

UNCLASSIFIED

AD NUMBER
ADB009388
NEW LIMITATION CHANGE
TO Approved for public release, distribution unlimited
FROM Distribution authorized to U.S. Gov't. agencies only; Test and evaluation; May 1975. Other requests shall be referred to Air Force Materials Laboratory, Nonmetallic Materials Division, Polymer Branch, Attn: AFML/MBP, Wright-Patterson AFB, OH 45433.
AUTHORITY
AFWAL ltr, NOV 1982

THIS PAGE IS UNCLASSIFIED

AFML-TR-75-202

Part I

ADB009388

OFFICIAL FILE COPY

**CORRELATIONS BETWEEN POLYMER  
STRUCTURE AND GLASS TRANSITION  
TEMPERATURE I. POLYSILOXANES,  
POLYARYLENE-SILOXANES AND  
POLYXYLENE-SILOXANES.**

*POLYMER BRANCH  
NONMETALLIC MATERIALS DIVISION*

OCTOBER 1975

TECHNICAL REPORT AFML-TR-75-202 Part I

Distribution limited to U.S. Government agencies only; (test and evaluation). May 1975. Other requests for this document must be referred to the Air Force Materials Laboratory, Nonmetallic Materials Division, Polymer Branch, AFML/MBP, Wright-Patterson Air Force Base, Ohio 45433.

AIR FORCE MATERIALS LABORATORY  
AIR FORCE WRIGHT AERONAUTICAL LABORATORIES  
Air Force Systems Command  
Wright-Patterson Air Force Base, Ohio 45433

**BEST AVAILABLE COPY**

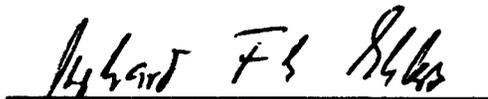
200 40 22 4083

## NOTICE

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operations, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

Copies of this report should not be returned unless return is required by security considerations, contractual obligations, or notice on a specific document.

This technical report has been reviewed and is approved for publication.



G. F. L. EHLERS  
Project Monitor

FOR THE COMMANDER



R. L. VAN DEUSEN, Chief  
Polymer Branch  
Nonmetallic Materials Division

## UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER AFML-TR-75- 202 , Pt. I	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Correlations Between Polymer Structure and Glass Transition Temperature. I. Polysiloxanes, Polyarylenesiloxanes and Polyxylylenesiloxanes		5. TYPE OF REPORT & PERIOD COVERED Progress Report September 1973-April 1975
7. AUTHOR(s) Gerhard F. L. Ehlers and Kurt R. Fisch		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS Air Force Materials Laboratory (AFML/MBP) Air Force Systems Command Wright-Patterson Air Force Base, Ohio 45433		8. CONTRACT OR GRANT NUMBER(s)
11. CONTROLLING OFFICE NAME AND ADDRESS Air Force Materials Laboratory Air Force Systems Command Wright-Patterson Air Force Base, Ohio 45433		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 7340/734004/734004/02
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE October 1975
		13. NUMBER OF PAGES 24
		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Distribution limited to U. S. Government agencies only; (test and evaluation). May 1975. Other requests for this document must be referred to the Air Force Materials Laboratory, Nonmetallic Materials Division, Polymer Branch, AFML/MBP, Wright-Patterson Air Force Base, Ohio 45433.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number)		
Polymer	Polysiloxanes	
Structure	Polyarylenesiloxanes	
Glass Transition Temperature	Polyxylylenesiloxanes	
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The glass transition temperatures of a number of polysiloxanes, polyarylenesiloxanes, poly(fluoro)alkylene siloxanes and polyxylylenesiloxanes were determined to provide much needed structure-property correlations for concurrent research efforts focused upon the tailoring of molecular backbone structures as a means of achieving desired property balance in novel polymers. These data supplemented with data from the literature were used to determine the effect of structural features on the glass transition temperature.		

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

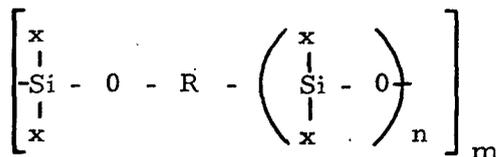
BEST AVAILABLE COPY

UNCLASSIFIED

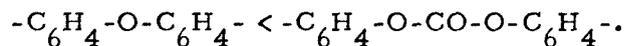
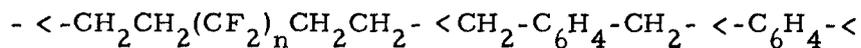
SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

20. ABSTRACT (continued)

Increases in glass transition temperatures were observed for polymers with larger and bulkier substituents on the silicone. The presence of aliphatic and aromatic moieties in the siloxane chain also coincided with higher glass transition temperatures. For the general structure



discussed in this report, the following order of increasing Tg was observed by modifying R as shown below:



UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

RESTRICTION COPY

## FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division. The work was initiated under Project No. 7340, "Nonmetallic and Composite Materials", Task 734004, "New Organic and Inorganic Polymers". It was administered under the direction of the Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, with Dr. G. F. L. Ehlers (AFML/MBP) as Project Scientist.

This report covers work conducted from September 1973 to April 1975 by G. F. L. Ehlers and K. R. Fisch. It was submitted for publication by the authors in April 1975.

## TABLE OF CONTENTS

SECTION		PAGE
I	Introduction	1
II	Discussion and Results	2
	1. Polysiloxanes	2
	2. Polyarylenesiloxanes	5
	3. Poly(fluoro)alkylene siloxanes	12
	4. Polyxylylenesiloxanes	12
III	Experimental	16
IV	Conclusions	17
V	References	19

## ILLUSTRATIONS

FIGURE		PAGE
1.	Glass Transition Temperatures of Polydimethyl-phenylmethyl siloxanes	20
2.	The Effect of the Number of Siloxane Units on the Tg of Polyarylenesiloxanes	21
3.	The Effect of Increasing Trifluoropropyl Content on the Tg of Polyxylylenesiloxanes	22
4.	The Effect of the Number of Siloxane Units on the Tg of Polyxylylenesiloxanes	23
5.	Actual and Projected Glass Transition Temperatures of Polysiloxanes, Polyarylenesiloxanes and Polyxylylenesiloxanes	24

## TABLES

TABLE		
I	Glass Transition Temperatures of Polysiloxanes	3
II	Glass Transition Temperatures of Polyarylenesiloxanes	9
III	Glass Transition Temperatures of Poly(fluoro)alkylene siloxanes	12
IV	Glass Transition Temperatures of Polyxylylenesiloxanes	13

## SECTION I

### Introduction

The glass transition temperatures of novel research polymers from AFML inhouse and contractual polymer synthesis programs are an important criterion for determining the specific use and use temperature range of these polymers. Transitions of a wide variety of polymers have been investigated in this laboratory during the last several years, initially by differential thermal analysis, but more recently by differential scanning calorimetry and thermomechanical analysis. While the results could not initially be correlated to any great extent, the data obtained from increasing numbers of structurally related groups of polymers has provided the basis for deriving currently emerging interrelationships.

Based on the collected data and data supplement from the literature, attempts will be made in this and future reports to elucidate the relationships between glass transition temperatures and structures of various classes of polymers. It is anticipated that these structure-property correlations will provide much needed guidance to future polymer synthesis research aimed toward obtaining candidate materials with improved use temperature ranges and better balances of mechanical and physical properties.

## SECTION II

### Discussion and Results

#### 1. Polysiloxanes

While there is general agreement about the glass transition temperature of polydimethylsiloxane at infinite molecular weight ( $-123^{\circ}\text{C}$ , references 1-5), other polysiloxanes show vast discrepancies in the  $T_g$ 's obtained by different authors. Polmanteer and Hunter (reference 2) determined the glass transition temperatures of dimethyl and phenylmethylsiloxane copolymers (with 0.4 mole % methyl vinyl siloxane) by dilatometry and obtained progressively higher  $T_g$ 's with increasing phenylmethylsiloxane content (Figure 1). A polymer consisting of 99.9% phenylmethylsiloxane had a  $T_g$  of  $-86^{\circ}\text{C}$ . Later, Polmanteer and coworkers (reference 3) determined the  $T_g$ 's of filled and vulcanized dimethyl-phenylmethylsiloxane copolymers through linear expansion measurements. Here a  $T_g$  of  $-30^{\circ}\text{C}$  was found for the oriented (by unidirectional milling) and a  $T_g$  of  $-41^{\circ}\text{C}$  for the nonoriented phenylmethyl siloxane elastomer. Figure 1 shows the effect of orientation on the  $T_g$ 's of the copolymers.

