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AFML-TR-75-202

Part I

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**CORRELATIONS BETWEEN POLYMER
STRUCTURE AND GLASS TRANSITION
TEMPERATURE I. POLYSILOXANES,
POLYARYLENESILOXANES AND
POLYXYLYLENESILOXANES.**

*POLYMER BRANCH
NONMETALLIC MATERIALS DIVISION*

OCTOBER 1975

TECHNICAL REPORT AFML-TR-75-202 Part I

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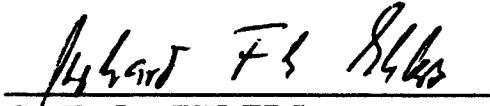
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This technical report has been reviewed and is approved for publication.


G. F. L. EHLERS
Project Monitor

FOR THE COMMANDER


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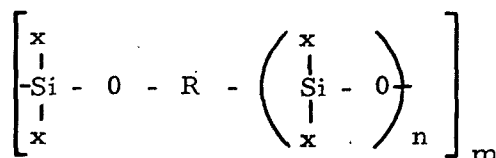
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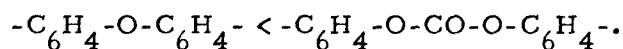
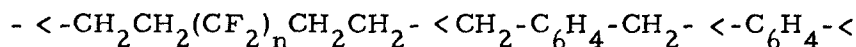
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20. ABSTRACT (continued)

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 T_g was observed by modifying R as shown below:



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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.

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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°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°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°C was found for the oriented (by unidirectional milling) and a T_g of -41°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°C for a copolymer of dimethylsiloxane with 25% phenylmethylsiloxane (Polmanteer's results are in the -100°C range), and Borisov and coworkers (reference 7) reported a T_g of -129°C for Polyphenylmethylsiloxane (Polmanteer's values are -30 and -86°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°C for polydiethylsiloxane. Recently, Beatty and Karasz (reference 10) clearly identified a discontinuity in C_r at 130°K (-143°C) as the T_g of polydiethylsiloxane and considered the transition found by Lee and coworkers at -72°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_g (°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	"
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Table I (continued)

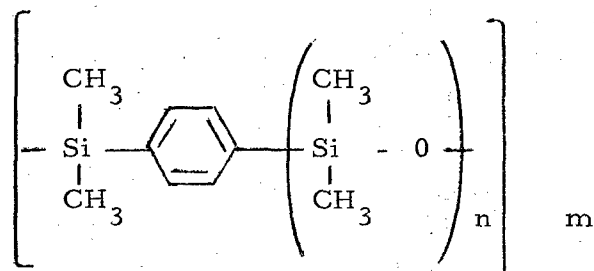
Structure	$T_g(^{\circ}\text{C})$	Reference
GEC Polymer (highly viscous liquid)		
$ \begin{array}{c} \text{CH}_3 \\ \\ -\text{Si}-0- \\ \\ \text{CH}_2\text{CH}_2\text{CH}_2\text{O}-\text{CF}_3 \\ \text{CF}_3 \end{array} $	-85	AFML data
GEC Polymer (tacky gum)		
$ \begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \\ \quad \quad \\ -\text{Si}-0-\text{Si}-0-\text{Si}-0- \\ \quad \quad \\ \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_2\text{CH}_2\text{CH}_2\text{O}-\text{CF}_3 \\ \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_g 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_g 's of about the same magnitude.

In view of the discrepancies observed for the T_g 's of polysiloxanes, very little can be said about structure - T_g 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

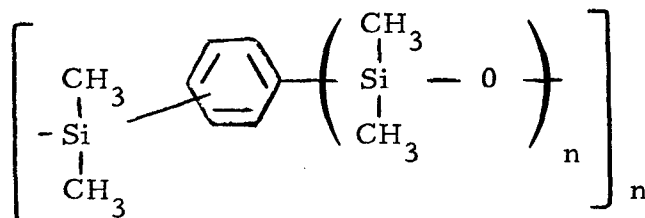


the glass transition temperature decreases with increasing n , as expected (references 11, 12, 13):

n	$T_g(^{\circ}\text{C})$
1	-23
2	-53
	-63
3	-62
	-62
	-81
4	-72
	-72
5	-80

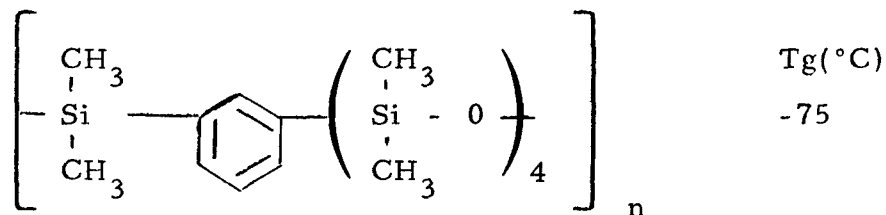
The scatter of these data, as also shown in Figure 2, is believed to be more the result of impure or differently crosslinked polymers than caused by differences in the method, or by the accuracy of the T_g determination. For $n = \infty$, the T_g 's are expected to approach the -123°C value of polydimethylsiloxane.

