3.5
0.5	1.9	1.9	1.6	1.6	58.7	49.6	24.0
I = from Randall [109], II = Jancke method [95], $\langle n\rangle_0$ = dimethyl sequence lengths, $\langle n\rangle_1$ = diphenyl sequence lengths							

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Table 14. Influence of Reaction Time on Polymerizations Conducted at 158°C with 1.0 mole% KOH, 58 mole% D_4" Charged.

$\langle n \rangle_0$		$\langle n \rangle_1$		R (exp)	R (rand)	Rxn Time (hrs)
I	II	I	II			
2.2	3.2	2.1	3.1	42.5	45.5	0.5
2.3	2.5	2.5	1.9	47.1	48.9	2.5
1.8	1.9	2.1	2.1	51.2	49.7	6.0
1.8	1.9	1.7	1.7	57.5	49.4	11.5
1.6	1.7	1.9	2.0	55.4	49.0	26.5
I = from Randall [109], II = Jancke method [95], $\langle n \rangle_0$ = dimethyl sequence lengths, $\langle n \rangle_1$ = diphenyl sequence lengths						

Table 15. Influence of Reaction Time on Polymerizations Conducted with 0.8 mole% KOH, 30 mole% D_4" Charged.

Rxn Temp. (°C)	$\langle n \rangle_0$		$\langle n \rangle_1$		R (exp)	R (rand)	Time (hrs)
	I	II	I	II			
131	2.7	1.7	2.4	2.5	47.9	48.5	0.5
131	3.3	4.1	1.5	1.6	36.5	40.2	1.0
131	3.6	3.5	1.3	1.4	44.0	48.4	3.0
131	3.1	3.0	1.4	1.4	45.2	47.8	5.0
88	4.4	4.3	1.2	1.2	33.1	36.9	1.5
88	2.8	2.9	1.5	1.6	45.9	45.6	5.5

I = from Randall [109], II = Jancke method [95], $\langle n \rangle_0$ = dimethyl sequence lengths, $\langle n \rangle_1$ = diphenyl sequence lengths

Table 16. ^{29}Si NMR Results of Polymerizations Conducted with 0.7 mole% TMAH at 89°C.

Mole% D_4" charged	$<n>_0$		$<n>_1$		R (exp)	R (rand)	Rxn Time (hrs)
	I	II	I	II			
58	2.5	2.6	1.8	1.9	44.5	48.0	2.75
58	1.9	1.9	1.8	1.9	52.8	49.8	4.0
58	1.8	1.8	1.8	1.8	56.2	49.8	17.0
30	3.5	3.4	1.2	1.3	44.8	40.1	3.0
30	4.0	4.6	1.3	1.3	34.7	35.5	8.5
30	2.1	2.2	1.7	1.8	49.5	52.0	93.5
I = from Randall [109], II = Jancke method [95], $<n>_0$ = dimethyl sequence lengths, $<n>_1$ = diphenyl sequence lengths							

6.0 CONCLUSIONS

The use of non-aqueous reversed-phase HPLC and capillary
GC have proven to be useful techniques for the investigation
of the ring-opening polymerization of cyclic siloxanes in the
presence of bis(α,ω-aminopropyl)-1,3-tetramethyldisiloxane.
Due to electronegativity effects, octamethyl-
cyclotetrasiloxane reacted more rapidly with basic siloxano-
late catalysts than the functional disiloxane under a variety
of reaction conditions. It was also determined that octa-
phenylcyclotetrasiloxane inially reacted with the potassium
siloxanolate catalyst more rapidly than the dimethyl-substi-
tuted cyclic, apparently also because of electronic consid-
erations. When the tetramethylammonium catalyst was used
however, the dimethyl-substituted cyclic reacts slightly
faster, due to steric factors in the reaction with the di-
phenyl-substituted cyclic. However, probably because the
diphenylsiloxanolate anion is a less nucleophilic anion than
the corresponding dimethylsiloxanolate anion, the overall
rate of polymerization is observed to decrease. Presumably,
the rate of chain transfer to polymer is also decreased by
the presence of the diphenylsiloxanolate.

It is suggested that ^{29}Si NMR has enormous potential for
the study of polysiloxane co-oligomerization. The sequence
distributions in polydimethyl-co-diphenylsiloxane oligomers

were measured as a function of a variety of reaction conditions. The co-oligomer composition seems to be the dominant factor influencing the sequence distributions as one approaches equilibrium. For example, a tendency towards an alternating distribution was observed in co-oligomers with nearly a 50/50 molar composition of dimethyl/diphenyl siloxane units. A co-oligomer with $\approx$30 mole% diphenylsiloxane units had a tendency towards a blocky distribution. Importantly, these results can be considered to represent statistical distributions since in a 30 mole% diphenylsiloxane co-oligomer, one would expect a somewhat blocky distribution, while in a 50/50 co-oligomer, a statistical distribution with short sequences might be expected.

Presumably, greater changes in the sequence distributions would be observed early in the polymerizations, particularly where heterogeneous conditions still persist. In fact, slightly longer sequences were sometimes observed at short reaction times. In some cases, perhaps due to the fact that the D_4'' ring opens more quickly than the D_4, longer distributions of diphenylsiloxane units were observed initially. However, occasionally slightly longer sequence lengths of dimethylsiloxane units were observed. This could be attributed to chain transfer reactions to polymer. The silicon-oxygen bonds in cyclic (larger than D_3) and linear siloxanes are of similar reactivity. Therefore, one would expect that, with a dimethylsiloxanolate anion particularly,

silicon-oxygen bonds within diphenylsiloxane units would be more readily attacked than the corresponding dimethylsiloxane units within a given chain. This could explain the slightly longer dimethylsiloxane sequence lengths in the co-oligomers observed early in the polymerization. This could not be fully studied by ^{29}Si NMR since equilibration samples could not be removed for analysis until the reaction mixture was completely homogeneous.

Another attractive feature of ^{29}Si NMR is the ability to distinguish qualitatively between linear and cyclic species very easily. The presence of "mixed" cyclics can also be plainly observed, however the calculation of the mole% cyclics present in a given sample is not feasible at this time because of the extensive model compound work which would be required. A large variety of peaks due to mixed cyclics were observed in high temperature reactions with nearly 50/50 molar compositions. This is presumably due to an increased amount of backbiting, coupled with a nearly alternating distribution of comonomer units. The exact distribution of comonomer units will produce a wide variety of _types_ of cyclics, although not necessarily a larger amount of total cyclics. Each mixed cyclic can give rise to at least 2, sometimes more, ^{29}Si NMR peaks, further complicating the situation. At this time, it is not possible to determine the cyclic peaks in the dimethyl region of the spectrum which correspond to cyclic peaks in the same ring in the diphenyl

region. Since each peak due to a silicon nucleus in a ring does not represent a separate ring, simply comparing the intensity of the linears with the cyclics does not give the % of cyclics remaining.

These studies, coupled with HPLC studies of the rates of disappearance of starting materials, provide useful information towards the synthesis of well-defined functional polysiloxane oligomers for the preparation of segmented copolymers.

REFERENCES

1. Stark, F. O., Falender, J. R., Wright, A. P., in Comprehensive Organometallic Chemistry The Synthesis, Reactions and Structures of Organometallic Compounds, Sir GeoffreyWilkinson, FRS, editor, Pergamon Press (1983).

2. Wright, P. V., in Ring-Opening Polymerizations, K. J. Ivin, T. Saegusa, editors, Elsevier Press (1984).

3. Voronkov, M. G., Mileshkevich, V. P., Yuzhelevskii, Yu. A., in The Siloxane Bond, Consultants Bureau (1978).

4. Noll, W., Chemistry and Technology of Silicones, Academic Press, (1968).

5. Meals, R., Encyclopedia of Chemical Technology, 18, 2nd edition, 221-260 (1969).

6. Riffle, J. S., Yilgor, I. Banthia, A. K., Wilkes, G. L., McGrath, J. E., in Epoxy Resins II, R. S. Bauer, editor, ACS Symposium Series No. 221 (1983).

7. Yilgor, I., Riffle, J. S., McGrath, J. E., in Reactive Oligomers, F. Harris, H. J. Spinelli, editors, ACS Symposium Series No. 283, 161 (1985).

8. Johnson, B. C., Ph. D. thesis, VPI&SU, June, 1984, and forthcoming publications.

9. Tran, C., Ph. D. thesis, VPI&SU, November, 1984, and forthcoming publications.

10. Yorkgitis, E., Tran, C., Eiss, N. S., Yu, T. Y., Yilgor, I., Wilkes, G. L., McGrath, J. E., in Rubber-Modified Thermoset Resins, C. K. Riew, J. K. Gillham, editors, Adv. Chem. Series No. 208 (1984).