Russian workers obtained quite different results for phenyl substituted siloxanes. Andrianov and Yakushkina (reference 6) obtained a  $T_g$  of  $-72^{\circ}\text{C}$  for a copolymer of dimethylsiloxane with 25% phenylmethylsiloxane (Polmanteer's results are in the  $-100^{\circ}\text{C}$  range), and Borisov and coworkers (reference 7) reported a  $T_g$  of  $-129^{\circ}\text{C}$  for Polyphenylmethylsiloxane (Polmanteer's values are  $-30$  and  $-86^{\circ}\text{C}$ ). It is believed that discrepancies like these result from the presence of low molecular weight (cyclic) materials or impurities. Differences in the degree of crosslinking may also contribute to the wide scatter of results.

Work by Lee and coworkers (reference 5 and 8) showed that larger alkyl substituents resulted in increased  $T_g$ :

	$T_g$ ( $^{\circ}\text{C}$ )
Polydimethylsiloxane	-123
Polydiethylsiloxane	-72
Polydipropylsiloxane	-46

Dolgoplosk and coworkers (reference 9), on the other hand, found a  $T_g$  of  $-123^{\circ}\text{C}$  for polydiethylsiloxane. Recently, Beatty and Karasz (reference 10) clearly identified a discontinuity in  $\text{Cr}$  at  $130^{\circ}\text{K}$  ( $-143^{\circ}\text{C}$ ) as the  $T_g$  of polydiethylsiloxane and considered the transition found by Lee and coworkers at  $-72^{\circ}\text{C}$  to be related to a solid-solid transition.

Table I summarizes the glass transition temperatures found in the literature, as well as AFML data:

TABLE I

Glass Transition Temperatures of Polysiloxanes

	<u>Structure</u>	<u>T<sub>g</sub> (°C)</u>	<u>Reference</u>
100%	$\begin{array}{c} \text{CH}_3 \\   \\ -\text{Si}-\text{O}- \\   \\ \text{CH}_3 \end{array}$	-123	1, 2, 3, 4, 5
90%	" , 10%	-112 to -121	2, 3
	$\begin{array}{c} \text{CH}_3 \\   \\ -\text{Si}-\text{O}- \\   \\ \text{C}_6\text{H}_5 \end{array}$		
75%	" , 25%	-97 to -102 -72	2, 3 6
70%	" , 30%	-93 to -100	2, 3
40%	" , 60%	-65 to -91	2, 3
	100%	-30 to -86 -123	2, 3 7
	$\begin{array}{c} \text{C}_2\text{H}_5 \\   \\ -\text{Si}-\text{O}- \\   \\ \text{C}_2\text{H}_5 \end{array}$	-123 -72 -143	9 8 10
	$\begin{array}{c} \text{C}_3\text{H}_7 \\   \\ -\text{Si}-\text{O}- \\   \\ \text{C}_3\text{H}_7 \end{array}$	-46	8

Table I (continued)

	Structure	$T_g$ (°C)	Reference		
75%	$\begin{array}{c} \text{CH}_3 \\   \\ -\text{Si}-\text{O}- \\   \\ \text{CH}_3 \end{array}$	25%	$\begin{array}{c} \text{CH}_3 \\   \\ -\text{Si}-\text{O}- \\   \\ \text{CH}_2 \\   \\ \text{CH}_2 \\   \\ \text{C}_6\text{H}_5 \end{array}$	-102	6
75%	"	25%	$\begin{array}{c} \text{CH}_3 \\   \\ -\text{Si}-\text{O}- \\   \\ \text{O} \\   \\ \text{Si}(\text{CH}_3)_3 \end{array}$	-125	6
	$\begin{array}{c} \text{CH}_3 \\   \\ -\text{Si}-\text{O}- \\   \\ \text{C}_{10}\text{H}_7 \end{array}$			-131 (?)	7

Dow Corning LS-422 (pliable gum)

presumably	$\begin{array}{c} \text{CH}_3 \\   \\ -\text{Si}-\text{O}- \\   \\ \text{CH}_2 \\   \\ \text{CH}_2 \\   \\ \text{CF}_3 \end{array}$	+ 2 mole % vinyl pendant groups	-74	AFML data
------------	---	---------------------------------------	-----	-----------

Dow Corning LS-53 (filled, cured rubber sheet)

presumably	$\begin{array}{c} \text{CH}_3 \\   \\ -\text{Si}-\text{O}- \\   \\ \text{CH}_2 \\   \\ \text{CH}_2 \\   \\ \text{CF}_3 \end{array}$		-75	"
------------	---	--	-----	---

Table I (continued)

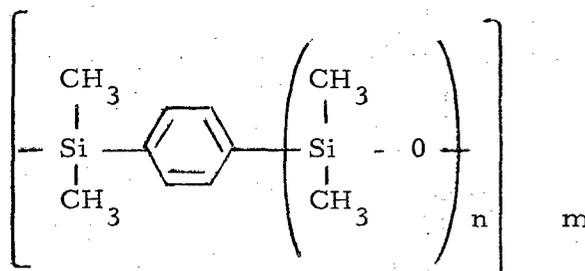
Structure	T <sub>g</sub> (°C)	Reference
GEC Polymer (highly viscous liquid)		
$  \begin{array}{c}  \text{CH}_3 \\    \\  -\text{Si} - \text{O} - \\    \\  \text{CH}_2\text{CH}_2\text{CH}_2\text{O} \\    \\  \text{CF}_3 \\    \\  \text{CF} \\    \\  \text{CF}_3  \end{array}  $	-85	AFML data
GEC Polymer (tacky gum)		
$  \begin{array}{c}  \text{CH}_3 \\    \\  -\text{Si} - \text{O} - \\    \\  \text{CH}_3  \end{array}  - \text{O} -   \begin{array}{c}  \text{CH}_3 \\    \\  -\text{Si} - \text{O} - \\    \\  \text{CH}_3  \end{array}  - \text{O} -   \begin{array}{c}  \text{CH}_3 \\    \\  -\text{Si} - \text{O} - \\    \\  \text{CH}_2\text{CH}_2\text{CH}_2\text{O} - \text{CF}_3 \\    \\  \text{CF} \\    \\  \text{CF}_3  \end{array}  $	-50	"

Differences in molecular weight may account for the fact that the last structure in Table I has a higher T<sub>g</sub> than the preceding one; the opposite would have been expected. It is also remarkable that LS-422, LS-53 and the first GEC polymer listed in Table I, which range from a liquid to a solid rubber at room temperature, have T<sub>g</sub>'s of about the same magnitude.

In view of the discrepancies observed for the T<sub>g</sub>'s of polysiloxanes, very little can be said about structure - T<sub>g</sub> relationships. Increasing amounts of bulkier substituents on the silicon increase the glass transition temperature, with the possible exception of the lowest members of the homologous series, such as polydiethylsiloxane.

## 2. Polyarylene siloxanes

In the polymer system

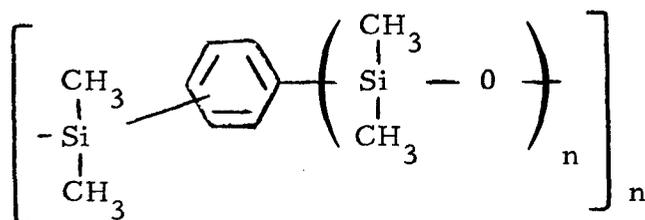


the glass transition temperature decreases with increasing n, as expected (references 11, 12, 13):

<u>n</u>	<u>Tg(°C)</u>
1	-23
2	-53
	-63
3	-62
	-62
	-81
4	-72
	-72
5	-80

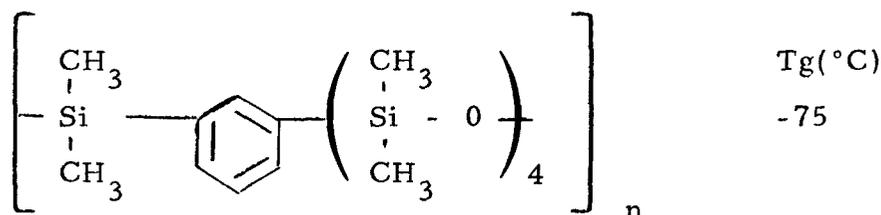
The scatter of these data, as also shown in Figure 2, is believed to be more the result of impure or differently crosslinked polymers than caused by differences in the method, or by the accuracy of the Tg determination. For n = infinite, the Tg's are expected to approach the -123°C value of polydimethylsiloxane.

