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Exactly Alternating Silarylene–Siloxane Polymers. 9. Relationships between Polymer Structure and Glass Transition Temperature

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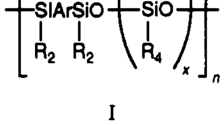
ABSTRACT: Glass transition temperatures, T_g, of 49 different silarylene–siloxane polymers, of which 33 were exactly alternating, were examined and correlated with the polymer structures. The relationships established were the following: (1) the T_gs of silarylene–siloxane polymers decreased with an increase in the content of the siloxane main-chain groups and approached those typical for the closely related alkyl-substituted polysiloxanes when the ratio of the siloxane to the silarylene–siloxane groups in the repeating units was higher than 4; (2) in the silarylene–siloxane polymer series in which this ratio was varied from zero to 4, the T_g correlated well with the values predicted by the Gordon–Taylor copolymer equation; (3) the stiffening effect of seven different aromatic main-chain groups was established, and the order of their effectiveness in that respect is presented; (4) as expected from the free volume theory of glass transition, bulky side-chain substituents, such as phenyl, cyanoalkyl, or fluoroalkyl groups, in the exactly alternating silarylene–siloxane polymer series, increased the T_g, and this increase was proportional to the relative content of these bulky groups; (5) an interesting effect of the unsaturated side groups, such as vinyl and allyl, on decreasing the exactly alternating silarylene–siloxane polymers T_g values was observed, and the magnitude of this effect was proportional to the relative content of the side units, but it was also found to be sensitive to the nature of other side groups and to the aromatic main-chain units present in the polymer structure.

Introduction

Many modern technologies, particularly in some of the most rapidly advancing industries, such as the aerospace industry, the fabrication of computer chips, and the development of membrane and chromatographic separation processes, have increasingly demanded new high-temperature resistant elastomers which would be able to exhibit and retain useful mechanical, electrical, and/or specific surface properties over as wide range of operating temperatures as possible, but at least from about -30 °C to about 350–400 °C or above. In order to fulfill such requirements, considerable research has been directed to the search for new polymers which would be able to satisfy these demands, and among those investigated, the silarylene–siloxane polymers of the generalized structure I have emerged as the most promising potential candidates to satisfy the purpose.[1]



$$\left[\underset{R_2}{\overset{R_1}{\mathrm{Si}}}\mathrm{Ar}\underset{R_2}{\overset{R_1}{\mathrm{Si}}}\mathrm{O} \left(\underset{R_4}{\overset{R_3}{\mathrm{Si}}}\mathrm{O} \right)_x \right]_n$$

I

Initial interest in these polymers was based on expectations that because of their close structural relationship to the well-known polysiloxanes, $-(\mathrm{SiO})_n-$, the silarylene–siloxane polymers, I, which may be viewed as modified polysiloxanes in which a fraction of the siloxane oxygens is regularly replaced by organic aromatic groups, so that each repeating unit contains one silarylene–siloxane, -SiArSiO-, and a specified number, x, of the siloxane, -SiO-, groups, might exhibit favorable combinations of properties by retaining some desirable characteristics of the corresponding polysiloxanes, while at the same time gaining improvements in other properties of the "parent" polymers.

Thus, because the polysiloxanes are almost unique among other polymers for their highly pronounced macromolecular chain flexibility, which allows them to exhibit pronounced elasticity at unusually low temperatures, such as -100 °C and lower, polymers of type I could also be expected to show unusually low temperature flexibility, although some stiffening of the silarylene–siloxane main-chain backbones, relative to the flexibility of the pure polysiloxanes, would, of course, be expected to occur with large, bulky, and rigid aromatic units between the $-(\mathrm{SiO})_x-$ segments. Nevertheless, some members of the silarylene–siloxane polymer family should retain at least some degree of this highly desirable property.