11. Brandt, P. J. Andolino, Ph. D. thesis, VPI&SU, February 1986, and forthcoming publications.

12. Kantor, S. W., Grubb, W. T., Osthoff, R. C., J. Amer. Chem. Soc., 76, 5190 (1954).

13. Jacobson, H., Stockmayer, W. H., J. Phys. Chem., 18, 1600 (1950).

14. Flory, P. J., Semlyen, J. A., J. Amer. Chem. Soc., 88, 3209 (1966).

15. Flory, P. J., Suter, U. W., Mutter, M., J. Amer. Chem. Soc., 98, 5733 (1976).

16. Carmichael, J. B., Jeffel, J., J. Phys. Chem., 69 (7), 2213 (1965).

17. Carmichael, J. B., Gordon, D. J., Ferguson, C. E., J. of Gas Chromatography, 347 (1966).

18. Wright, P. V., Semlyen, J. A., Polymer, 11 (9), 462 (1970).

19. Wright, P. V., Semlyen, J. A., Polymer, 10, 543, (1969).

20. Brown, J. F., Slusarczuk, G. M., J. Amer. Chem. Soc., 87, 931 (1965).

21. Beevers, M. S., Semlyen, J. A., Polymer, 12 (6), 373 (1971).

22. Hurd, D. T., Osthoff, R. C., Corrin, M. L., J. Amer. Chem. Soc., 76, 249 (1954).

23. Gilbert, A. R., Kantor, S. W., J. Polym. Sci., 40, 35 (1959).

24. Grubb, W. T., Osthoff, R. C., J. Amer. Chem. Soc., 77, 1405 (1955).

25. Mazurek, M., Chojnowski, J., Macromolecules, 11, 347 (1978).

26. Mazurek, M., Chojnowski, J., Makromol. Chem., 178, 1005 (1977).

27. Kucera, M., Jelinek, M., Vsolomol. Soedin., 2, 1860 (1960).

28. Kleinert, J. C., Weschler, C. J., Anal. Chem., 52, 1245 (1980).

29. Beevers, M. S., Semlyen, J. A., Polymer, 13, 385 (1972).

30. Carmichael, J. B., Heffel, J., J. Phys. Chem., 69 (7), 2218 (1965).

31. Chan, L. L., Smic, J. J., J. Amer. Chem. Soc., 89, 17 (1967).

32. Izatt, R. M., Eatough, D. J., Christensen, J. J., J. Chem. Rev., 74, 162 (1974).

33. Suryanarayanan, B., Peace, B. W., Mayhan, K. G., J. Polym. Sci., Polym. Chem. Ed., 12, 1089 (1974).

34. Suryanarayanan, B., Peace, B. W., Mayhan, K. G., J. Polym. Sci., Polym. Chem. Ed., 12, 1109 (1974).

35. Fessler, W. A., Juliano, P. C., Polym. Prepr., 12, 151 (1971).

36. Gangi, J. B., Bettelheim, J. A., J. Polym. Sci. A-2, 4011 (1964).

37. Murray, J. G., Polym. Prepr., 6, 163 (1965).

38. Cooper, G. D., Elliott, J. R., J. POlym. Sci. A-1 (4) 603 (1966).

39. Laita, Z., Hlozek, P., Bucek, B., Jelinek, M., J. Polym. Sci., Part C, No. 16, 669 (1967).

40. Andrianov, K. A., Yakushkina, S. Ye., Koretko, I. I., Lavrukhin, B. D., Petrova, I. I., Polym. Sci. USSR, 13, 3097 (1971).

41. Andrianov, K. A., Yakushkina, K. A., Guniava, L. N., Polym. Sci. USSR, 8, 2398 (1967).

42. Andrianov, K. A., Iakushkina, S. E., Polym. Sci. USSR, 1, 221 (1960).

43. Andrianov, K. A., Yakushkina, Polym. Sci. USSR, 8, 384 (1966).

44. Baratova, T. N., Mileshkevich, V. P., Gurari, V. I., Polym. Sci. USSR, 24 (1), 27 (1982).

45. Andrianov, K. A., Rodionova, E. F., Luk'yanova, L. V., Vysokomol. Soedin., 14B, 331 (1972).

46. Andrianov, K. A., Rodionova, E. F., Vysokomol. Soedin., 13B, 829 (1971).

47. Andrianov, K. A., Zavin, B. G., Sablina, G. F., Polym. Sci. USSR, 14, 1294 (1972).

48. Andrianov, K. A., Slonimskii, G. L., Levin, V. Yu., Godovskii, Yu. K., Kuznetsov, I. K., Ivankin, D. Ya., Moskalenko, V. A., Kuteinikova, L. I., Polym. Sci. USSR, <u>12</u>, 1436 (1970).

49. Andrianov, K. A., Pavlova, S. A., Tverdokhlebova, I. I., Petrova, N. V., Larina, T. A., Sablina, G. F., in <u>Preprints of International Symposium on Macromolecular Chemistry</u>, Vol. 2, Sect. 1, Helsinki, 1972, p.875.

50. Laita, Z., Jelinek, M., Polym. Sci. USSR, <u>5</u>, 342 (1964).

51. Polymer Handbook, 2nd edition, J. Brandrup, E. H. Immergut, editors, Wiley-Interscience (1975).

52. Lai. S., Locke, D. C., J. of Chrom., <u>252</u>, 325 (1982).

53. Snyder, L. R., Kirkland, J. J., <u>Introduction to Modern Liquid Chromatography</u>, Wiley-Interscience, New York, 2nd edition, 679, (1979).

54. Kirkland, J. J., Chromatographia, <u>8</u>, 661 (1975).

55. Holt-Sockett, P., Hannah, R. W., Slavin, W., Chromatographia, <u>11</u>, 634 (1978).

56. Fukuda, M., Takamatsu, T., Tago, T., Sato, T., Kobunshi Ronbunshu, <u>36</u>, 7 (1979); C. A. 90, 122148h (1979).

57. Bui, K. H., Armstrong, D. W., J. Liq. Chrom., <u>7</u> (1), 29 (1984).

58. Armstrong, D. W., Bui, K. H., Anal. Chem., <u>54</u> (4), 706 (1982).

59. Armstrong, D. W., Bui, K. H., Boehm, R. E., J. Liq. Chrom., <u>6</u> (1), 1 (1983).

60. Boehm, R. E., Martire, D. C., Armstrong, D. W., Bui, K. H., Macromolecules <u>16</u>, 466 (1983).

61. Larmann, J. P., De Stefano, J. J., Goldberg, A. P., Stout, R. W., Snyder, L. R., Stadalius, M. A., J. Chrom., <u>255</u>, 163 (1983).

62. Regnier, F. E., Gooding, K. M., Anal. Biochem., <u>103</u>, 1 (1980).

63. Vigh, F., Varga-Puchony, Z., Hlavay, J., Papp-Hites, E., J. Chrom., <u>236</u>, 51 (1982).

64. Hearn, M. T. W., Grego, B., J. Chrom., 218, 497 (1981).

65. Nice, E. C., Capp, M. W., Cooke, N., O'Hare, M. J., J. Chrom., 218, 569 (1981).

66. Lewis, R. V., Fallon, A., Stein, S., Kenneth, D., Udenfriend, S., Anal. Biochem., 104, 153 (1980).

67. Jones, B. N., Lewis, R. V., Paabo, S., Kojima, K., Kimura, S., Stein, S., J. Liq. Chrom., 3, 1373 (1980).

68. Hollaway, W. L., Prestidge, R. L., Bhown, A. S., Mole, J. E., Bennet, J. C., in Recent Developments in Chromatography and Electrophoresis, 10, A. Frigerio, M. McCamish, editors, Elsevier, p. 131 (1980).

69. Krajnik, V., Bozek, P., Kondelikova, J., Kralicek, J. J. Chrom., 250, 138 (1982).

70. Krajnik, V., Bozek, V., Kondelikova, J., Kralicek, J., J. Chrom., 240, 539 (1982).

71. Moore, J. C., J. Polym. Sci., A-2, 835 (1964).

72. Takeuchi, T., Ishii, D., J. Chrom., 257, 327 (1983).

73. Ishiguro, S., Inoue, Y., Hosogane, T., J. Chrom., 239, 651 (1982).

74. Yau, W. W., Kirkland, J. J., Bly, D. D., Modern Size-Exclusion Liquid Chromatography, Wiley-Interscience, New York, Chapt. 1, 1979.

75. Giddings, J. C., Anal. Chem., 39 (8), 1027 (1967).

76. Issaq, H. J., J. Liq. Chrom., 7 (5), 883 (1984).

77. Issaq, H. J., J. Liq. Chrom., 7 (3), 474 (1984).

78. Sormani, P. M., McGrath, J. E., Polym. Prepr., 26 (1), 258 (1985).

79. Sormani, P. M., Minton, R. J., McGrath, J. E., in Ring-Opening Polymerization Kinetics, Mechanisms, and Synthesis, J. E. McGrath, editor, ACS Symposium Series No. 286, Chapt. 11 (1985).