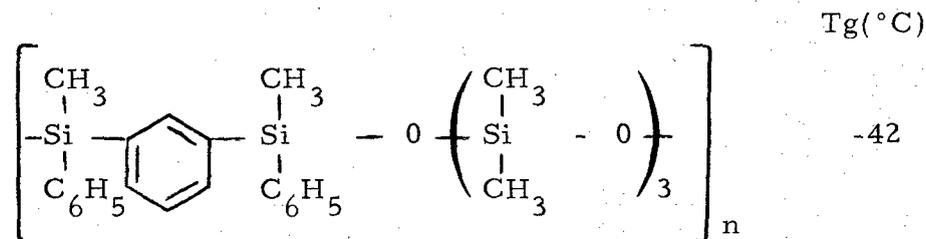
The replacement of p-phenylene by m-phenylene in the above structure seems to have no distinct effect (references 11, 12, 13):



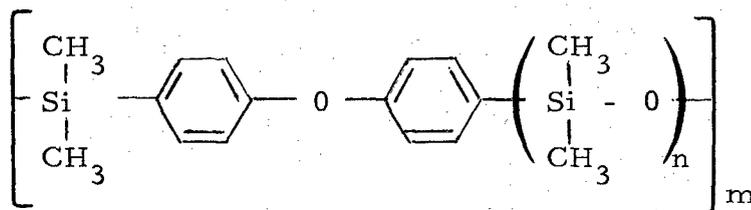
<u>n</u>	<u>meta or para</u>	<u>Tg (°C)</u>
2	p	-53; -63
2	m	-46
4	p	-72
4	m	-75

Replacing two of the methyl groups, attached to silicone atoms adjacent to the phenylene ring, by phenyl results in a considerable increase in Tg (reference 13):





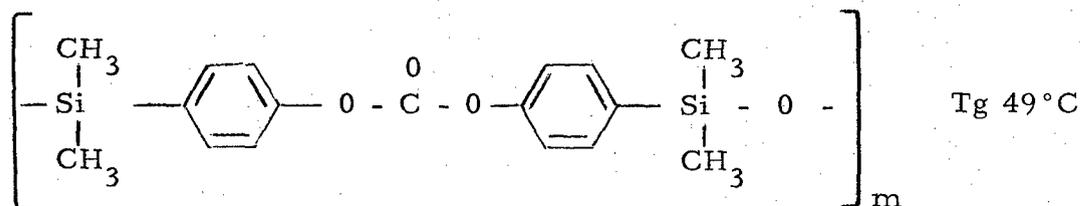
Very remarkable is the fact that the introduction of a diphenylether linkage for the phenylene linkage increases the Tg (reference 13; see also Figure 2):



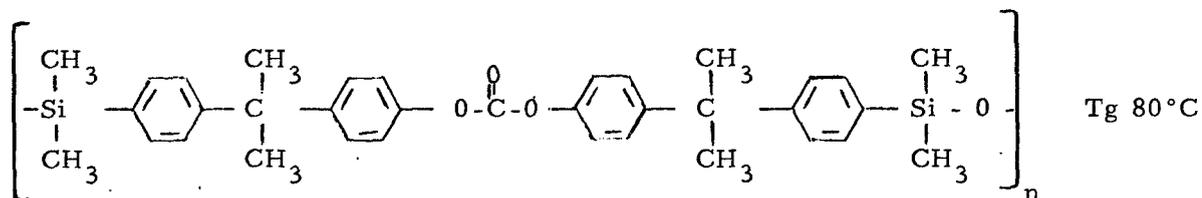
<u>n</u>	<u>Tg(°C)</u>
3	-37
4	-52
5	-65

It appears that, in spite of its flexibility, the large aromatic diphenylether unit increases the rigidity of the very flexible siloxane chains more than the shorter phenylene moiety. The same observation has been made with the polyxylylene siloxanes (See under 3).

An even larger increase of the glass transition has been observed by introducing the diphenylcarbonate linkage:



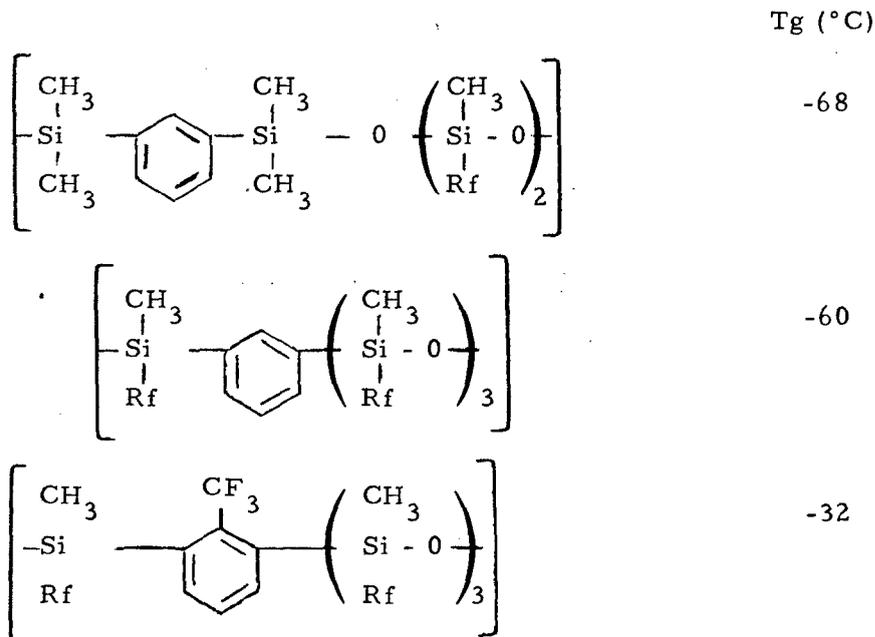
Finally, the polymer



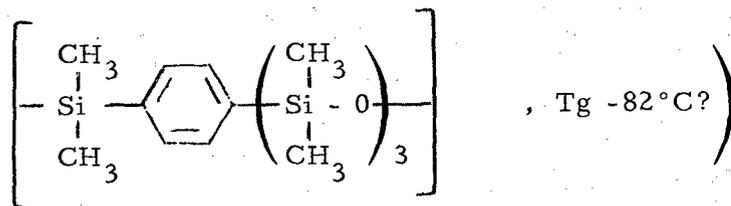
can be visualized as the structure of Lexan, with every second  $\text{---O---C(=O)---O---}$  moiety replaced by  $\text{---Si(CH}_3)_2\text{---O---Si(CH}_3)_2\text{---}$ . The replacement resulted in a lowering of the

Tg by  $70^\circ\text{C}$  (Tg of Lexan:  $150^\circ\text{C}$ ).

A comparison of the glass transition temperatures of polyarylene-siloxanes with fluoroaliphatic pendant groups (and 3% vinyl)

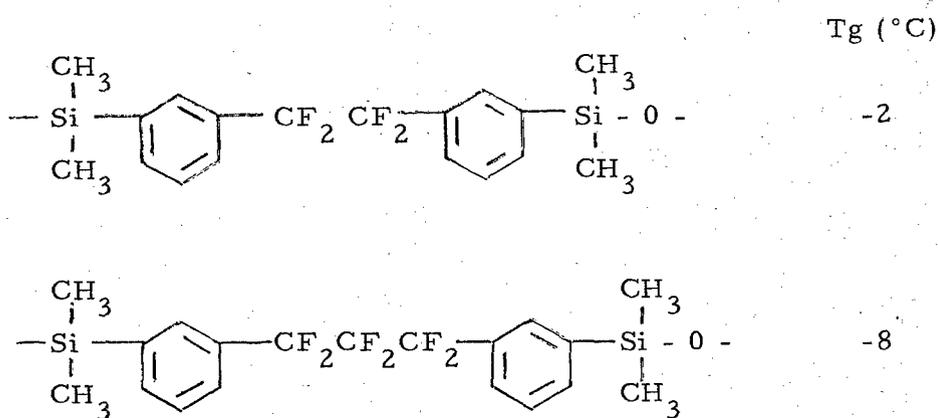


seems to suggest that the replacement of methyl groups on the silicone by  $\text{---CH}_2\text{CH}_2\text{CF}_3$  increases the Tg (compare also the first structure with the previous described structure)



Introduction of  $-\text{CF}_3$  into the ring in 2-position increases Tg considerably.