On the other hand, it could clearly be expected that the presence of large and bulky, thermally stable aromatic groups in the silarylene–siloxane polymer main-chain backbones should successfully contribute to increasing their high-temperature stability with respect to the corresponding polysiloxanes, because the size and rigidity of the aromatic groups should be able to prevent the formation of silarylene–siloxane ring structures and thereby also prevent the polysiloxane cyclization depolymerization reactions.[2]

Indeed, the results obtained in our past studies have clearly shown these initial expectations to be correct, as it has been found that many silarylene–siloxane polymers exhibit high enough elasticity well below -30 °C and that at the same time most of them do not undergo substantial thermal degradation until about 400 °C or higher.[1] Furthermore, it has also been shown that, as expected, the limiting temperatures within which these polymers can be used depend on their particular structural features and that three main factors which determine their properties and thermal stability are (1) the relative contents of the silarylene–siloxane and the siloxane groups, x in structure

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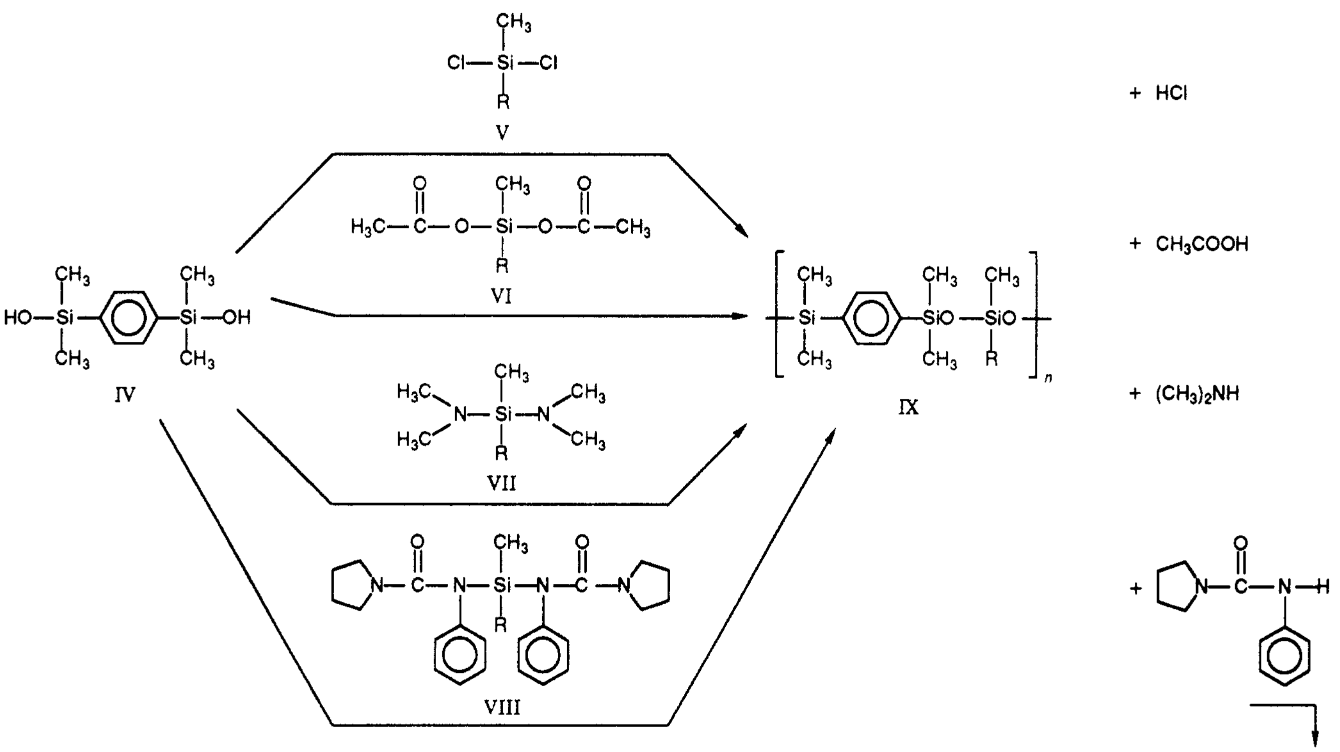
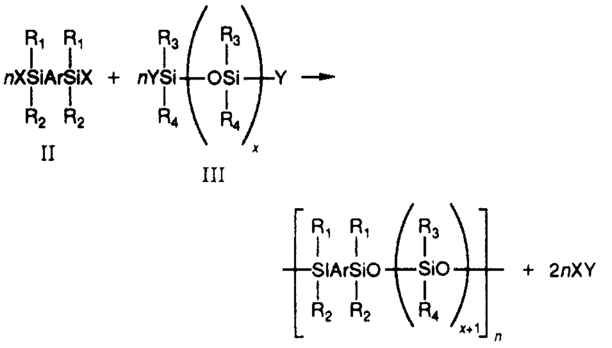
Scheme I



I, (2) the nature of the aromatic groups, Ar in structure I, and (3) the type and the amount of the side groups, R_i in structure I.