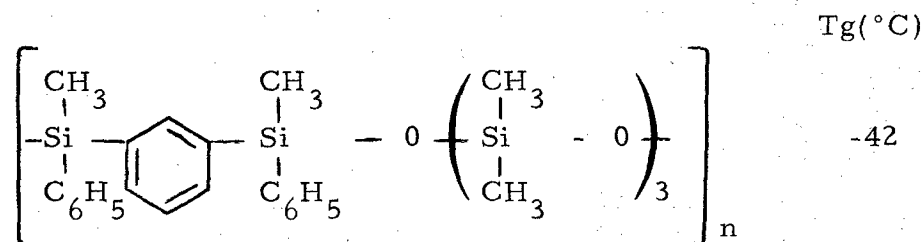
The replacement of *p*-phenylene by *m*-phenylene in the above structure seems to have no distinct effect (references 11, 12, 13):



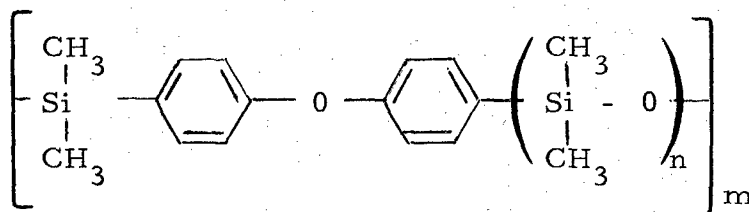
n	<u>meta or para</u>	<u>$T_g (^{\circ}\text{C})$</u>
2	p	-53; -63
2	m	-46
4	p	-72
4	m	-75

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





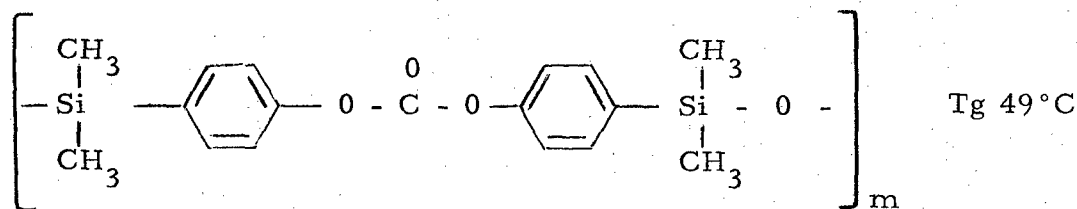
Very remarkable is the fact that the introduction of a diphenylether linkage for the phenylene linkage increases the Tg (reference 13; see also Figure 2):



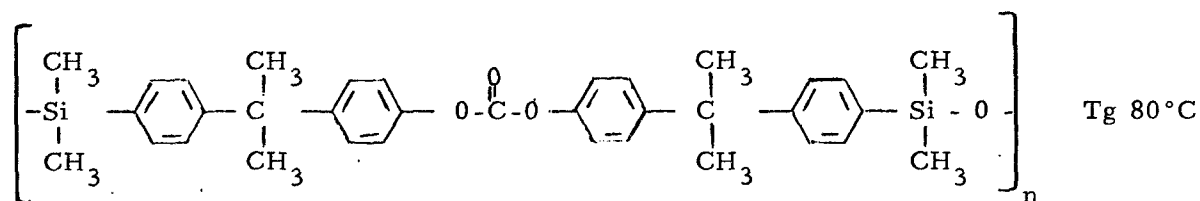
<u>n</u>	<u>Tg(°C)</u>
3	-37
4	-52
5	-65

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



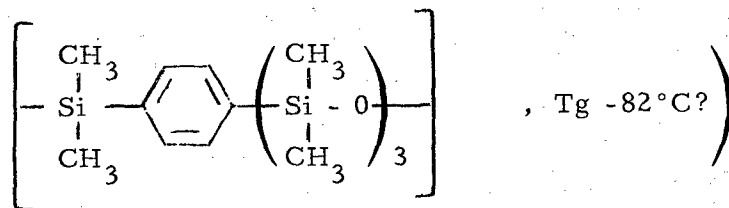
can be visualized as the structure of Lexan, with every second $-\text{O}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{O}-$ moiety replaced by $-\text{Si}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{O}}}-\text{Si}-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{O}}}-$. The replacement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

Tg by 70°C (Tg of Lexan: 150°C).