80. Andrews, G., Macromolecules, 14 (5), 1603 (1981).

81. Andrews, G., Macromolecules, 15 (6), 1580 (1982).

82. Krstulovic, A. M., Brown, P. R., _Reversed-Phase High-Performance Liquid Chromatography: Theory, Practice, and Biomedical Applications_, Wiley-Interscience, New York, (1982).

83. Molnar, I., editor, _Practical Aspects of Modern HPLC_, Proceedings Dec. 7-8, 1981 - Berlin (West), Walter de Gruyter, Berlin, New York (1982).

84. Yilgor, I., Riffle, J. S., Wilkes, G. L., McGrath, J. E., Polym. Bull., _8_, 535 (1982).

85. Yilgor, I., Sha'aban, A. K., Steckle, W. P. Jr., Tyagi, D., Wilkes, G. L., McGrath, J. E., Polymer, _25_, 1800 (1984).

86. Webster, D. C., Andolino, P. J., Riffle, J. S., Keohan, F. L., McGrath, J. E., Polym. Prepr., _24_ (1), 161 (1983).

87. Noshay, A., McGrath, J. E., _Block Copolymers: Overview and Critical Survey_, Academic Press, Chapt. 7 (1977).

88. Mori, S., Furusawa, M., Takeuchi, T., Anal. Chem., _42_, 661 (1970).

89. Lee, M. L., Yang, F. J., Bartle, K. D., _Open Tubular Gas Chromatography Theory and Practice_, Wiley-Interscience (1984).

90. Williams, E. A., in _Annual Reports on NMR Spectroscopy_, Vol. 15, G. A. Webb, editor, Academic Press, London, Chapt. 3 (1983).

91. Levy, G. C., Cargioli, J. D., in _Nuclear Magnetic Resonance Spectroscopy of Nuclei other than Proton_, T. Axenrod, G. A. Webb, editors, Wiley-Interscience, New York, Chapt. 17 (1974).

92. Marsmann, H., in _NMR, Basic Principles and Progress_, Oxygen-17 and Silicon-29, P. Diehl, E. Fluck, R. Kosfeld, editors, Springer-Verlag, Chapt. 2 (1981).

93. Marsmann, H. C., Meyer, E., Vongehr, M., Weber, E. F., Makromol. Chem., _184_, 1817 (1983).

94. Engelhardt, G., Jancke, H., Magi, M., Pehk, T., Lippmaa, E., J. Organometallic Chem., _28_, 293 (1971).

95. Engelhardt, G., Jancke, H., Polym. Bull., _5_, 577 (1981).

96. Harris, R. K., Kimber, B. J., J. Organometallic Chem., 70, 43 (1974).

97. Harris, R. K., Robins, M. L., Polymer 19,1123 (1978).

98. Brandt, P. J. Andolino, Subramanian, R., Sormani, P. M., Ward, T. C., McGrath, J. E., Polym. Prepr., 26 (2), 213 (1985); J. Polym. Sci., Polym. Chem. Ed. (in press).

99. Lauterbur, P. C., in Determination of Organic Structure by Physical Methods, E. C., Nachod, W. D. Phillips, editors, Academic Press, New York (1962).

100. Farrar, T. C., Becker, E. D., Pulse and Fourier Transform NMR, Academic Press, New York (1971).

101. Freeman, R., Pachler, K. G. R., LaMar, G. N., J. Chem. Phys., 55, 4586 (1971).

102. Gransow, O. A., Burke, A. R., Vernon, W. D., J. Amer. Chem. Soc., 94, 2550 (1972).

103. Linde, S. Aa., Jakobsen, H. J., Kimber, B. J., J. Amer. Chem. Soc., 97, 3219 (1975).

104. Bertrand, R. D., Moniz, W. B., Garoway, A. N., Chingas, G. C., J. Amer. Chem. Soc., 100, 5227 (1978).

105. Harris, R. K., Kimber, B. J., Appl. Spectrosc. Rev., 10, 117 (1975).

106. Engelhardt, G., Magi, M., Lippmaa, E., J. Organometallic Chem., 54, 115 (1973).

107. Harwood, H. J., Ritchey, W. M., J. Polym. Sci., Polym. Lett., 2, 601 (1964).

108. Jancke, H., Engelhardt, G., Kiregsmann, H., Plaste und Kautschuk, 26, 612 (1979).

109. Randall, J. C., Polymer Sequence Distributions - C-13 NMR Methods, Academic Press (1977).

110. McNair, H. M., Ogden, M. W., Hensley, J. L., American Laboratory, 15, (August, 1985).

APPENDIX A. SYNTHESIS AND CHARACTERIZATION OF

POLYESTER-SILOXANE COPOLYMERS

A.1.1   INTRODUCTION

Since the pioneering work of Carothers [1] and Flory [2,3] the field of polyesters has been of interest to polymer chemists. A wide variety of structures and properties of the resulting polyesters are available. There are a variety of synthetic techiques utilizing a variety of functionalities - alcohols, acids, and esters - available to prepare these materials. It is also possible to modify polyesters by the incorporation of functionally-terminated polysiloxane oligomers [4]. This chapter will deal primarily with preliminary studies of the preparation of polyesters via an ester-interchange technique or the Schotten-Baumann reaction, modified by the incorporation of bis(α,ω-aminopropyl)polydimethylsiloxane.

A.1.2   LITERATURE REVIEW

The synthesis of polyarylesters may be accomplished through a number of experimental techniques. This important subject is treated in a number of reviews and texts on po-

lymer chemistry [5-9]. One possible route is by the direct esterification of a diacid with a glycol. Since an excess of the glycol is generally used, the process ultimately becomes an ester-interchange reaction.

Probably one of the most important routes commercially for the synthesis of polyesters is the ester-interchange process, illustrated for the synthesis of poly(ethylene terephthalate) in scheme 5.

$$CH_3O-\overset{\overset{O}{\|}}{C}-\langle\bigcirc\rangle-\overset{\overset{O}{\|}}{C}-OCH_3 \quad + \quad HO(CH_2)_4OH$$

catalyst, argon

$\simeq$ 180°C

$$H-O(CH_2)_4O-\overset{\overset{O}{\|}}{C}-\langle\bigcirc\rangle-\overset{\overset{O}{\|}}{C}-O(CH_2)_4OH \quad + \quad CH_3OH$$

$\simeq$260°C

vacuum

$$\left[\overset{\overset{O}{\|}}{C}-\langle\bigcirc\rangle-\overset{\overset{O}{\|}}{C}-O-(CH_2)_4-O\right]_x$$
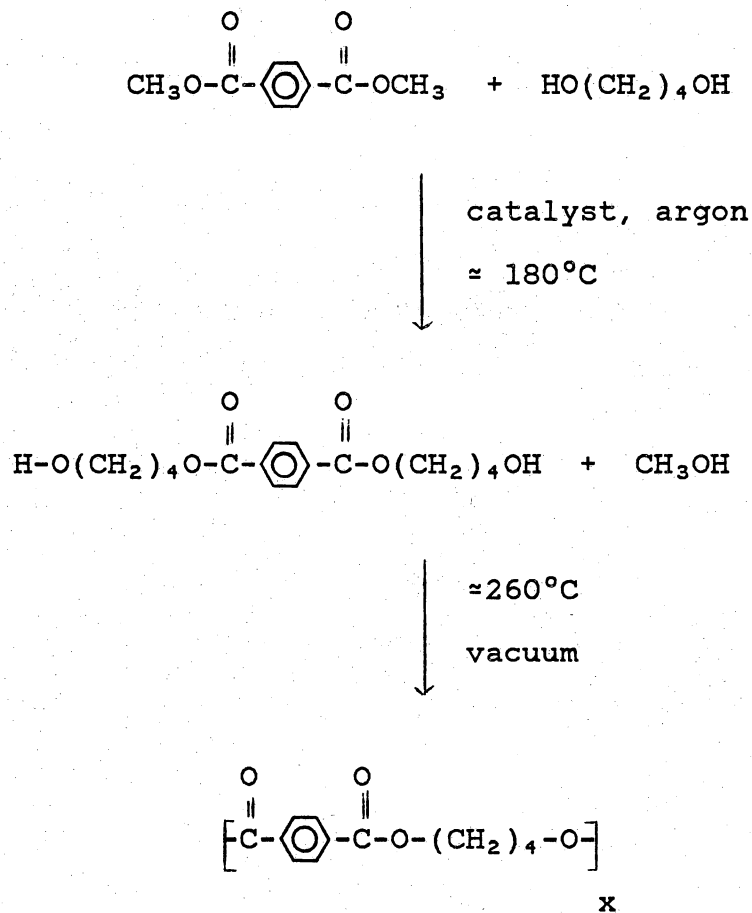
Scheme 5. Synthesis of poly(ethylene terephthalate) via an ester-interchange process.