Various synthetic approaches and procedures have been tried and developed for preparation of these polymers.[1] These are all based on step-growth condensation polymerization reactions in which various disilarylene monomers II, such as dichlorosilarylenes (X = Cl), diaminosilarylenes (X = NH_2), dimethoxysilarylenes (X = OCH_3), or arylene disilanols (X = OH), are reacted with suitable difunctional, reactive silanes or siloxanes, III, as shown by the generalized eq 1.



$$n\,\mathrm{X}\underset{R_2}{\overset{R_1}{\mathrm{Si}}}\mathrm{Ar}\underset{R_2}{\overset{R_1}{\mathrm{Si}}}\mathrm{X} + n\,\mathrm{Y}\underset{R_4}{\overset{R_3}{\mathrm{Si}}}\left(\mathrm{O}\underset{R_4}{\overset{R_3}{\mathrm{Si}}}\right)_x\mathrm{Y} \longrightarrow \left[\underset{R_2}{\overset{R_1}{\mathrm{Si}}}\mathrm{Ar}\underset{R_2}{\overset{R_1}{\mathrm{Si}}}\mathrm{O}\left(\underset{R_4}{\overset{R_3}{\mathrm{Si}}}\mathrm{O}\right)_{x+1}\right]_n + 2n\mathrm{XY} \qquad (1)$$

II III

Of the disilarylene monomers examined, the arylene disilanols (IV) were the easiest to prepare in good yields and high enough purities, as well as to handle and use. The best synthetic procedures were found to be those based on the reactions of these monomers with different dichloro-[3,4] (Y = Cl; V), diacetoxy-[5] (Y = $O(O)CCH_3$; VI), diamino-[6-8] (Y = NH_2; VII), or diureidosilanes[9-11] (Y = $N(C_6H_5)C(O)N(CH_2)_4$; VIII) as shown in Scheme I.

Most of these reactions can be routinely performed to yield high molecular weight ($\bar{M}_w$ above about 100 000) polymers,[4,7-11] and the versatility of these reactions in preparing different polymers is only limited by the availability of arylene disilanols (IV) and difunctional silane or siloxane monomers (III). Consequently, a wide variety of different silarylene–siloxane polymers has been prepared, and these were excellent candidates for studying the effects of structural changes in the main-chain backbones and side groups on the physical properties of polymers which possess inherently flexible chains.

In the previous reports of this series we described the preparation and some structure–property relationships observed for the exactly alternating members of this silarylene–siloxane polymer family, for which, as shown in structure IX of Scheme I, the value of x in structure I is equal to unity.[4,7-11] In these studies particular attention was placed on the preparation of these polymers[4,9-11] and on the properties which were relevant for their behavior both at elevated temperatures[12,13] and under stress.[14] In this report, we describe effects of the silarylene–siloxane polymer structure on their low-temperature properties, specifically on the glass transition temperature, T_g, and in order to present a coherent picture of these relationships, we compare these properties with the corresponding relationships which have been established for the parent polysiloxanes.

Experimental Section

Polymers. The silarylene–siloxane polymers examined in this work are described in Table I. All of these polymers were prepared by step-growth polymerization reactions in which either 1,4-bis(dimethylhydroxysilyl)benzene (IV with Ar being p-C_6H_4) or 1,4-bis(dimethylhydroxysilyl)phenyl ether (IV with Ar being p-$C_6H_4OC_6H_4$) was reacted with selected bisureido, or dichlorosilanes, as specified in that table, according to the procedures described earlier.[4,10,11] Of the monomers used, the 1,4-bis(dimethylhydroxysilyl)benzene was purchased from Petrarch Systems Silanes and Silicones, while the dichlorosilanes were purchased from the Aldrich Chemical Co. The disilanol was used in the polymerization reactions without further purification, while the silanes were distilled prior to use as described previously.[4] The 1,4-bis(dimethylhydroxysilyl)diphenyl ether and the diureidosilane monomers were prepared as described previously.[10,15,16] The structures of the polymers obtained were verified by elemental analyses, ^{1}H and ^{13}C NMR spectroscopies, and infrared spectrometry, and the molecular weights and molecular weight distributions were determined by GPC.[4,10]