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

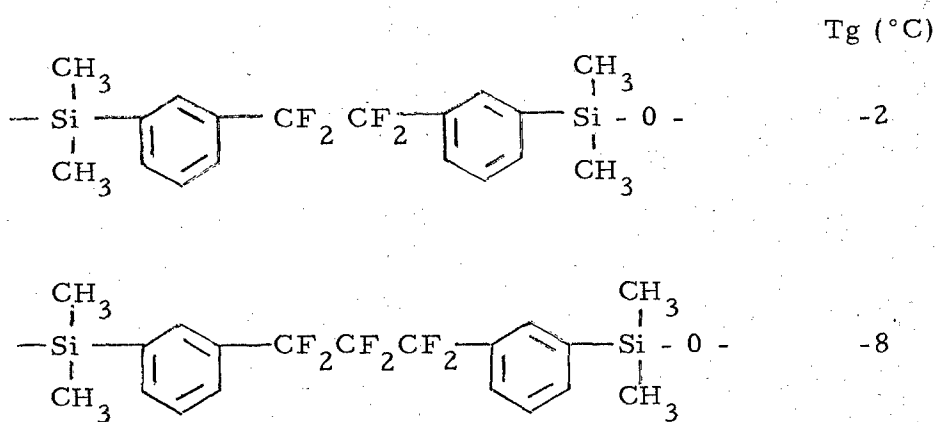
	Tg ($^\circ\text{C}$)
$\left[\begin{array}{c} \text{CH}_3 \\ \\ -\text{Si}- \\ \\ \text{CH}_3 \end{array} - \text{C}_6\text{H}_4 - \begin{array}{c} \text{CH}_3 \\ \\ -\text{Si}- \\ \\ \text{CH}_3 \end{array} - \text{O} \left(\begin{array}{c} \text{CH}_3 \\ \\ -\text{Si}- \\ \\ \text{Rf} \end{array} - \text{O} \right)_2 \right]$	-68
$\left[\begin{array}{c} \text{CH}_3 \\ \\ -\text{Si}- \\ \\ \text{Rf} \end{array} - \text{C}_6\text{H}_4 - \left(\begin{array}{c} \text{CH}_3 \\ \\ -\text{Si}- \\ \\ \text{Rf} \end{array} - \text{O} \right)_3 \right]$	-60
$\left[\begin{array}{c} \text{CH}_3 \\ \\ -\text{Si}- \\ \\ \text{Rf} \end{array} - \text{C}_6\text{H}_3(\text{CF}_3) - \left(\begin{array}{c} \text{CH}_3 \\ \\ -\text{Si}- \\ \\ \text{Rf} \end{array} - \text{O} \right)_3 \right]$	-32

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

(Table II continued)

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

(Table II continued)

Structure	Tg(°C)	Reference
$\left[\begin{array}{c} \text{CH}_3 \\ \\ \text{Si} - \text{C}_6\text{H}_4 - \text{C}(\text{CH}_3)_2 - \text{C}_6\text{H}_4 - \text{O} - \overset{\text{O}}{\text{C}} - \text{O} - \text{C}_6\text{H}_4 - \text{C}(\text{CH}_3)_2 \\ \\ \text{CH}_3 \end{array} \right]_n$ $\left[\begin{array}{c} \text{CH}_3 \\ \\ \text{C}_6\text{H}_4 - \text{Si} - \text{O} - \\ \\ \text{CH}_3 \end{array} \right]_n$	80	AFML data
$\left[\begin{array}{c} \text{CH}_3 \\ \\ \text{Si} - \text{C}_6\text{H}_4 - \text{Si}(\text{CH}_3)_2 - \text{O} - \left(\begin{array}{c} \text{CH}_3 \\ \\ \text{Si} - \text{O} \\ \\ \text{Rf} \end{array} \right)_2 \\ \\ \text{CH}_3 \end{array} \right] \text{Rf} = \text{CH}_2\text{CH}_2\text{CF}_3$	-68	"
$\left[\begin{array}{c} \text{CH}_3 \\ \\ \text{Si} - \text{C}_6\text{H}_4 - \left(\begin{array}{c} \text{CH}_3 \\ \\ \text{Si} - \text{O} \\ \\ \text{Rf} \end{array} \right)_3 \\ \\ \text{Rf} \end{array} \right] \text{Rf} = \text{CH}_2\text{CH}_2\text{CF}_3$	-60	"
$\left[\begin{array}{c} \text{CH}_3 \quad \text{CF}_3 \\ \quad \\ \text{Si} - \text{C}_6\text{H}_4 - \left(\begin{array}{c} \text{CH}_3 \\ \\ \text{Si} - \text{O} \\ \\ \text{Rf} \end{array} \right)_3 \\ \\ \text{Rf} \end{array} \right] \text{Rf} = \text{CH}_2\text{CH}_2\text{CF}_3$	-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_2 groups in the nonaromatic poly(fluoro)alkylene siloxane system does not result in a significant change of T_g , as Table II shows.