This reaction is carried out in the presence of a proton-donating, metallic ion, or weak base catalyst. The first step is a capping reaction which produces primarily bis(2-hydroxyethyl)-terephthalate with continuous distillation of methanol. In the second stage the reaction temperature is raised above the melting point of the polymner and the excess glycol is removed by application of a vacuum, driving the equilibrium in favor of polymer formation.

This ester-interchange process has a number of attractive features. Since the polymerization can be performed in bulk, the requirement of high purity solvents to obtain high molecular weight polymers in step-growth polymerizations is avoided. In addition, the requirement for a strict stoichiometric balance of functional groups is avoided since the excess diol is distilled from the reaction mixture in the second stage of the polymerization. In fact, an excess of the diol is used initially to speed up the rate of the initial transesterification.

Another useful synthetic technique is the esterification of a diacid chloride with a glycol or bisphenol (the Schotten-Baumann reaction). In the case of aromatic monomers, the reaction is rapid and can proceed at room temperature. An acid-acceptor, such as triethylamine, is used to remove the HCl formed in the reaction and so force the equilibrium in the direction of polymer formation. This reaction is illus-

trated in scheme 6 for the reaction of bisphenol-A and tere-phthaloyl chloride in a methylene chloride/tetrahydrofuran solvent system using triethylamine as acid acceptor [10].

$$Cl-\overset{\overset{\displaystyle O}{\|}}{C}-\langle\bigcirc\rangle-\overset{\overset{\displaystyle O}{\|}}{C}-Cl \quad + \quad HO-\langle\bigcirc\rangle-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-\langle\bigcirc\rangle-OH$$

argon

CH_2Cl_2/THF

$(C_2H_5)_3N$

$$\left[O-\langle\bigcirc\rangle-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-\langle\bigcirc\rangle-O-\overset{\overset{\displaystyle O}{\|}}{C}-\langle\bigcirc\rangle-\overset{\overset{\displaystyle O}{\|}}{C} \right]_x$$
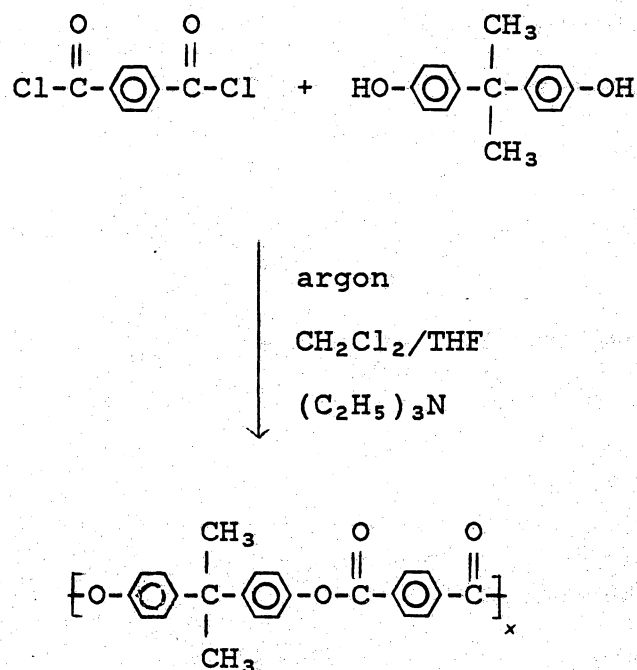
Scheme 6.   Illustration of the Schotten-Baumann reaction in
           the preparation of polyarylesters.

A.1.3 EXPERIMENTAL

A.1.3.1 SYNTHESIS OF BIS(α, ω-AMINOPROPYL)-TERMINATED
POLYDIMETHYLSILOXANE OLIGOMERS

    Polydimethylsiloxane oligomers were prepared by the
ring-opening polymerization of octamethylcyclotetrasiloxane

in the presnce of bis(α,

ω-aminopropyl)-1,3-tetramethyldisiloxane using tetramethyl-

ammonium siloxanolate catalyst as described in Chapter 3.

After 24 hours the reaction temperature was increased to ap-

proximately 150°C in order to decompose the catalyst. The

cyclics were then removed by vacuum distillation (0.2mm Hg

at 160°C). Number-average molecular weights were obtained

by potentiometric titration of the amine end group with

0.0995 N HCl (alcoholic, from Fisher) in 100 ml isopropanol

(Fisher, certified), using bromophenol blue as the indicator.

A.1.3.2 SYNTHESIS OF DIMETHYL TEREPHTHALATE-CAPPED POLYDIMETHYLSILOXANE

Dimethyl terephthalate was obtained from Eastman Kodak

and purified by recrystallization in ethanol (99%) according

to the following procedure: ≈ 100 g. dimethyl terephthalate

were dissolved in hot ethanol, resulting in a clear solution

which was filtered by gravity through fluted filter paper.

The filtrate was then allowed to crystallize with stirring.

The white, crystalline solid was dried in a vacuum oven at

low heat (≈60°C) overnight. The melting point range was

141.5-142.5°C (Literature: 141.0-141.8°C).

The dimethyl terephthalate and a magnetic stirring bar

were placed into a round bottom flask with an extended neck,

as shown in Figure 60, to allow as much as of the apparatus as possible to be immersed in a silicone oil bath. A side-arm allowed argon to flow into the flask. A drying tube was placed at the top of the addition funnel. The reaction flask was heated with stirring at 160°C until the dimethyl tereph-thalate melted, upon which slow addition of the polysiloxane via an addition funnel was then begun. As the first drops of polysiloxane were added to the liquid dimethyl terephtha-late a white solid was observed, due to the temperature of the liquid falling in the area contacted by the polysiloxane. This disappeared within a few minutes of formation. When addition of the polysiloxane was complete, the reaction mix-ture was allowed to stir under argon for ≃ 2 additional hours. The color of the reaction mixture at this time was a pale yellow. The addition funnel was then replaced by a ground glass stopper, and a vacuum was begun. The vacuum was gradually applied until the system could be fully opened to the vacuum pump without excessive bumping of the reaction mixture and allowed to stir until no further bubbling was observed, ≃ 12-24 hours. During this time, an increase in the viscosity of the system was observed and often a deepen-ing in the color of the system. The product was then poured into a sample jar until later use.

The product was characterized by Fourier-Transform In-frared (FTIR) Spectroscopy and high resolution ^{1}H nuclear
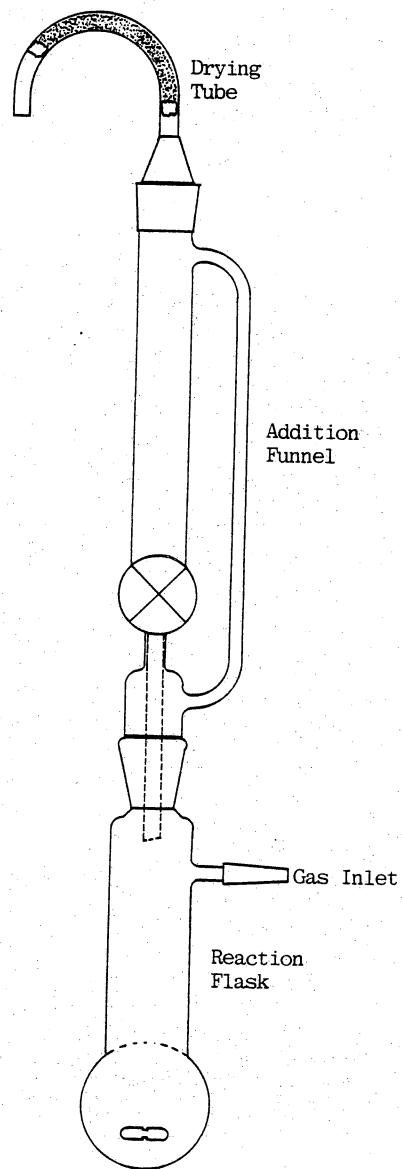
Figure 60. Apparatus for capping reaction of polysilox-
ane with fimethyl terephthalate.

magnetic resonance spectroscopy (see Chapter 4 for exper-
imental details of the ^{1}H NMR). FTIR spectra were obtained
on a Nicolet MX - 1 spectrometer. The molecular weight of
the product was measured by a Wescan Model No.233-200 vapor
pressure osmometer in toluene at 50°C. The intrinsic vis-
cosity was measured in methylene chloride at 25°C.