Glass Transition Temperatures. The glass transition temperatures of the polymers were determined using a Perkin-Elmer

Table I
Preparation and Molecular Weights of Exactly Alternating Silarylene–Siloxane Polymers, IX[a]

polym no.	aromatic group	R_3	R_4	silane monomers	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
1	p-C_6H_4	CH_3	CH_3	u	132 000	1.86
2		CH_3	$(CH_2)_2CH_3$	u	142 000	1.66
3		CH_3	$(CH_2)_2CN$	u	342 000	1.97
4		CH_3	$(CH_2)_3CN$	u	292 000	2.11
5		CH_3	$(CH_2)_2CF_3$	u	120 000	2.21
6		CH_3	$(CH_2)_2(CF_2)_5CF_3$	c	55 000	1.98
7		CH_3	$0.99\ CH_3 + 0.01\ CH{=}CH_2$	c	27 000	3.10
8		CH_3	$0.97\ CH_3 + 0.03\ CH{=}CH_2$	c	28 000	2.15
9		CH_3	$0.95\ CH_3 + 0.05\ CH{=}CH_2$	u	119 000	1.78
10		CH_3	$0.925\ CH_3 + 0.075\ CH{=}CH_2$	u	125 500	1.81
11		CH_3	$0.9\ CH_3 + 0.1\ CH{=}CH_2$	u	215 000	1.95
12		CH_3	$CH{=}CH_2$	u	199 000	1.92
13		CH_3	$CH_2CH{=}CH_2$	u	68 300	3.18
14		CH_3	$0.66\ CH_3 + 0.33\ C_6H_5 + 0.01\ CH{=}CH_2$	c	33 000	2.20
15		CH_3	$0.33\ CH_3 + 0.66\ C_6H_5 + 0.01\ CH{=}CH_2$	c	71 000	2.96
16		CH_3	$0.99\ C_6H_5 + 0.01\ CH{=}CH_2$	c	51 000	3.92
17		CH_3	$0.97\ C_6H_5 + 0.03\ CH{=}CH_2$	c	123 000	3.97
18		CH_3	$0.9\ H + 0.1\ CH{=}CH_2$	u	875 000	1.95
19		CH_3	$0.85\ H + 0.15\ CH{=}CH_2$	u	650 000	1.87
20		CH_3	$0.85\ (CH_2)_2(CF_2)_5CF_3 + 0.15\ CH{=}CH_2$	c	49 000	2.05
21		C_6H_5	$CH{=}CH_2$	u	86 000	4.35
22		C_6H_5	$CH_2CH{=}CH_2$	u	120 000	1.80
23		$(CH_2)_3CN$	$(CH_2)_3CN$	u	77 700	1.99
24		H	$(CH_2)_2CF_3$	c	43 000	1.75
25		$0.85\ H + 0.15\ CH_3$	$0.85\ (CH_2)_2CF_3 + 0.15\ CH{=}CH_2$	u	37 000	2.11
26	p,p'-$C_6H_4OC_6H_4$	CH_3	CH_3	u	214 000	2.13
27		CH_3	$0.95\ CH_3 + 0.05\ CH{=}CH_2$	u	74 000	1.86
28		CH_3	$0.925\ CH_3 + 0.075\ CH{=}CH_2$	u	184 000	1.78
29		CH_3	$CH{=}CH_2$	u	232 000	1.63
30	$0.5\ p$-$C_6H_4 + 0.5\ p,p'$-$C_6H_4OC_6H_4$	CH_3	CH_3	u	163 000	1.86
31		CH_3	$0.95\ CH_3 + 0.05\ CH{=}CH_2$	u	239 500	1.89
32		CH_3	$0.925\ CH_3 + 0.075\ CH{=}CH_2$	u	164 500	1.78
33		CH_3	$CH{=}CH_2$	u	218 500	1.70

[a] u = ureidosilane, VIII; c = chlorosilane, V. See Scheme I.