In the polymers



the introduction of another  $-\text{CF}_2-$  moiety in the chain results in a slight increase in flexibility (decrease in Tg)(reference 11).

Table II summarizes the Tg data on polyarylenesiloxanes.

TABLE II

Glass Transition Temperatures of Polyarylenesiloxanes

<u>Structure</u>	<u>Tg(<math>^\circ\text{C}</math>)</u>	<u>Reference</u>
$\left[ \text{Si} \begin{array}{c}   \\ \text{CH}_3 \\   \\ \text{CH}_3 \end{array} - \text{C}_6\text{H}_4 - \left( \text{Si} \begin{array}{c}   \\ \text{CH}_3 \\   \\ \text{CH}_3 \end{array} - \text{O} \right)_n \right]_m$		
<u>n:</u>		
1	-23	10
2	-53	10
	-63	11

(Table II continued)

Structure	$T_g(^{\circ}\text{C})$	Reference
$\left[ \begin{array}{c} \text{CH}_3 \\   \\ \text{---Si---} \\   \\ \text{CH}_3 \end{array} \text{---} \text{C}_6\text{H}_4 \text{---} \left( \begin{array}{c} \text{CH}_3 \\   \\ \text{---Si---} \\   \\ \text{CH}_3 \end{array} \right)_n \right]_m$	$\frac{n:}{3}$ -62 -62 -81 $\frac{n:}{4}$ -72 -72 $\frac{n:}{5}$ -80	10 12 AFML data 10 12 12
$\left[ \begin{array}{c} \text{CH}_3 \\   \\ \text{---Si---} \\   \\ \text{C}_6\text{H}_5 \end{array} \text{---} \text{C}_6\text{H}_4 \text{---} \text{Si} \begin{array}{c} \text{CH}_3 \\   \\ \text{---} \\   \\ \text{C}_6\text{H}_5 \end{array} \text{---} 0 \left( \begin{array}{c} \text{CH}_3 \\   \\ \text{---Si---} \\   \\ \text{CH}_3 \end{array} \right)_3 \right]_n$	$\frac{n:}{2}$ -46 $\frac{n:}{4}$ -75	AFML data 12
$\left[ \begin{array}{c} \text{CH}_3 \\   \\ \text{---Si---} \\   \\ \text{CH}_3 \end{array} \text{---} \text{C}_6\text{H}_4 \text{---} 0 \text{---} \text{C}_6\text{H}_4 \text{---} \left( \begin{array}{c} \text{CH}_3 \\   \\ \text{---Si---} \\   \\ \text{CH}_3 \end{array} \right)_n \right]_m$	$\frac{n:}{3}$ -37 $\frac{n:}{4}$ -52 $\frac{n:}{5}$ -65	12 12 12
$\left[ \begin{array}{c} \text{CH}_3 \\   \\ \text{---Si---} \\   \\ \text{CH}_3 \end{array} \text{---} \text{C}_6\text{H}_4 \text{---} 0 \text{---} \text{C}(=\text{O}) \text{---} 0 \text{---} \text{C}_6\text{H}_4 \text{---} \text{Si} \begin{array}{c} \text{CH}_3 \\   \\ \text{---} \\   \\ \text{CH}_3 \end{array} \text{---} 0 \right]_m$	49	AFML data

(Table II continued)

Structure	T <sub>g</sub> (°C)	Reference
$\left[ \begin{array}{c} \text{CH}_3 \\   \\ \text{Si} - \text{C}_6\text{H}_4 - \text{C}(\text{CH}_3)_2 - \text{C}_6\text{H}_4 - \text{O} - \overset{\text{O}}{\parallel} \text{C} - \text{O} - \text{C}_6\text{H}_4 - \text{C}(\text{CH}_3)_2 \\   \\ \text{CH}_3 \end{array} \right]_n$ $\left[ \begin{array}{c} \text{CH}_3 \\   \\ \text{C}_6\text{H}_4 - \text{Si} - \text{O} - \\   \\ \text{CH}_3 \end{array} \right]_n$	80	AFML data
$\left[ \begin{array}{c} \text{CH}_3 \\   \\ \text{Si} - \text{C}_6\text{H}_4 - \text{Si}(\text{CH}_3)_2 - \text{O} - \left( \text{Si}(\text{CH}_3)_2 - \text{O} \right)_2 \\   \\ \text{CH}_3 \end{array} \right] \text{Rf} = \text{CH}_2\text{CH}_2\text{CF}_3$	-68	"
$\left[ \begin{array}{c} \text{CH}_3 \\   \\ \text{Si} - \text{C}_6\text{H}_4 - \left( \text{Si}(\text{CH}_3)_2 - \text{O} \right)_3 \\   \\ \text{Rf} \end{array} \right] \text{Rf} = \text{CH}_2\text{CH}_2\text{CF}_3$	-60	"
$\left[ \begin{array}{c} \text{CH}_3 \quad \text{CF}_3 \\   \quad   \\ \text{Si} - \text{C}_6\text{H}_4 - \left( \text{Si}(\text{CH}_3)_2 - \text{O} \right)_3 \\   \\ \text{Rf} \end{array} \right] \text{Rf} = \text{CH}_2\text{CH}_2\text{CF}_3$	-32	"
$\left[ \begin{array}{c} \text{CH}_3 \\   \\ \text{Si} - \text{C}_6\text{H}_4 - \text{CF}_2\text{CF}_2 - \text{C}_6\text{H}_4 - \text{Si}(\text{CH}_3)_2 - \text{O} - \\   \\ \text{CH}_3 \end{array} \right]_n$	-2	"
$\left[ \begin{array}{c} \text{CH}_3 \\   \\ \text{Si} - \text{C}_6\text{H}_4 - \text{CF}_2\text{CF}_2\text{CF}_2 - \text{C}_6\text{H}_4 - \text{Si}(\text{CH}_3)_2 - \text{O} - \\   \\ \text{CH}_3 \end{array} \right]_n$	-8	"

3. Poly(fluoro)alkylene siloxanes.

Contrary to the observations at the end of the previous chapter, the increase of CF<sub>2</sub> groups in the nonaromatic poly(fluoro)alkylene siloxane system does not result in a significant change of Tg, as Table II shows.

TABLE III

Glass Transition Temperatures of Poly(fluoro)alkylene siloxanes

<u>Structure</u>	<u>Tg(°C)</u>	<u>Reference</u>
$  \begin{array}{c}  \text{CH}_3 \\    \\  -\text{Si} - \text{CH}_2\text{CH}_2(\text{CF}_2)_n\text{CH}_2\text{CH}_2 - \\    \\  \text{CH}_2 \\    \\  \text{CH}_2 \\    \\  \text{CF}_3  \end{array}  $	$  \begin{array}{c}  \text{CH}_3 \\    \\  -\text{Si} - \text{O} - \\    \\  \text{CH}_2 \\    \\  \text{CH}_2 \\    \\  \text{CF}_3  \end{array}  $	
	<u>n:</u>	
	*) 2	-26
	**) 8	-24
		AFML
		"

\*) assumed to be the structure of FCS 210

\*\*) assumed to be the structure of FCS 810

4. Polyxylylene siloxanes.

A series of polyxylylene siloxanes synthesized by Rosenberg and Choe in our Polymer Branch Laboratories (reference 14) permit some conclusions as to the effect of the number of siloxane units, and the effect of silicone substituents, on the glass transition temperature. The results are listed in Table IV. All of the determinations are AFML data.