A.1.3.3 SYNTHESIS OF POLY(BUTYLENE
TEREPHTHALATE-CO-DIMETHYLSILOXANE)

The synthesis of these copolymers was done in bulk via
an ester-interchange process. Dimethyl terephthalate, poly-
siloxane capped with dimethyl terephthalate, as described in
section A.1.3.2, 1,4-butane diol (>99% from DuPont), and
calcium acetate were placed into the reactor shown in
Figure 61 equipped with an overhead mechanical stirrer, an
argon inlet and a drying tube. Heating was accomplished by
means of a fluidized bed reactor or heating mantle. As some
of the dimethyl terephthalate sublimed onto the cooler por-
tions of the reaction vessel, heat was applied to melt it
back into the reaction mixture. The reaction temperature was
kept at ≈180°C for ≈12 hours, until little or no dimethyl
terephthalate was observed to sublime. The reaction mixture
was then cooled, the antimony trioxide added, ("Baker Ana-
lyzed" Reagent) and the temperature raised to ≈230°C. After

several hours reaction, a vacuum was begun to remove the excess butane diol. The reaction was allowed to proceed ≈12 hours, until the pressure in the system was ≈0.25 mm Hg. A typical recipe is as follows:

- 6 g. polysiloxane (Mn=1910 g/mole before capping,0.002 moles)

- 3.35 g. butane diol(0.0372 moles)

- 2g. dimethyl terephthalate(0.0155 moles)

- 0.02 g. calcium acetate(0.0001 moles)

- 0.02 g. antimony trioxide(0.0001 moles)

The products were extracted in a soxlet extractor with hot methylene chloride for 24 hours. These materials were analyzed by Fourier-Transform Infrared Spectroscopy to determine the presence of the ester functionality. Wide-angle x-ray patterns were obtained to investigate the presence of crystallinity in the polymers. A Phillips table-top x-ray generator was employed in conjunction with a standard vacuum-sealed Statton camera. The samples were in the form of a powder in a quartz tube. Exposure times were approximately
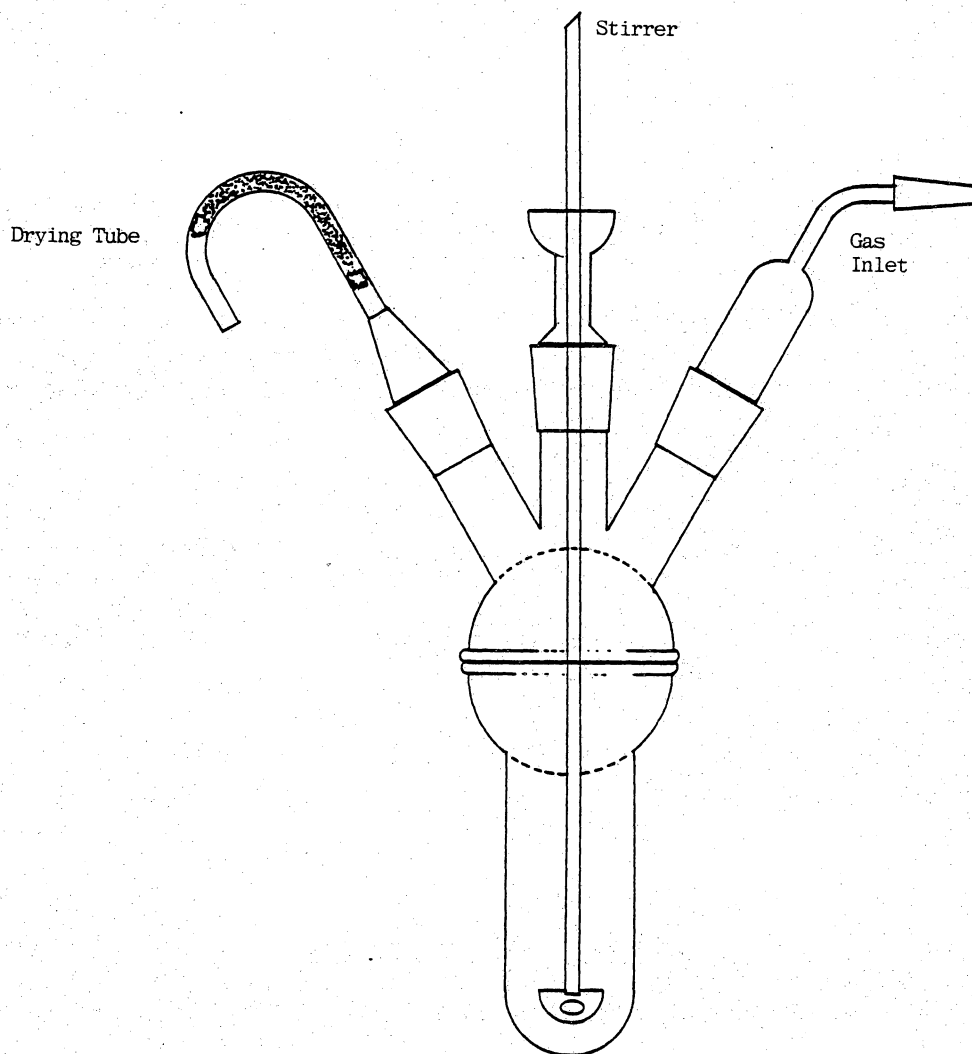
Figure 61. Melt polymerization reactor.

10 hours. Intrinsic viscosities were measured either in 1,1,1,3,3,3-hexafluoro-2-propanol at 40°C or a 50/50 mixture of phenol and tetrachloroethane at 25°C. Differential scanning calorimetry was used to determine glass transition, melting, and crystallization temperatures. Scans were done at a heating rate of 5°C/min. on a Perkin-Elmer DSC Model-2.

A.1.3.4 SYNTHESIS OF POLY(BUTYLENE TERE/ISOPHTHALATE-CO-DIMETHYLSILOXANE)

These materials were prepared by a bulk process and also by a solution process. In the bulk process, dimethyl terephthalate-capped polydimethylsiloxane, dimethyl terephthalate, butane diol, dimethyl isophthalate and catalysts were put into the reaction vessel as described previously in section A.1.3.3.

The solution process entailed the reaction of the acid chlorides with butane diol and aminopropyl-terminated polydimethylsiloxane. Terephthaloyl and isophthaloyl chloride were purified by recrystallization from hot hexane, analogously to the procedure described for dimethyl terephthalate. Methylene chloride was used as solvent and purified by distillation over calcium hydride. Triethylamine was used as acid acceptor, and also purified by distillation over calcium hydride [10].

The polysiloxane and triethylamine were dissolved in methylene chloride and placed under argon in a four-neck flask. The acid chlorides were dissolved in methylene chloride and added dropwise via an addition funnel. A one to one stoichiometry of functional groups was used. Upon addition of the acid chloride solution, a fine, white precipitate and a slight increase ($\approx 5^{\circ}$C) in temperature were observed. After addition of the acid chlorides was complete, the reaction was allowed to stir for several hours. The reaction mixture was filtered by vacuum through a Buchner funnel to remove the salts. The methylene chloride solution was then washed until neutral with a 10% aqueous sodium bicarbonate solution and then precipitated in 50/50 methanol/isopropanol. The resulting polymer was collected by filtration and dried under vacuum overnight. The polyester-siloxanes were analyzed by FTIR, ^{1}H NMR, differential scanning calorimetry, and wide-angle x-ray scans as described previously in section A.1.3.3. Intrinsic viscosities were measured in methylene chloride at 25°C.

A.1.4 RESULTS AND DISCUSSION

A.1.4.1 REACTION OF DIMETHYL TEREPHTHALATE AND AMINOPROPYL-TERMINATED POLYDIMETHYLSILOXANE

The reaction of dimethyl terephthalate with aminopropyl-terminated polydimethylsiloxane is illustrated in scheme 7. This reaction proceeds readily; however long reaction times were required to approach 100% conversion. The reaction was considered to be completed when the bubbling due to the presence of methanol at high temperatures under a vacuum subsided.

These materials were extremely viscous, possibly due to strong hydrogen bonding between chains due to the amide linkages. The increase in viscosity could have been due to a large increase in molecular weight. However, the titrated polysiloxane molecular weight was 1910 g/mole. Shown in Table 17 are the results obtained for a series of experiments at varying amounts of dimethyl terephthalate charged. The possible effect of the hydrogen bonding is illustrated by a comparison of the % reaction, $[\eta]$ and Mn.

$$CH_3-O-\overset{O}{\overset{||}{C}}-\langle O \rangle-\overset{O}{\overset{||}{C}}-OCH_3 \quad + \quad NH_2(CH_2)_3\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-O-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-O-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}(CH_2)_3NH_2$$

1. argon, 160°C

2. vacuum

$$CH_3O\overset{O}{\overset{||}{C}}\langle O \rangle CHNH(CH_2)_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-O-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-O-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-(CH_2)_3NHC\overset{O}{\overset{||}{}}-\langle O \rangle \overset{O}{\overset{||}{C}}-OCH_3$$

$$+ \quad CH_3OH$$
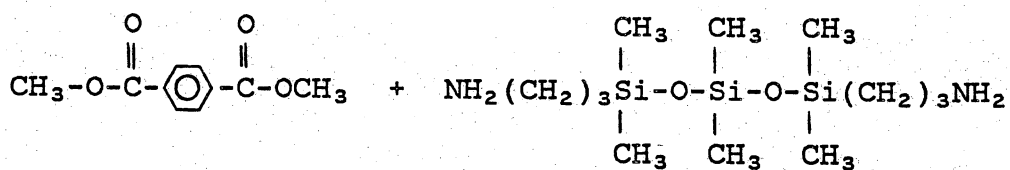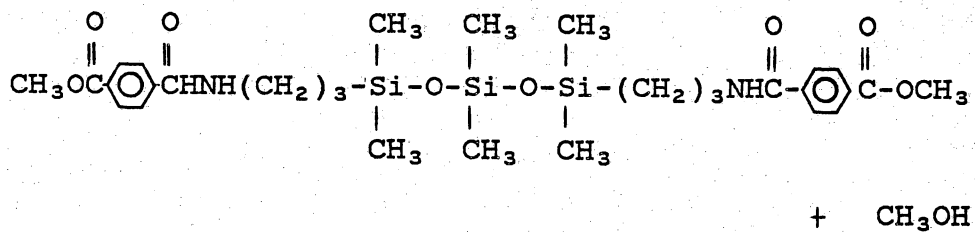
Scheme 7. Reaction of dimethyl terephthalate with
Polydimethylsiloxane.