TABLE III

Glass Transition Temperatures of Poly(fluoro)alkylene siloxanes

<u>Structure</u>	<u>$T_g(^{\circ}\text{C})$</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{Si}-\text{O}- \\ \qquad \qquad \qquad \\ \text{CH}_2 \qquad \qquad \qquad \text{CH}_2 \\ \qquad \qquad \qquad \\ \text{CH}_2 \qquad \qquad \qquad \text{CH}_2 \\ \qquad \qquad \qquad \\ \text{CF}_3 \qquad \qquad \qquad \text{CF}_3 \end{array} $		
$n:$		
*) 2	-26	AFML
**) 8	-24	"

*) 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

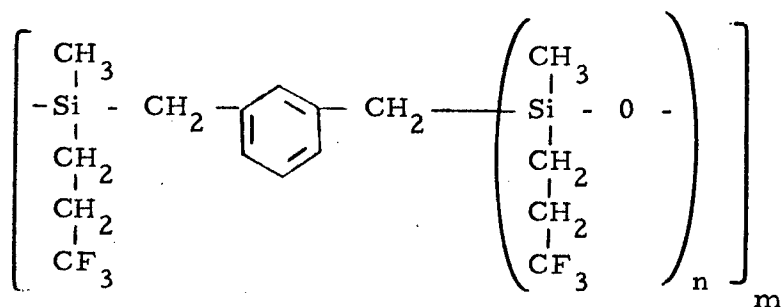
Glass Transition Temperatures of Polyxilylene Siloxanes

<u>Structure</u>			<u>Tg(°C)</u>
$\left[\begin{array}{c} \text{CH}_3 \\ \\ -\text{Si}- \\ \\ \text{CH}_3 \end{array} \text{CH}_2 - \text{C}_6\text{H}_4 - \text{O} - \text{C}_6\text{H}_4 - \text{CH}_2 - \begin{array}{c} \text{CH}_3 \\ \\ -\text{Si}- \\ \\ \text{CH}_3 \end{array} - \text{O} - \right]$			-18
$\left[\begin{array}{c} \text{CH}_3 \\ \\ -\text{Si}- \\ \\ \text{R}_1 \end{array} \text{CH}_2 - \text{C}_6\text{H}_4 - \text{CH}_2 - \begin{array}{c} \text{CH}_3 \\ \\ -\text{Si}- \\ \\ \text{R}_2 \end{array} - \text{O} - \right]$			
R ₁	R ₂		
CH ₃	CH ₃		-41
CF ₃ CH ₂ CH ₂	CF ₃ CH ₂ CH ₂		-19
$\left[\begin{array}{c} \text{CH}_3 \\ \\ -\text{Si}- \\ \\ \text{R}_1 \end{array} \text{CH}_2 - \text{C}_6\text{H}_4 - \text{CH}_2 - \begin{array}{c} \text{CH}_3 \\ \\ -\text{Si}- \\ \\ \text{R}_2 \end{array} - \text{O} - \begin{array}{c} \text{CH}_3 \\ \\ -\text{Si}- \\ \\ \text{R}_3 \end{array} - \text{O} - \right]_n$			
R ₁	R ₂	R ₃	
CH ₃	CH ₃	CH ₃	
CH ₃	CH ₃	CF ₃ CH ₂ CH ₂	-62
CF ₃ CH ₂ CH ₂	CF ₃ CH ₂ CH ₂	CH ₃	-52
CF ₃ CH ₂ CH ₂	CF ₃ CH ₂ CH ₂	CF ₃ CH ₂ CH ₂	-44
CF ₃ CH ₂ CH ₂	CF ₃ CH ₂ CH ₂	CF ₃ CH ₂ CH ₂ (97%)	-35
		+ CH ₂ = CH (3%)	-35.5

(Table IV continued)

Structure				Tg(°C)
$ \begin{array}{ccccccc} \text{CH}_3 & & & & \text{CH}_3 & & \text{CH}_3 \\ & & & & & & \\ -\text{Si}- & \text{CH}_2- & \text{C}_6\text{H}_4 & -\text{CH}_2- & -\text{Si}- & \text{O}- & -\text{Si}- & \text{O}- & -\text{Si}- & \text{O}- \\ & & & & & & & & \\ \text{R}_1 & & & & \text{R}_2 & & \text{R}_3 & & \text{R}_4 \end{array} $				
R ₁	R ₂	R ₃	R ₄	
CH ₃	CH ₃	CH ₃	CH ₃	-77
CH ₃	CH ₃	CF ₃ CH ₂ CH ₂	CF ₃ CH ₂ CH ₂	-59
CF ₃ CH ₂ CH ₂	CF ₃ CH ₂ CH ₂	CF ₃ CH ₂ CH ₂	CF ₃ CH ₂ CH ₂	-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.

n	$T_g(^{\circ}C)$	$T_g(^{\circ}C)$
1	-23	-41
2	-53 ^{x)}	-62
3	-67 ^{x)}	-77

x) from plot 1 in Figure 2

The comparison shows the flexibilizing effect of the CH_2 -group to a varying extent.