TABLE IV

Glass Transition Temperatures of Polyxilylene Siloxanes

Structure	Tg(°C)
$\left[ \begin{array}{c} \text{CH}_3 \\   \\ -\text{Si}- \\   \\ \text{CH}_3 \end{array} - \text{CH}_2 - \text{C}_6\text{H}_4 - \text{O} - \text{C}_6\text{H}_4 - \text{CH}_2 - \begin{array}{c} \text{CH}_3 \\   \\ -\text{Si}- \\   \\ \text{CH}_3 \end{array} - \text{O} \right]_n$	-18
$\left[ \begin{array}{c} \text{CH}_3 \\   \\ -\text{Si}- \\   \\ \text{R}_1 \end{array} - \text{CH}_2 - \text{C}_6\text{H}_4 - \text{CH}_2 - \begin{array}{c} \text{CH}_3 \\   \\ -\text{Si}- \\   \\ \text{R}_2 \end{array} - \text{O} \right]_n$	
$\begin{array}{cc} \text{R}_1 & \text{R}_2 \\ \text{CH}_3 & \text{CH}_3 \\ \text{CF}_3\text{CH}_2\text{CH}_2 & \text{CF}_3\text{CH}_2\text{CH}_2 \end{array}$	-41 -19
$\left[ \begin{array}{c} \text{CH}_3 \\   \\ -\text{Si}- \\   \\ \text{R}_1 \end{array} - \text{CH}_2 - \text{C}_6\text{H}_4 - \text{CH}_2 - \begin{array}{c} \text{CH}_3 \\   \\ -\text{Si}- \\   \\ \text{R}_2 \end{array} - \text{O} - \begin{array}{c} \text{CH}_3 \\   \\ -\text{Si}- \\   \\ \text{R}_3 \end{array} - \text{O} \right]_n$	
$\begin{array}{ccc} \text{R}_1 & \text{R}_2 & \text{R}_3 \\ \text{CH}_3 & \text{CH}_3 & \text{CH}_3 \\ \text{CH}_3 & \text{CH}_3 & \text{CF}_3\text{CH}_2\text{CH}_2 \\ \text{CF}_3\text{CH}_2\text{CH}_2 & \text{CF}_3\text{CH}_2\text{CH}_2 & \text{CH}_3 \\ \text{CF}_3\text{CH}_2\text{CH}_2 & \text{CF}_3\text{CH}_2\text{CH}_2 & \text{CF}_3\text{CH}_2\text{CH}_2 \\ \text{CF}_3\text{CH}_2\text{CH}_2 & \text{CF}_3\text{CH}_2\text{CH}_2 & \text{CF}_3\text{CH}_2\text{CH}_2(97\%) \\ & & + \\ & & \text{CH}_2 = \text{CH} (3\%) \end{array}$	-62 -52 -44 -35 -35.5

(Table IV continued)

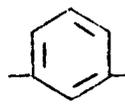
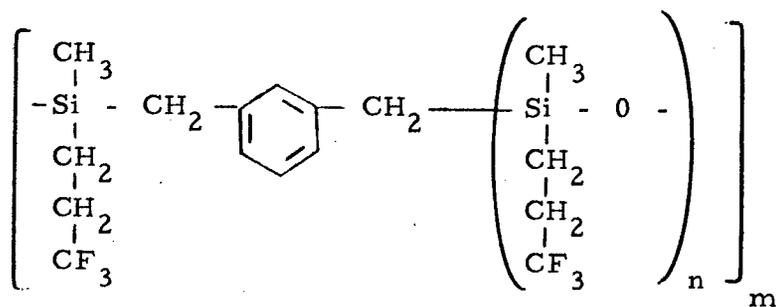
Structure				Tg(°C)
$\begin{array}{c} \text{CH}_3 \\   \\ -\text{Si}- \\   \\ \text{R}_1 \end{array}$	$\text{CH}_2$ -  - $\text{CH}_2$	$\begin{array}{c} \text{CH}_3 \\   \\ -\text{Si}- \\   \\ \text{R}_2 \end{array}$	$0 - \begin{array}{c} \text{CH}_3 \\   \\ -\text{Si}- \\   \\ \text{R}_3 \end{array} - 0 - \begin{array}{c} \text{CH}_3 \\   \\ -\text{Si}- \\   \\ \text{R}_4 \end{array} - 0 -$	
R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	R <sub>4</sub>	
CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	-77
CH <sub>3</sub>	CH <sub>3</sub>	CF <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub>	CF <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub>	-59
CF <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub>	CF <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub>	CF <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub>	CF <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub>	-38

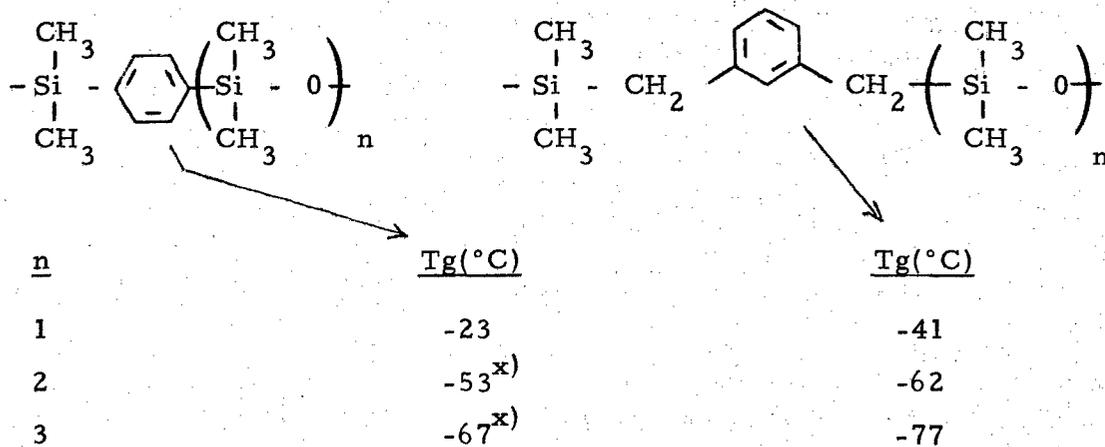
Table IV shows again, as discussed before, the rigidifying effect of the diphenylether linkage compared to the phenylene linkage. By replacing methyl groups with trifluoropropyl groups, the glass transition temperature increases rather consistently by 9°C per replaced unit. (See also Figure 3). Increasing the number of dimethylsiloxane units from 1 to 2 decreases the Tg by 21°C, and from 2 to 3 units by 15°C. (Figure 4). The effect of additional dimethylsiloxane units is expected to decrease slowly, and for an infinite number of units the Tg is identical to that of polydimethyl siloxane (-123°C). The Tg of the trifluoropropyl substituted polymer system



also decreases with increasing n, but, as Figure 4 shows, the glass transition temperature begins already to level off at n = 3. At n = infinite, the Tg would be -75°C (see Chapter 1).

Another comparison can be made between three of the xylylene siloxane polymers and their phenylene counterparts described in Chapter 2. Although the former are meta substituted, and the latter para, it has been shown in

Chapter 2 that m-phenylene siloxanes give Tg's in the same order of magnitude as p-phenylene siloxanes.



x) from plot 1 in Figure 2

The comparison shows the flexibilizing effect of the CH<sub>2</sub>-group to a varying extent.

## SECTION III

### EXPERIMENTAL

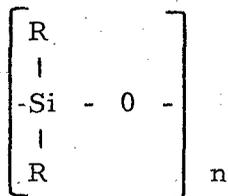
The glass transition temperatures of the polymers, as far as they had been determined in the PolymerBranch were obtained almost exclusively by differential scanning calorimetry (DSC), using the duPont 990 Thermal Analyzer. Heating rates of  $\Delta T = 20^\circ\text{C}/\text{min}$  were applied, and the extrapolated onset of the baseline shift in DSC was taken as the glass transition temperature. Only in isolated cases was thermomechanical analysis (TMA) used for clarification, either with the expansion mode (point of rate change of expansion) or penetration mode (point of highest rate of penetration). All measurements were made at least in duplicate.

The methods and conditions which were used to determine the Tg data reported in the literature - and used here - were not explored. Strictly speaking, only data obtained by the same author under the same conditions can be compared.

## SECTION IV

### CONCLUSIONS

#### Polysiloxanes

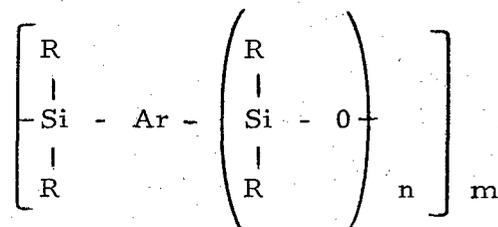


Widely scattered glass transition temperatures of dimethyl-methylphenyl siloxane copolymers suggest that the polymers investigated by some authors were impure or ill defined.

Introduction of larger alkyl substituents or phenyl for methyl in dimethylsiloxane increases Tg, with the possible exception of the lowest members of the homologous series, such as polydiethyl siloxane.

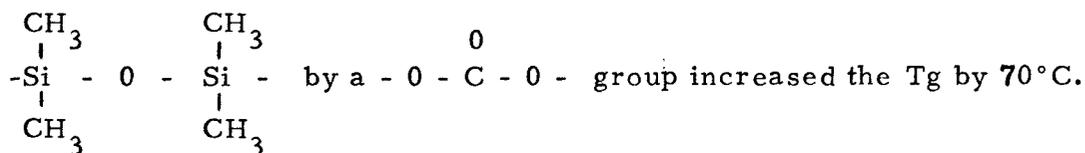
The physical nature of a polysiloxane at room temperature may not give a clue as to its glass transition temperature. Materials of widely different physical conditions, from highly viscous liquids to rubber sheets, had Tg's of the same order of magnitude.