Table 17. Results for the Capping of Polysiloxane with
Dimethyl Terephthalate.

Sample	$[\eta]^1$	Molecular Weight[2]	% Reaction by ^{1}H NMR	Molar ratio of DMT to PSX charged	Rxn Time (hrs.)
5.73	0.13	4360	88	1.1	7
5.75	0.08	4020	98	1.1	10
5.82	0.08	3800	91	1.5	11
5.83	0.2	6000	92	1.5	23
6.36	0.05	3244	83	1.5	21
6.42	0.19	3080	98	1.5	19
6.53.		3840	96	1.5	24

[1] in methylene chloride at 25°C., [2] by VPO

Sample 6.42 has a relatively high intrinsic viscosity (0.19) and a high conversion (98%) but a low titrated molecular weight. Sample 5.83 has a comparable intrinsic viscosity (0.20), slightly lower conversion (92%) but a higher number-average molecular weight by VPO. FTIR spectroscopy revealed the presence of the amide functionality; no absorption due to an acid functionality was observed. A representative FTIR spectrum is shown in Figure 62. This was important because these materials were to be used in an ester-interchange reaction to prepare siloxane modified-poly(butylene terephthalate). ^{1}H NMR was used to calculate the amount of reaction that occurred, by comparing the integral for a methylene unit in the unreacted aminopropyl group with the integral for the same methylene group in the reacted aminopropyl group.

No solvent system could be found to extract any excess dimethyl terephthalate from the reaction product. Since additional dimethyl terephthalate was to be used in the preparation of the polyester-co-dimethylsiloxane, this was not considered to be a problem. Also, the nature of the ester-interchange process eliminates the need for a stoichiometric balance of functional groups at the start of the polymerization. For this reason also, the presence of a very small amount of unreacted aminopropyl groups should not be a problem.
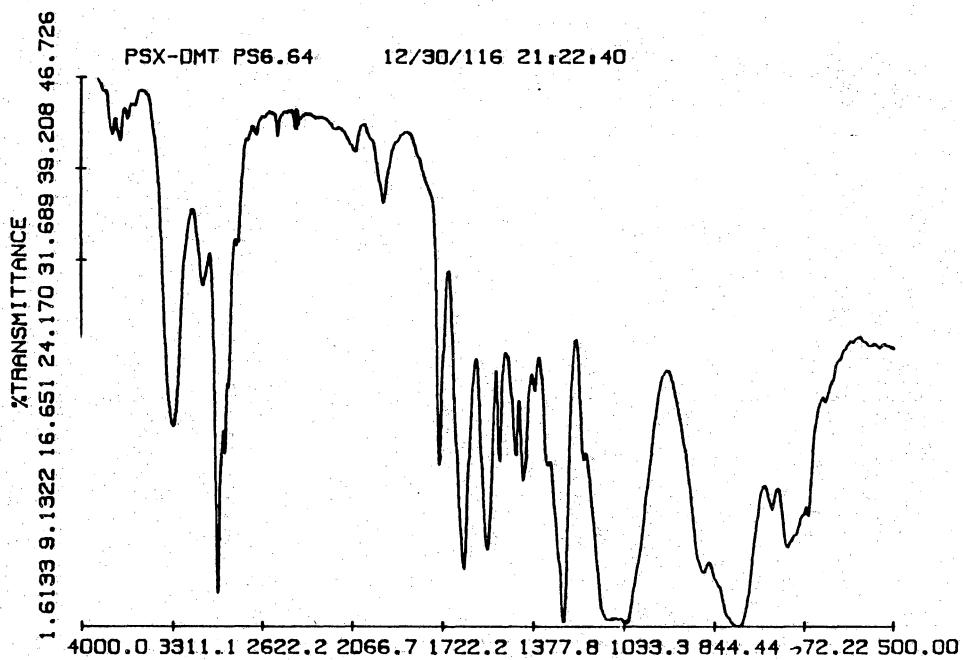
Figure 62.   FTIR spectrum of the product of the reaction
             of dimethyl terephthalate and polysiloxane.

Appendix A. Synthesis and Characterization of
Polyester-siloxane Copolymers   180

A.1.4.2 PREPARATION OF POLY(BUTYLENE TEREPHTHALATE-CO-DIMETHYLSILOXANE)

The preparation of poly(butylene terephthalate-co-dimethylsiloxane) is shown in scheme 8. There were some experimental difficulties involved in the preparation of these materials. The dimethyl terephthalate had a tendency to sublime out of the reaction mixture and had to be repeatedly melted back down into the bottom of the reaction mixture.

Once formed, these polymers were extremely insoluble, presumably due to the presence of crystallinity. Shown in Table 18 are the results obtained from DSC and intrinsic viscosity measurements. Each sample shows a strong melting and crystallization transition; a glass transition temperature corresponding to the polyester could not be observed.

The intrinsic viscosities measured do not indicate very high molecular weight polymers. This is possibly due to incomplete removal of the excess butane diol, due to difficulties in obtaining a sufficient vacuum, with stirring, of the reaction mixture. However, while the values for the intrinsic viscosities were not very high, the polymers seemed to be quite stable in solution. Flow times remained constant for a given concentration for periods between runs of at least 30 minutes.

$$CH_3OC\text{-}\langle O \rangle\text{-}COCH_3 \quad + \quad HO(CH_2)_4OH$$

with both C=O as shown (O double bonds).

$$+ \quad CH_3OC\text{-}\langle O \rangle\text{-}CNH - PSX - NHC\text{-}\langle O \rangle COCH_3$$

1. calcium acetate, argon, 180°C

2. antimony trioxide, 240°C, vacuum

$$\left[O\text{-}(CH_2)_4\text{-}OC\text{-}\langle O \rangle\text{-}CNH - PSX - NHC\text{-}\langle O \rangle C\right]_x \left[O\text{-}(CH_2)_4\text{-}O\text{-}C\text{-}\langle O \rangle\text{-}C\right]_y$$
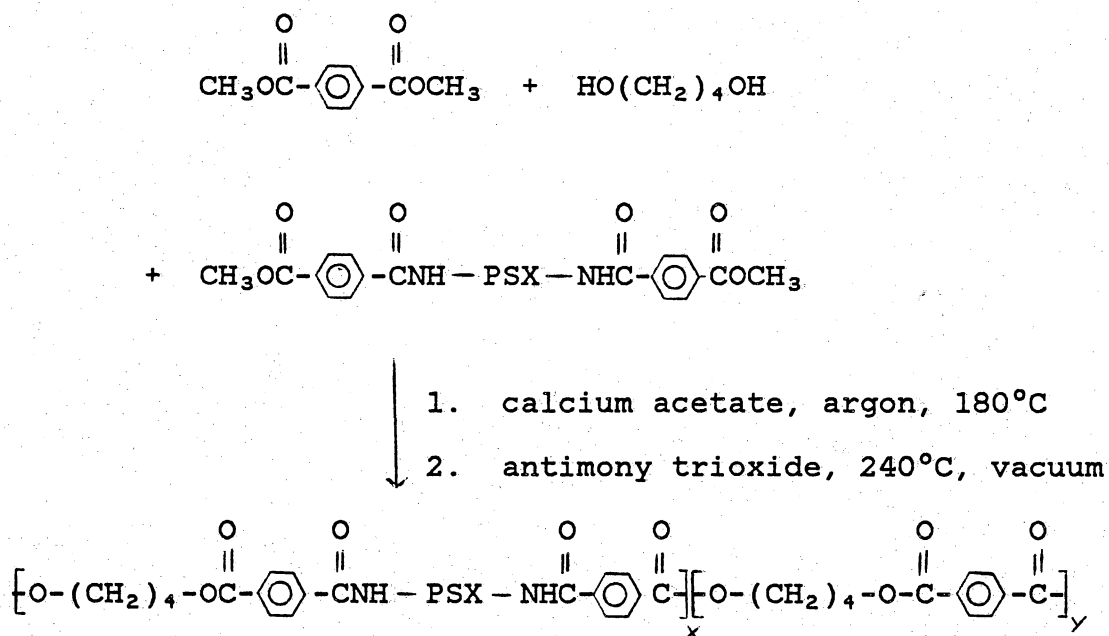
Scheme 8. Synthesis of poly(butylene terephthalate-co-dimethylsiloxane by ester-interchange process.