SECTION III

EXPERIMENTAL

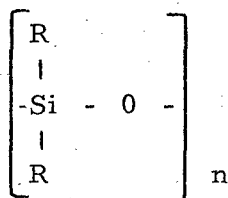
The glass transition temperatures of the polymers, as far as they had been determined in the PolymerBranch were obtained almost exclusively by differential scanning calorimetry (DSC), using the duPont 990 Thermal Analyzer. Heating rates of $\Delta T = 20^{\circ}\text{C}/\text{min}$ were applied, and 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

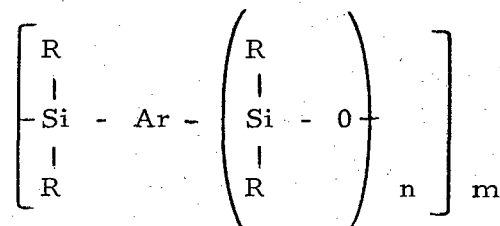


Widely scattered glass transition temperatures of dimethyl-methylphenyl siloxane copolymers suggest that the polymers investigated by some authors were impure or ill defined.

Introduction of larger alkyl substituents or phenyl for methyl in dimethyl-siloxane 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 CF₃ 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 $\text{--O--}\overset{\text{O}}{\text{C}}\text{--O--}$ moiety by itself is relatively rigid compared to the siloxane unit: replacement of a

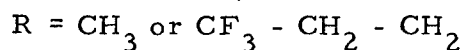
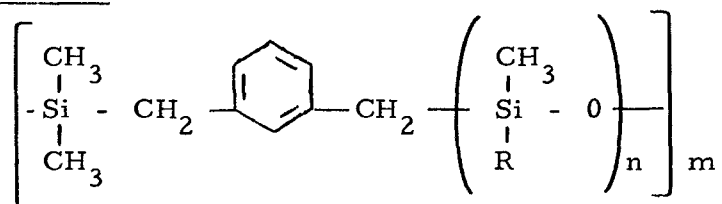
$\begin{array}{c} \text{CH}_3 \\ | \\ -\text{Si}- \\ | \\ \text{CH}_3 \end{array} - \text{O} - \begin{array}{c} \text{CH}_3 \\ | \\ -\text{Si}- \\ | \\ \text{CH}_3 \end{array}$ by a $-\text{O}-\overset{\text{O}}{\text{C}}-\text{O}-$ group increased the Tg by 70°C.

As far as the silicon substituents are concerned, the replacement of a methyl group by phenyl increases Tg considerably, but the introduction of CF₃-CH₂-CH₂ linkages seems to have relatively little effect (~ 4 to 7°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 CF₃CH₂CH₂ increase Tg by about 9°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 Tg, initially by 15-20°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 Tg by 10 to 20°C.

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

SECTION V

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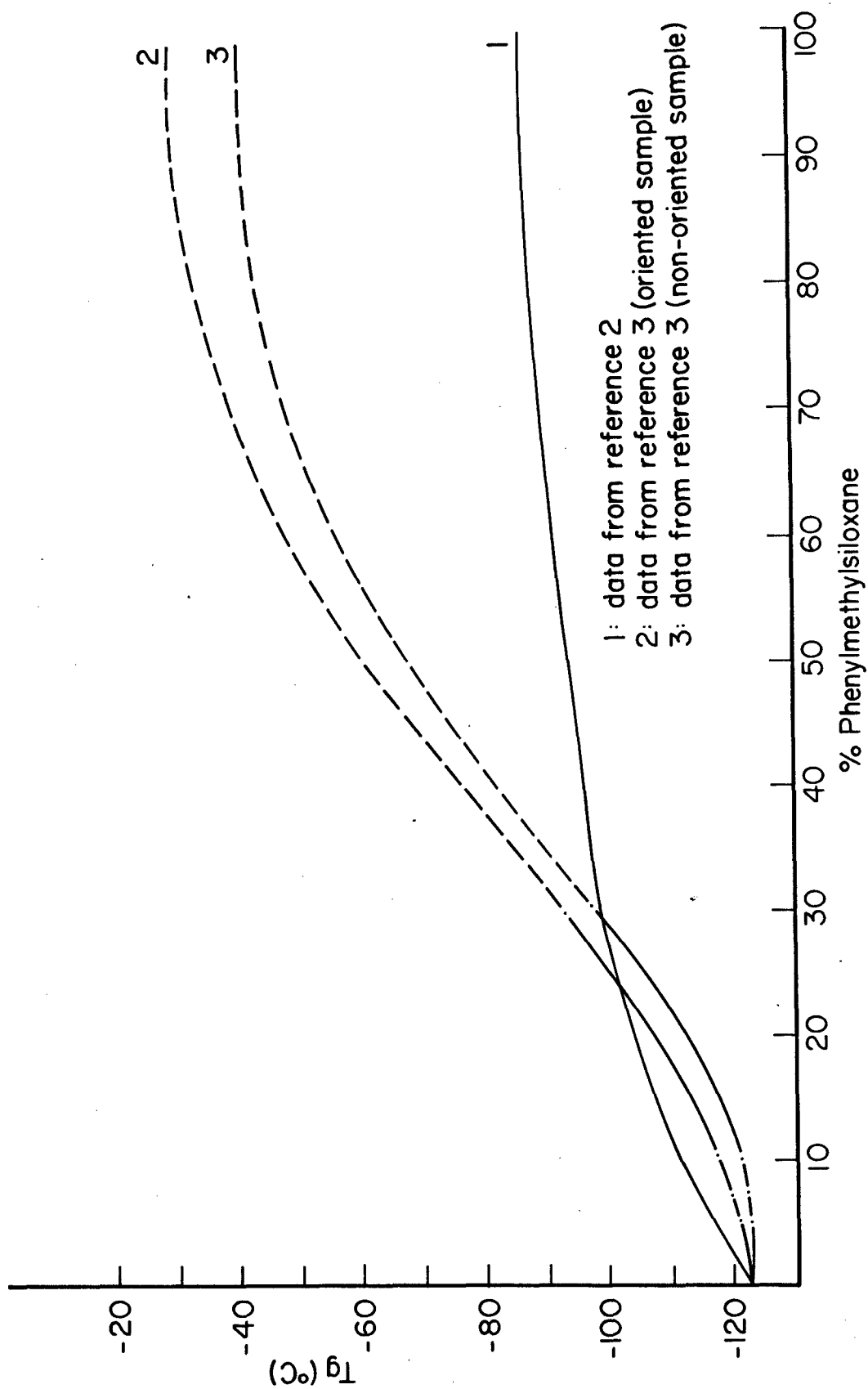