#### Polyarylenesiloxanes



The introduction of arylene units into the siloxane chain increases the Tg considerably. The stiffening effect of this moiety is so strong that differences between m - and p - phenylene are of negligible effect.

Introduction of a CF<sub>3</sub> group into the 2-position of a m-phenylene linkage increases the Tg considerably. The diphenylether linkage, being a larger aromatic unit than phenylene, increases the Tg even more, in spite of its flexible ether linkage. The same observation has been made for the polyxylylene-siloxanes. The introduction of the diphenylcarbonate moiety produces a still higher glass transition temperature. Even the  $\text{-O-C(=O)-O-}$  moiety by itself is relatively rigid compared to the siloxane unit: replacement of a

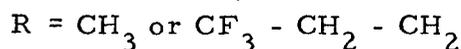
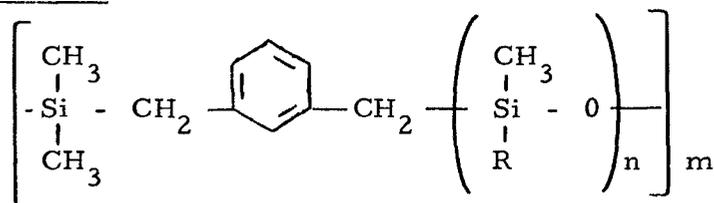


As far as the silicon substituents are concerned, the replacement of a methyl group by phenyl increases  $T_g$  considerably, but the introduction of  $\text{CF}_3\text{-CH}_2\text{-CH}_2$  linkages seems to have relatively little effect ( $\sim 4$  to  $7^\circ\text{C}$  per replaced methyl group).

### Poly(fluoro)alkylene siloxanes.

The number of perfluoromethylene groups in a structure as shown in Table III seems to have little effect on the glass transition temperature.

### Polyxylylenesiloxanes



Increasing amounts of  $\text{CF}_3\text{CH}_2\text{CH}_2$  increase  $T_g$  by about  $9^\circ\text{C}$  per replaced methyl group, while the addition of another  $\begin{array}{c} \text{CH}_3 \\ | \\ \text{-Si-} \\ | \\ \text{CH}_3 \end{array} - \text{O} -$  unit

decreases  $T_g$ , initially by  $15\text{-}20^\circ\text{C}$ , but less so with larger amounts of  $\begin{array}{c} \text{CH}_3 \\ | \\ \text{-Si-} \\ | \\ \text{CH}_3 \end{array} - \text{O} -$  units.

The xylylene moiety in the chain, compared with the phenylene moiety, lowers the  $T_g$  by  $10$  to  $20^\circ\text{C}$ .

Figure 5 gives an overview of the observed and projected glass transition temperatures of polysiloxanes, polyarylenesiloxanes and polyxylylenesiloxanes.

## SECTION V

### REFERENCES

1. G. M. Konkle, R. Selfridge and P. C. Servais, *Ind. Eng. Chem.* 39, 1410 (1947).
2. K. E. Polmanteer and M. J. Hunter, *J. Appl. Pol. Sci.* 1, 3 (1959).
3. K. E. Polmanteer, J. Thorne and J. D. Helmer, *Rubber Chem. and Tech.* 39, 1403 (1966).
4. R. F. Boyer, *Rubber Chem. and Tech.* 36, 1303 (1963).
5. C. L. Lee, O. K. Johannson, O. L. Flaningam and P. Hahn, *Pol. Preprints* 10, 1311 (1969).
6. K. A. Andrianov and S. E. Yakushkina, *Vysokomol. Soyed.* 4, 1193 (1962).
7. S. N. Borisov, A. V. Karmin, Ye. A. Cheruysheyev and V. S. Fikhtengol'ts, *Vysokomol. Soyed.* 4, 1507 (1962).
8. C. L. Lee, O. K. Johannson, O. L. Flaningam and P. Hahn, *Pol. Preprints* 10, 1319 (1969).
9. B. A. Dolgoplosk, A. L. Klebanskij, L. P. Fomina, V. S. Fikhtengol'ts and Ye. Yn. Shvarts, *DAN SSSR* 150, 813 (1963).
10. C. L. Beatty and F. E. Karasz, *J. Polym. Sci., Polym. Chem. Ed.* 13, 971 (1975).
11. V. C. R. McLoughlin and Patricia A. Grattan, Royal Aircraft Establishment Technical Report TR 71224 (1971).
12. R. E. Burks Jr., E. R. Covington, M. V. Jackson and J. E. Curry, *J. Polym. Sci., Polym. Chem. Ed.* 11, 319 (1973).
13. L. W. Breed, R. L. Elliot and M. E. Whitehead, *J. Polymer Sci. A-1*, 5, 2745 (1967).
14. H. Rosenberg and E. W. Choe, AFML-TR 75-182 (1975) (in print)