A.1.4.3 SYNTHESIS OF POLY(BUTYLENE TERE/ISOPHTHALATE-CO-DIMETHYLSILOXANE)

Due to the insolubility problems in the polymers pre-pared with only terephthalate linkages, it was desirable to prepare systems with a certain amount of isophthalate link-ages, thereby disrupting the crystallinity. This was done by the ester-interchange process as well through a solution process. The ester-interchange reaction is as shown for the terephthalate system in scheme 8, with the use of dimethyl

isophthalate as well as dimethyl terephthalate. The solution

process is illustrated in scheme 9.

ClC-⟨O⟩-CCl   +   ⟨O⟩-CCl   +   NH$_2$PSXNH$_2$

               |
               C
               Cl

+ HO(CH$_2$)$_4$OH

↓ methylene chloride, room temperature

    argon, (C$_2$H$_5$)$_3$N

$$\text{-NHPSXNHC-}\phi\text{-C--O(CH}_2\text{)}_4\text{OC-}\phi\text{-C--}$$

with O double-bonds:

-NHPSXNHC-⟨O⟩-ⁿC—O(CH$_2$)$_4$OC-⟨O⟩-C—
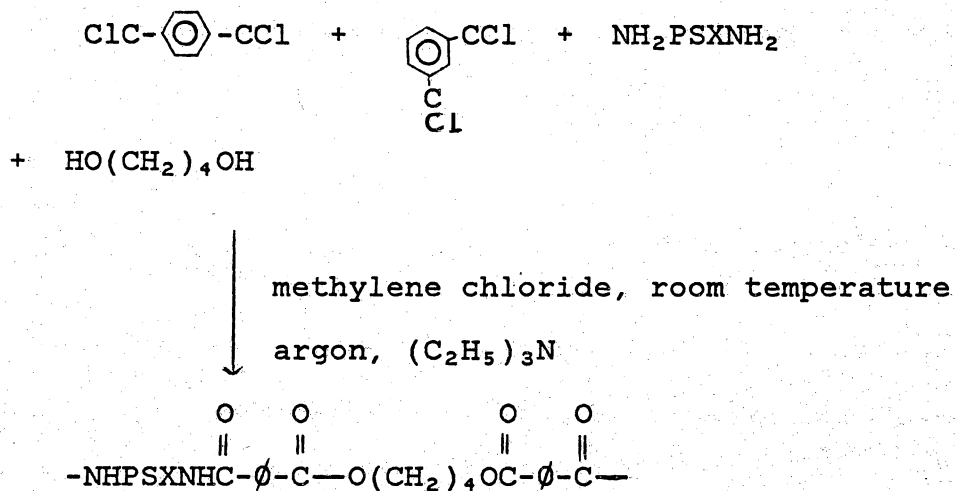
Scheme 9.   Solution technique for the preparation of

            poly(butylene tere/isophthalate-co-dimethyl-

            siloxane.

Table 18. Results for the Preparation of Poly(butylene terephthalate-co-dimethylsiloxane.

Sample[1]	Tm (°C.)	Tc (°C)	[η]	% PSX (theory)
6.23	213	192	-	0
6.30	217	196	-	12
6.30(R)	218	199	0.52[2]	-
6.40	203	182	-	40
6.40(R)	207	192	0.4[3]	-
6.56(R)	-	-	0.5[3]	65
6.56(E)	-	-	0.09[4]	-
[1] (R) insoluble, (E) soluble, in methylene chloride				
[2]hexafluoropropanol at 40°C, [3]50/50 phenol/tetrachloroethane at 25°C, [4]methylene chloride at 25°C.				

Shown in Table 19 are the results obtained on polymers prepared using both processes. A representative ^{1}H NMR spectrum is shown in Figure 63. In those cases where the resolution between the aromatic protons of the isophthalate and terephthalate repeat units was sufficient, the isophthalate contents are reported. The wt% polysiloxane was obtained by the following equations:

(19) $\dfrac{\text{aromatic }^1\text{H integral}}{8\ ^1\text{H's}}$ x repeat unit MW x 2

$\qquad\qquad$ = contribution by weight of isophthalate and terephthalate units

(20) $\dfrac{\text{butane diol }^1\text{H integral}}{8\ ^1\text{H's}}$ x repeat unit MW

$\qquad\qquad$ = contribution by weight of butane diol

(21) $\dfrac{\text{siloxane }^1\text{H integral}}{6\ ^1\text{H's}}$ x repeat unit MW

$\qquad\qquad$ = contribution by weight of polysiloxane

For example, in the case of polymer 6.88, prepared by a solution process, the sum of the integrals for the aromatic protons was 37.0. The contribution for the phthalate units

is thus 37/8 x 132 x 2 = 1221 parts. The integral for the protons in the butane diol segment was 74.5 and the contribution was 74.5/8 x 88.2 = 821 parts. The siloxane protons had a contribution of 46.0/6 x 74 = 567 parts. The composition of this polymer is thus 23% siloxane by weight. The calculation for the amount of isophthalate linkages, relative to the amount of terephthalate present, is simpler. In the same polymer, the terephthalate linkage gives a peak at 8.1 ppm with an integral of 61.3. The isophthalate linkage gives peaks at 8.6, 8.2 and 7.5 ppm with a total integral of 78.2. Since each type of linkage has the same molecular weight and number of protons, the amount of isophthalate content is given directly by a comparison of the integrals: 56%.

The amount of polydimethylsiloxane is generally lower than the charged amount. The presence of even lower molecular weight chains which may be somewhat soluble in the methanol/isopropanol mixture could account for the low incorporation of the polysiloxane.

These materials still possessed some crystallinity, as evidenced from wide-angle x-ray patterns. Representative patterns are shown in Figure 64. In addition, films cast from chloroform were cloudy, rather than transparent, due to crystallinity.

These polymers are apparently not of very high molecular weight, as evidenced by the values obtained for the intrinsic

viscosities. Although the acid chlorides were recrystallized and stored in a dessicator until use, perhaps the purity was not of a sufficiently high level to provide a high molecular weight polymer.
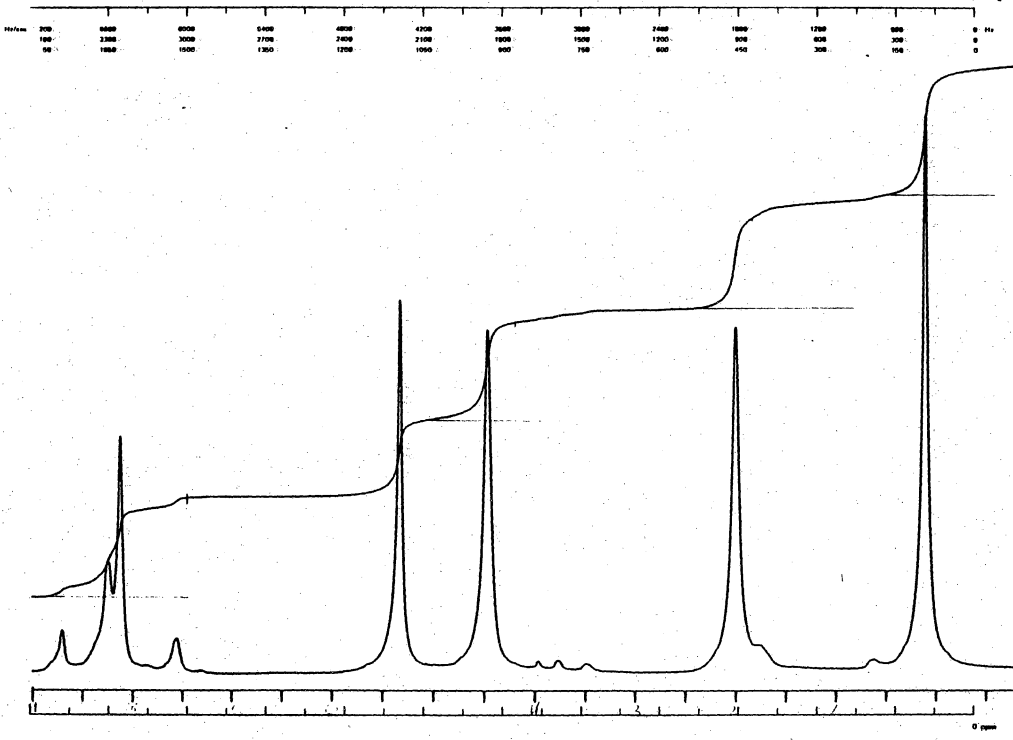
Figure 63. ¹H NMR spectrum of a poly(butylene
tere/isophahalate-co-dimethylsiloxane).