Figure 1: Glass Transition Temperatures of Polydimethyl-phenylmethyl Siloxanes

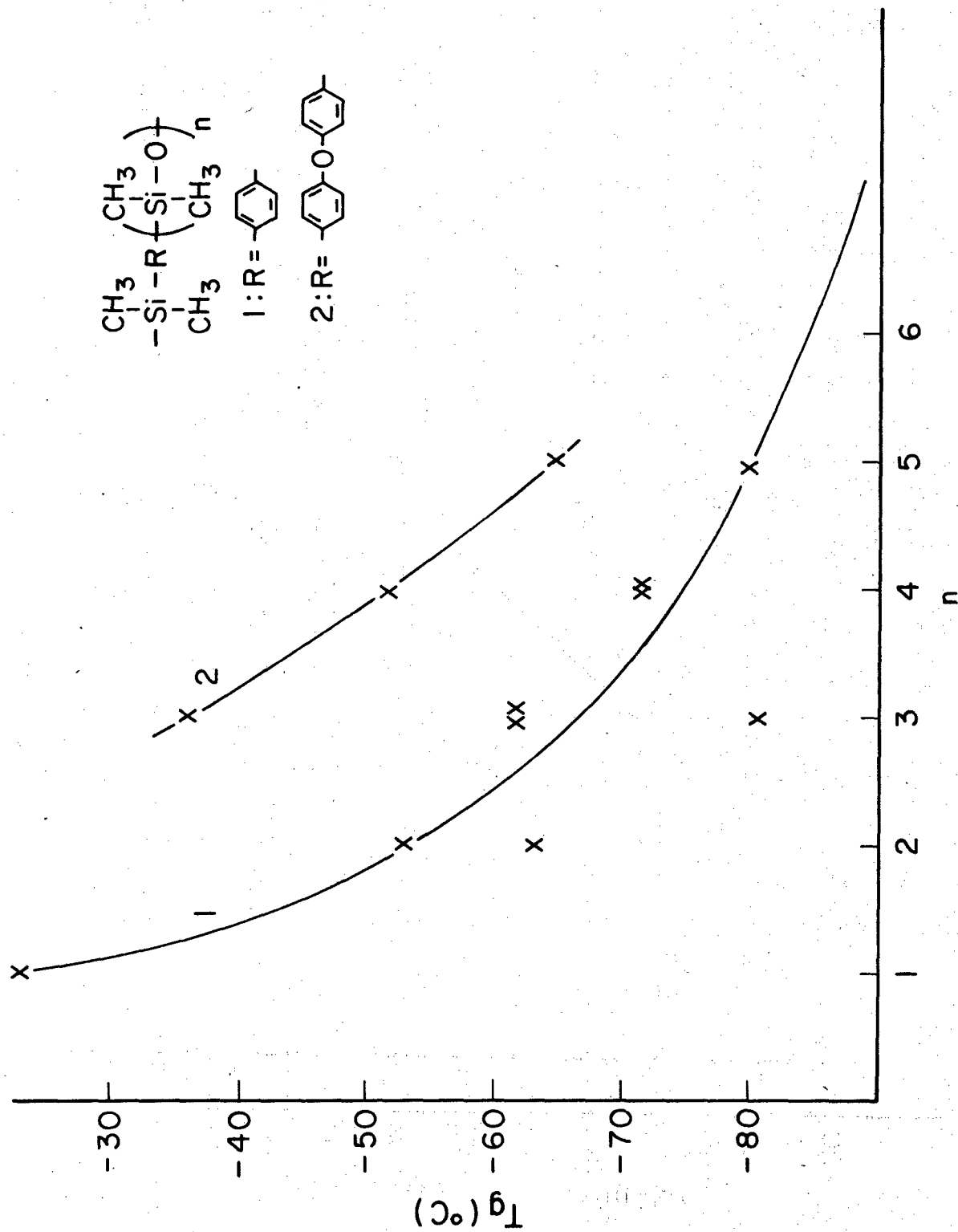


Figure 2: The Effect of