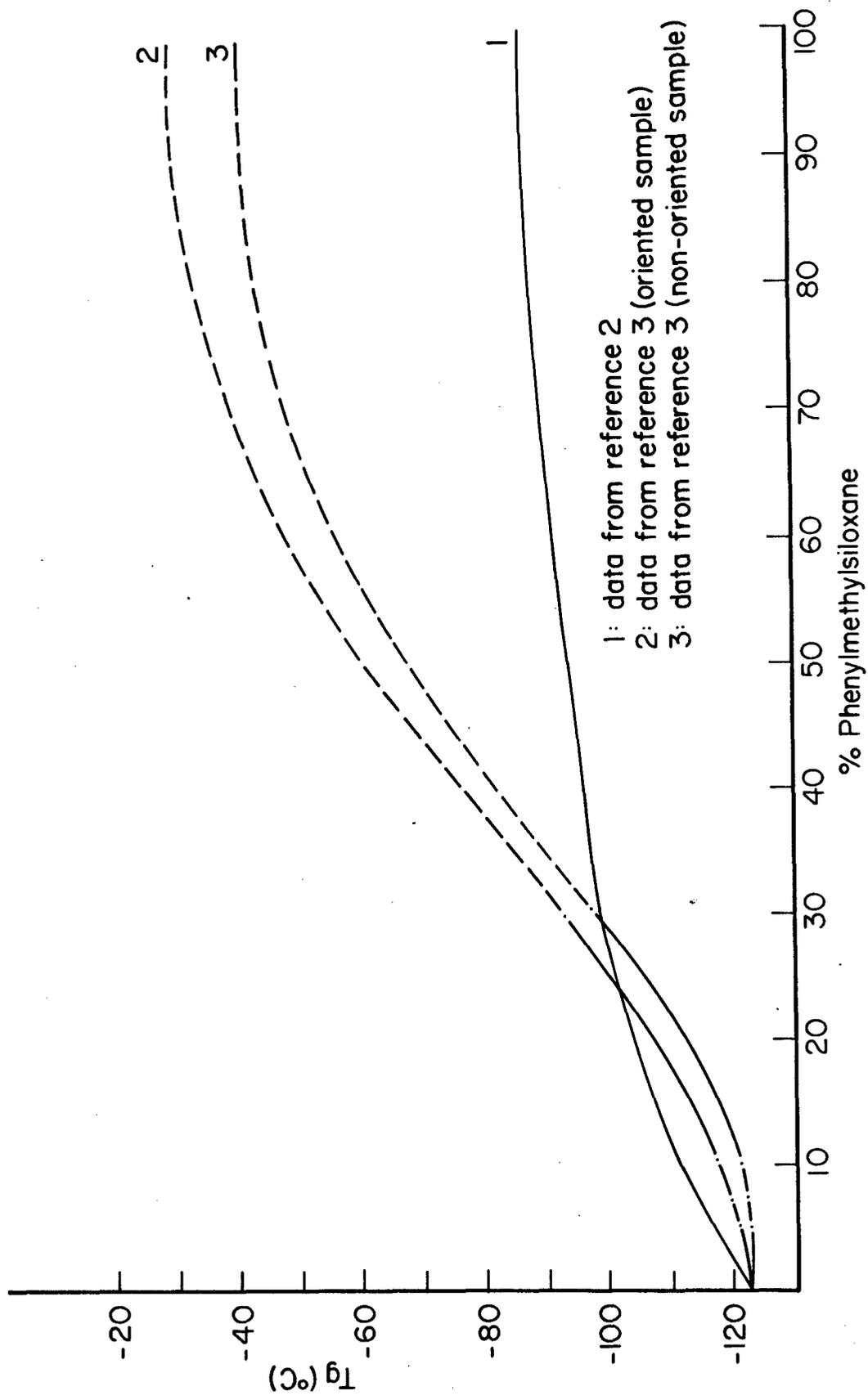


Figure 1: Glass Transition Temperatures of Polydimethyl-phenylmethyl Siloxanes

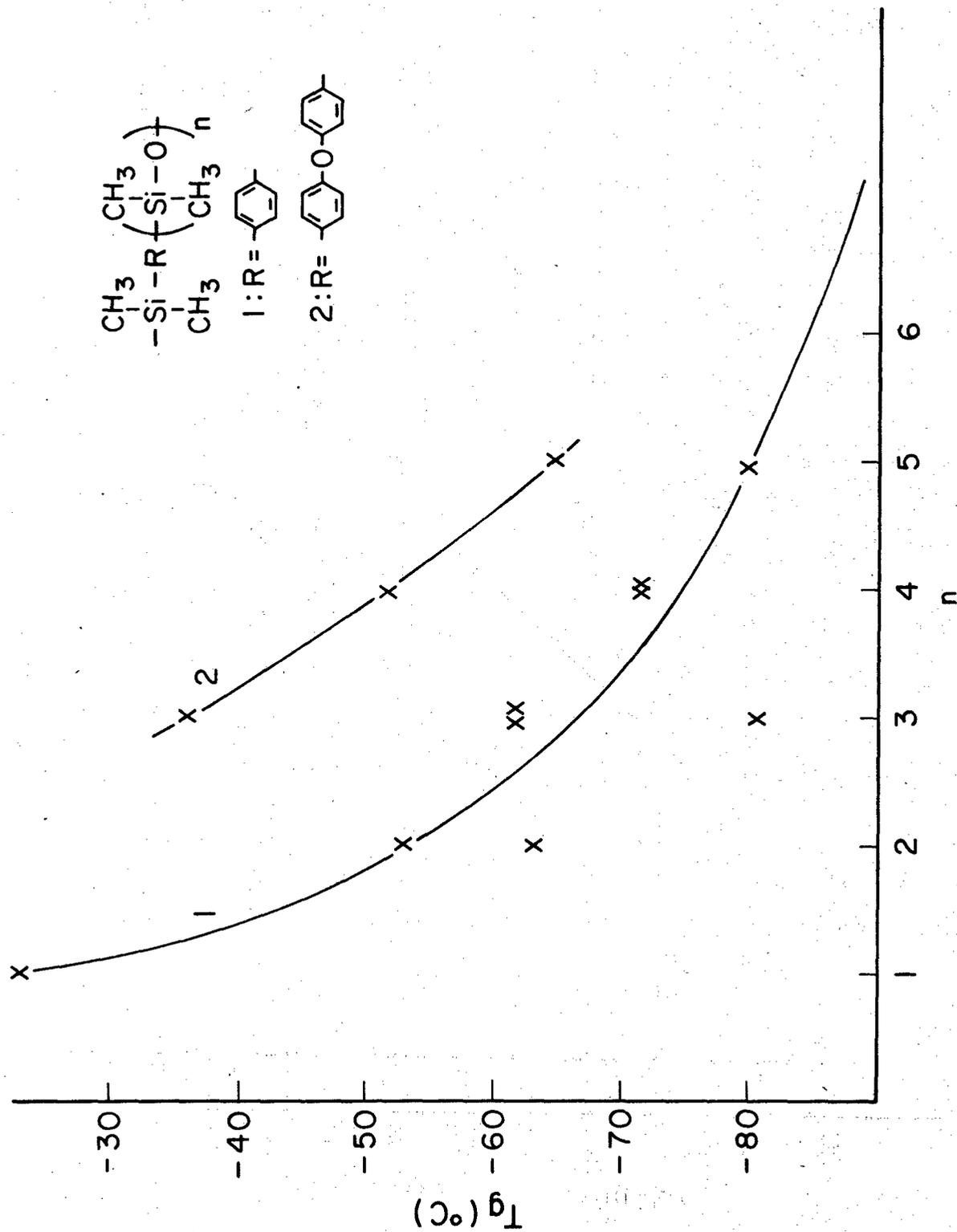


Figure 2: The Effect of the Number of Siloxane Units on the T<sub>g</sub> of Polyarylene Siloxanes

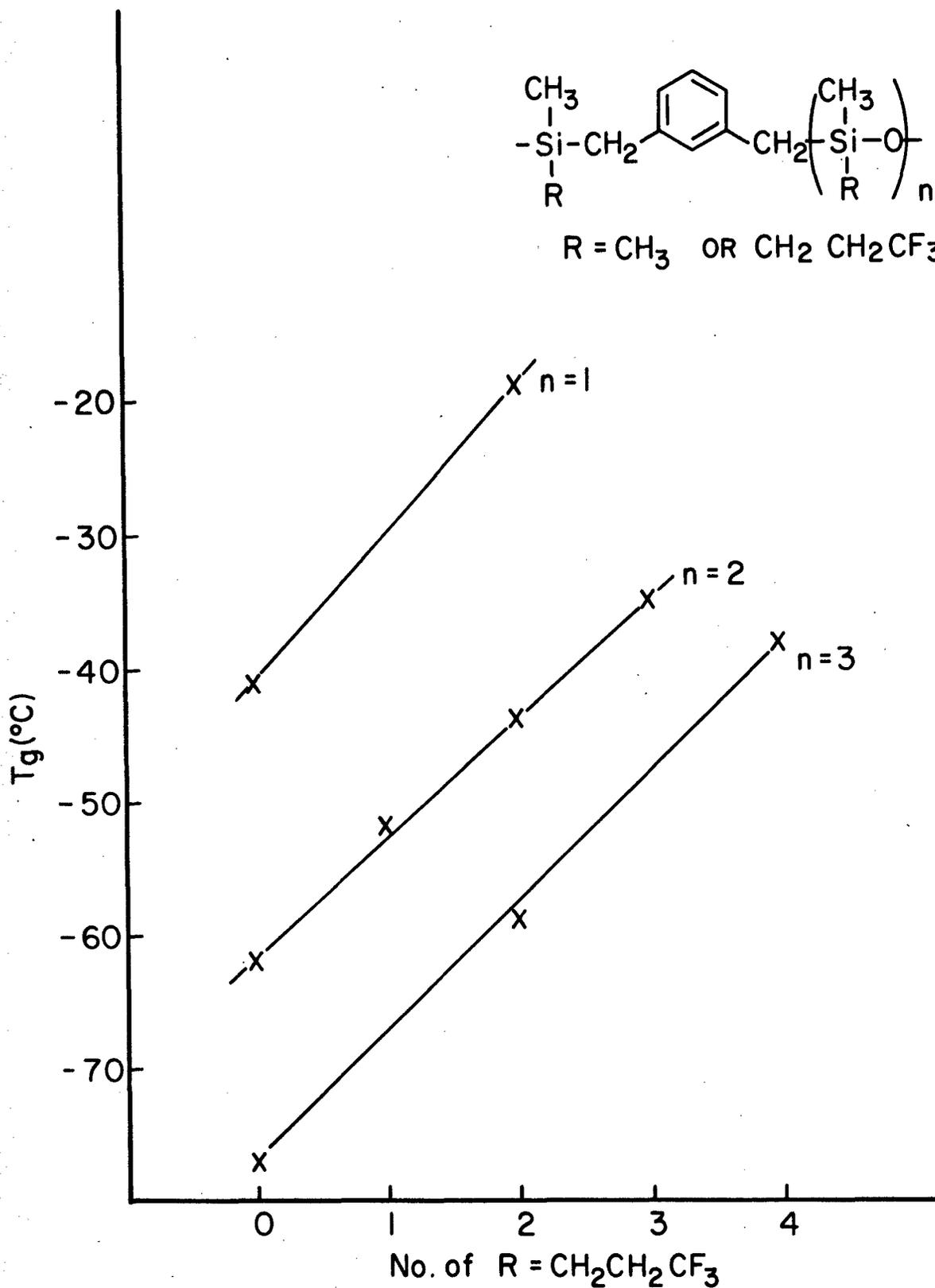
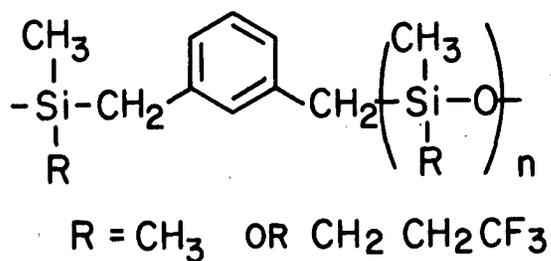