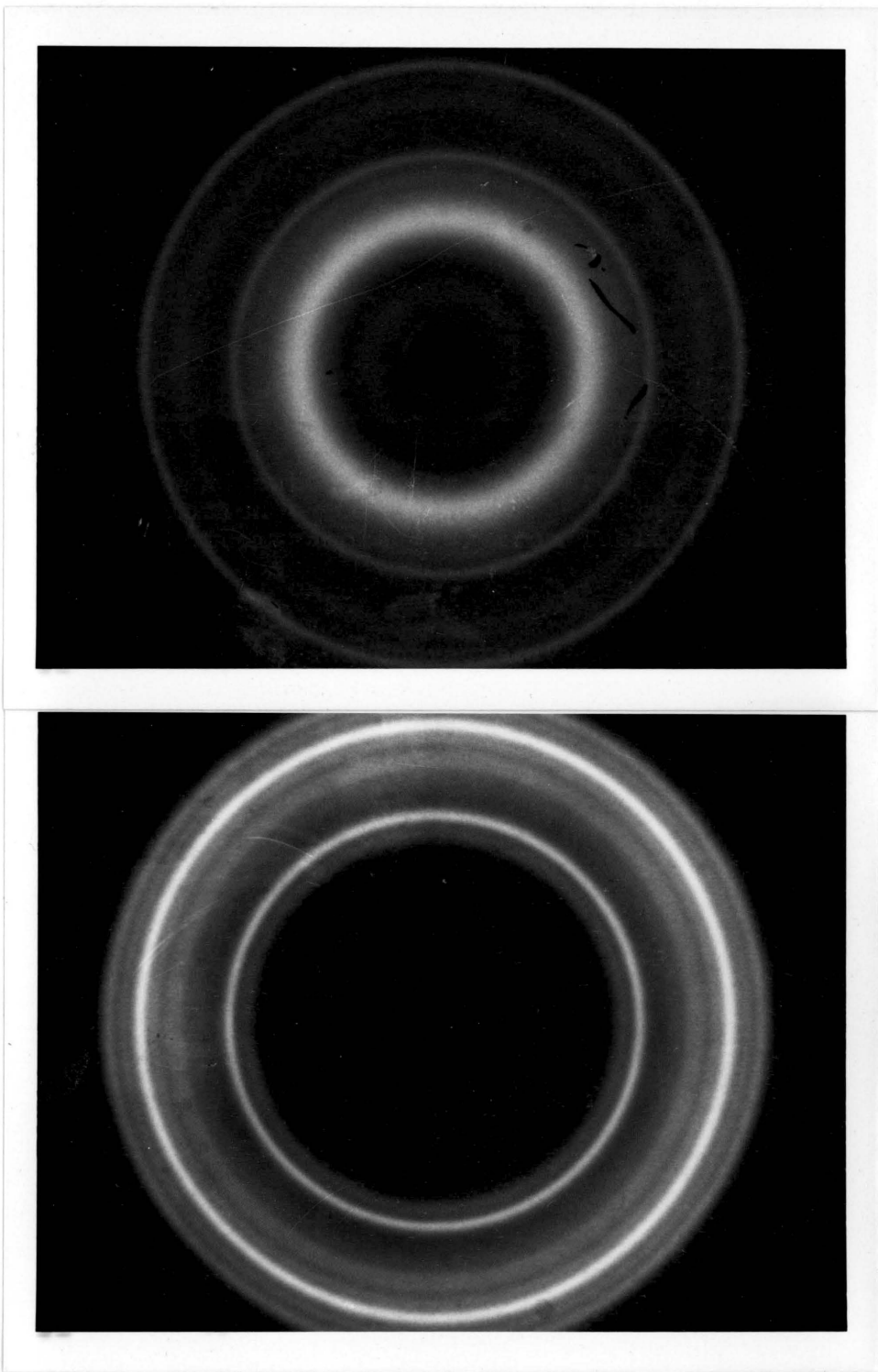Figure 64. WAXS patterns for polyesters prepared by so-
lution   technique.:   top=sample   6.86
bottom=sample 6.87 from Table 19.

Appendix A. Synthesis and Characterization of
Polyester-siloxane Copolymers   189

Table 19. Results for the Preparation of Poly(butylene tere/isophthalate-co-dimethylsiloxane.

Sample	Tm (°C.)	$[\eta]^1$	wt% PSX (theory)		% isophthalate
			found[2]	charged	
6.84	124	0.27	42	40	47
6.85[3][4]	-	0.26	18	40	-
6.86	185	0.19	-	-	46
6.87[3]	-	0.14	-	15	-
6.88	-	0.16	23	50	56
[1]in methylene chloride at 25°C, [2]by ^{1}H NMR,					
[3]bulk process; dimethyl terephthalate used.					
[4]Tg=36°C					
50 wt% isophthaloyl chloride charged relative to terephthoyl chloride.					

A.1.5 REFERENCES

1. Carothers, W. H., Chem. Rev., <u>8</u>, 353, (1931).

2. Flory, P. J., J. Amer. Chem. Soc., <u>61</u>, 3334 (1939).

3. Flory, P. J., J. Amer. Chem. Soc., <u>62</u>, 2261 (1940).

4. Brandt, P. J. Andolino, Ph. D. Thesis, VPI&SU, February, 1986.

5. Odian, G., <u>Principles of Polymerizations</u>, 2nd edition, Academic Press, New York, p. 102-105 (1981).

6. Morgan, P. W., <u>Condensation Polymers: By Interfacial and Solution Methods</u>, Interscience, New York (1965).

7. Lenz, R. W., <u>Organic Chemistry of Synthetic High Polymers</u>, Interscience, New York, chapter 4 (1967).

8. Bier, G., Polymer <u>15</u>, 527 (1958).

9. Goodman, J., Rhys, J. A., <u>Polyesters</u> Vol. I, Iliffe Books, Ltd. (1965).

10. Webster, D. C., Ph. D. Thesis, VPI&SU, January, 1984.

APPENDIX B. ^{29}SI NMR PULSE SEQUENCE

- Power gated heteronuclear broad band decoupling

- to minimize dielectric heating

- 1 ze   zero memory

- 2 D1 BB S1   BB dec. with power S1 during D1

- 3 D2 S2   Switch to power S2

- 4 GO=2   Aq. with power S2

- 5 DO   Decoupler off

- 6 Exit

- S1 typically 0.4 watt for NOE generation

- S2 typically 2-5 watt as needed for good decoupling

- D1 typically 1-5 times aq

- D2 typically 5-10 msec to allow power switching

THE RING-OPENING POLYMERIZATION OF

OCTAMETHYLCYCLOTETRASILOXANE

IN THE PRESENCE OF

BIS(α,ω-AMINOPROPYL)-1,3-TETRAMETHYLDISILOXANE

by

Patricia M. Sormani

J. E. McGrath, Chairman

Department of Chemistry

(ABSTRACT)

The ring-opening polymerization of octamethyl-cyclotetrasiloxane, D_4, in the presence of bis(α,ω-aminopropyl)-1,3-tetramethyldisiloxane using potassium siloxanolate and tetramethylammonium siloxanolate catalysts has been investigated. The use of reversed-phase high performance liquid chromatography (HPLC) and capillary gas chromatography (GC) allowed the disappearance of the starting materials to be monitored as a function of reaction temperature, time, targeted molecular weight, catalyst type and concentration. Due to electronegativity differences, the cyclic tetramer was found to react more quickly than the disiloxane under all conditions studied. This work was extended to the study of polydimethyl-co-diphenylsiloxane oligomers, prepared by the ring-opening copolymerization of D_4 with octaphenylcyclotetrasiloxane, D_4''. Reversed-phase HPLC was used to study the disappearance of the cyclic starting materials. Due to volatility considerations these oligomers were not analyzed by capillary GC. ^{29}Si NMR was

used to determine the number-average sequence length of each type of siloxane unit as a function of reaction conditions. The co-oligomer composition played the greatest role in determining the average sequence lengths. Oligomers with close to a 50/50 molar composition of dimethyl and diphenyl units showed a tendency towards an alternating distribution, while oligomers with an ≃27/83 molar composition displayed a tendency towards blockiness.

A series of polyester-siloxanes was prepared using both bulk and solution polycondensation techniques. Copolymers based on polybutylene terephthalate were highly insoluble, due to the presence of crystallinity in the systems. The incorporation of some isophthalate linkages increased the solubility of the polymer products, making the solution polymerization technique possible.