the Number of Siloxane Units on the T_g of Polyarylene Siloxanes

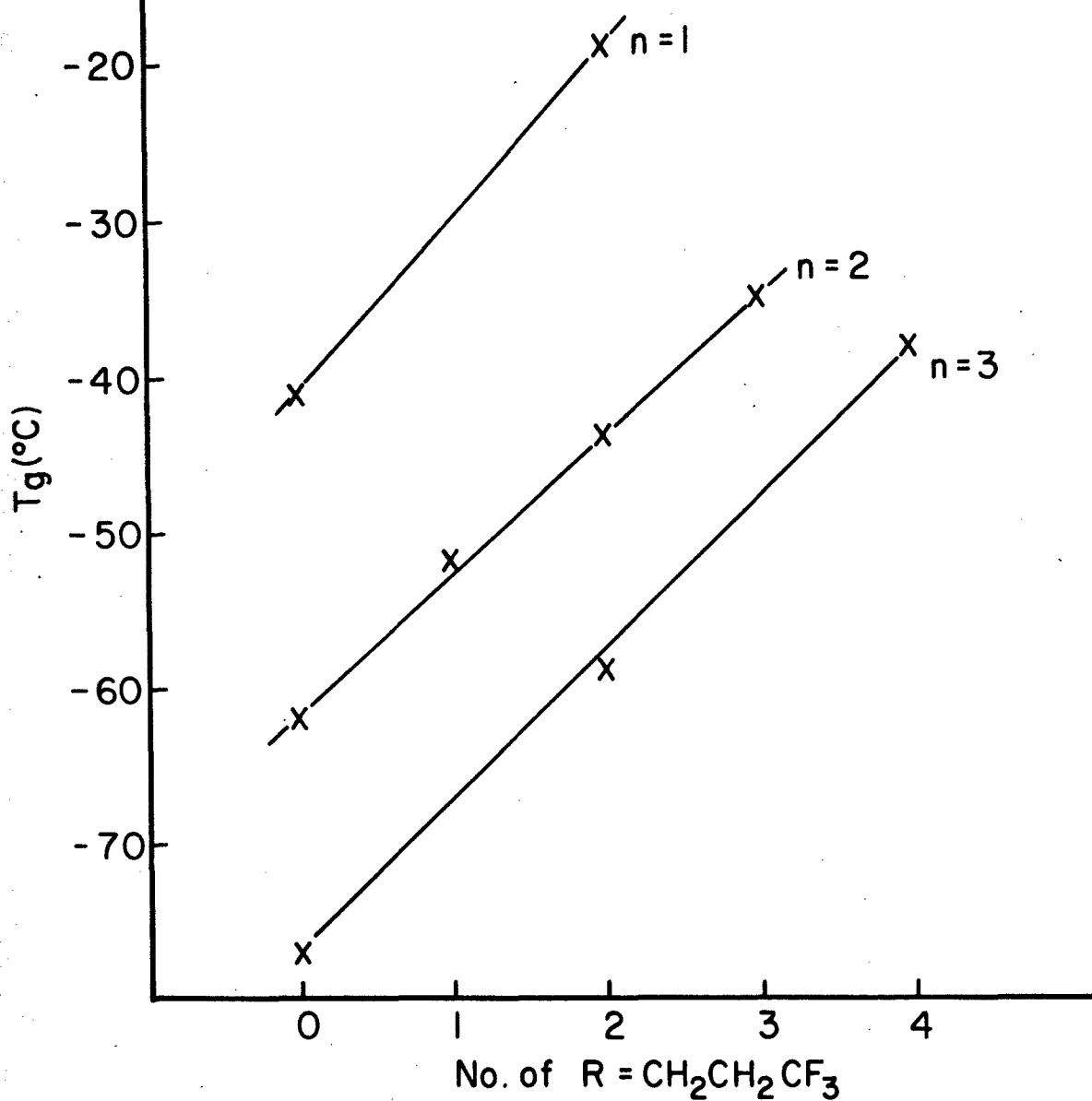
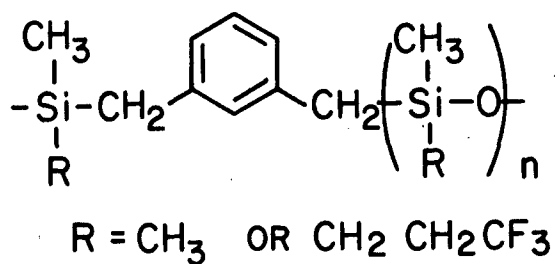