Figure 3: The Effect of Increasing Trifluoropropyl Content on the T<sub>g</sub> of Polyxylylene Siloxanes

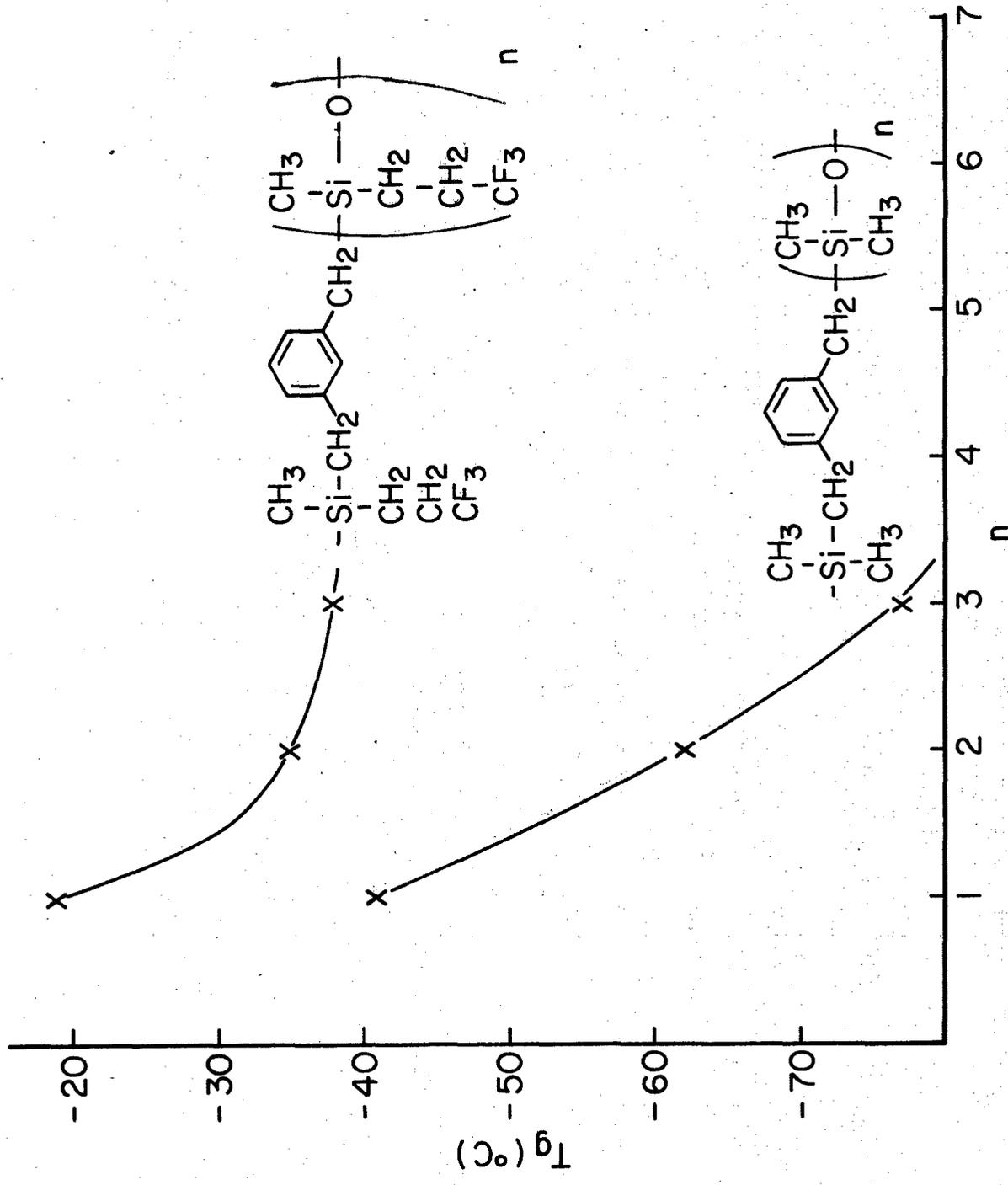


Figure 4: The Effect of the Number of Siloxane Units on the  $T_g$  of Polyxylylene Siloxanes

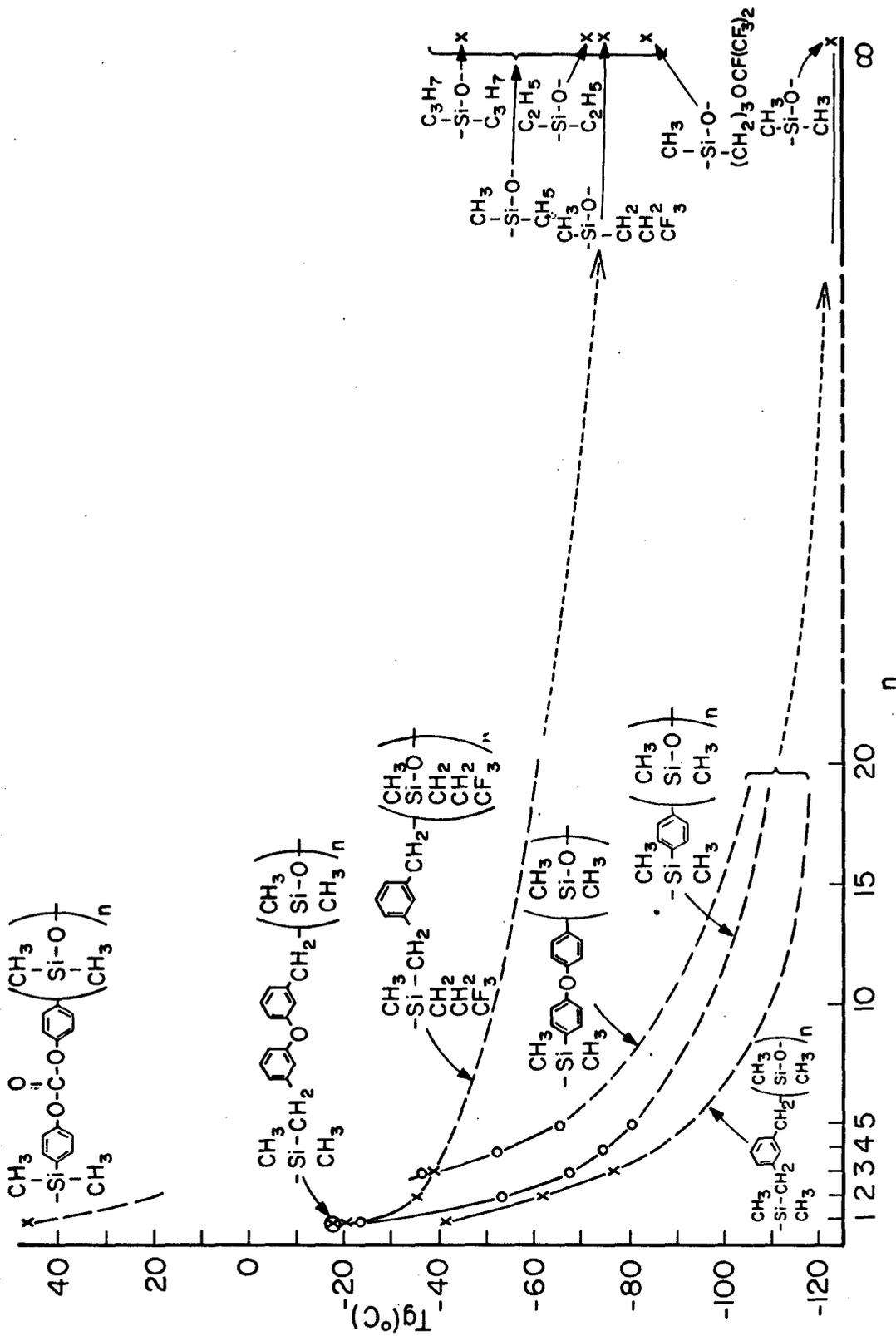


Figure 5: Actual and Projected Glass Transition Temperatures of Polysiloxanes, Polyarylene Siloxanes and Polyxylylene Siloxanes.