Figure 3: The Effect of Increasing Trifluoropropyl Content on the T_g of Polyxylylene Siloxanes

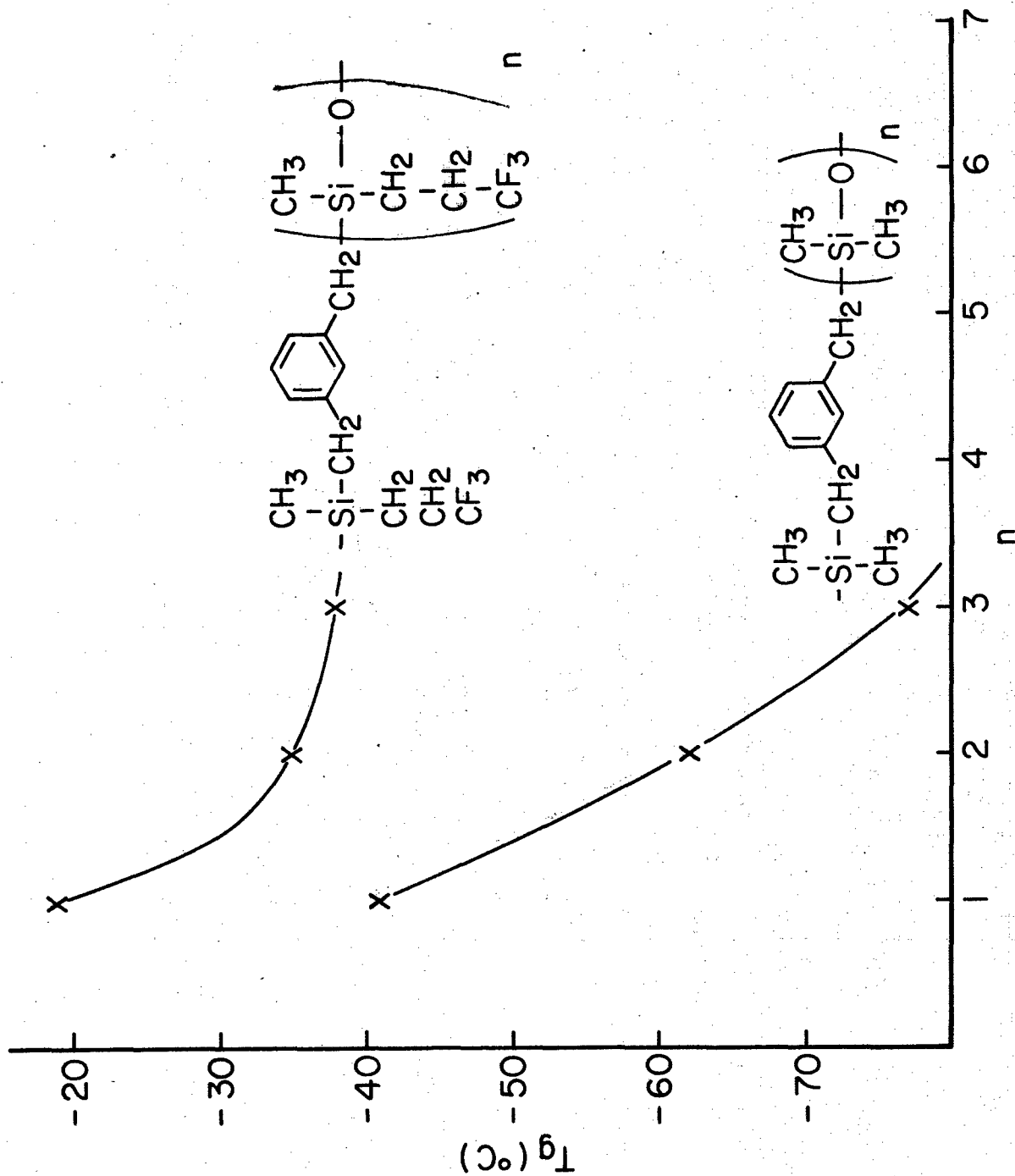


Figure 4: The Effect of the Number of Siloxane Units on the T_g of Polyxylylene Siloxanes