DSC-2 analyzer at heating rates of 5 and 20 °C/min. The temperature range examined was from −100 to +25 °C in all cases, and the temperature corresponding to half of the distance between the onset and the end of the temperature interval in which the changing base-line slope was observed in each particular thermogram was taken for the T_g value. Liquid nitrogen was used as the cooling fluid, and all measurements were performed in an inert, helium atmosphere with the samples which ranged from 10 to 25 mg in weight.

Results and Discussion

Elastomers are polymers which can rapidly recover their shapes after removal of relatively large strains (50% or more) and whose entropically derived equilibrium moduli increase with temperature. In order to comply to this description, these materials must be able to exhibit, at the molecular level and at the application temperatures, pronounced freedom of segmental motions through which they can successfully relax the applied stresses and recover their shapes.

The glass transition temperature of a polymer, T_g, can be viewed as a measure of the reorientational freedom of motion of the macromolecular chain segments, so that segmental motions are possible only above that temperature and are "frozen in" below it. Consequently, elastomeric behavior can appear only above T_g, and low T_g values are associated with flexible polymer chains and high T_g values with the rigid chain polymers.

A promising polymer candidate for a potentially useful elastomer is normally a highly viscous, amorphous fluid, which must have its glass transition temperature, T_g, somewhat below the lowest intended application temperature, but just how much below remains a question of experience rather than of some well-defined theoretical criterion. Nevertheless, as an approximation the T_g should be at least about 10–20 °C below the lowest intended use temperature, and for normal applications polymers with glass transition temperatures of about −50 °C or lower are the most effective.

On the basis of this empirical guideline, some polymers that qualify as potential candidates for useful elastomers under normal conditions are listed together with their respective glass transition temperatures in Table II.

Polysiloxanes. It can be seen from Table II that polysiloxanes as a class show lower T_g values than all other polymers known, and many members of this polymer family have values that are considerably below −50 °C. Consequently, these polymers clearly represent excellent candidates for useful elastomers, and it is for that reason that the search for high-temperature elastomers has been directed toward modified polysiloxanes, in which modifications were desired mostly in order to achieve improvements in their thermal stabilities.

The reasons for such low glass transition temperatures of the polysiloxanes (that is, for their exceptional elasticity at unusually low temperatures) lie in the following two fundamental structural properties of these polymers: (1) the highly pronounced inherent conformational flexibility of the $-(SiO)_n-$ main-chain backbones, and (2) the very weak *inter*molecular interactions between neighboring polymer segments.[1] The former property enables unusually pronounced mobility of the $-(SiO)_x-$ chain segments and molecules, while the latter accounts, in part, for the relatively large free volume between neighboring polymer chains.

Conformational Flexibility of Siloxane Polymers. The polysiloxane backbone, $-(SiO)_x-$, is one of the most

Table II
Glass Transition Temperatures of Selected Elastomers

polymer	T_g, °C	ref
polyacetaldehyde	-10	17
poly(oxymethylene)[a]	(-10 to -85)	18
polychloroprene (cis)	-20	18
poly(ethyl acrylate)	-22	17
poly(ethylethylene)	-24	18
poly(methylphenylsiloxane)	**-28**	19
poly(diphenylsiloxane-*co*-dimethylsiloxane) (50:50 mol %)	**-30**	19
poly(propylethylene)	-40	18
poly(oxyethylene)[b]	-41	18
polychloroprene (85% trans-1,4)	-45	17
poly(butylethylene)	-50	18
polysulfide rubber (Thiokol FA)	-50	17
poly(dioxynonylphosphazene)	-56	20
polybutadiene (trans-1,4)	-58	18
polyisoprene (trans-1,4)	-58	18
poly(ethylene-*co*-propylene) (50:50)	-60	17
poly(difluoroalkoxyphosphazenes)	-60	20
poly(diphenylsiloxane-*co*-dimethylsiloxane) (30:70 mol %)	**-64**	19
polyisobutylene	-70	17
polyisoprene (cis-1,4)	-70	17
poly(methyl-3,3,3-trifluoropropylsiloxane)	**-70**	19
natural rubber	-72	21
poly(dioxymethylphosphazene)	-76	20
poly(oxytrimethylene)	-78	18
poly(dioxyethylphosphazene)	-84	20
polybutadiene (20% 1,2)	-85	17
poly(methyl-*n*-octylsiloxane)	**-92**	19
poly(dioxypropylphosphazene)	-100	20
polybutadiene (cis-1,4)	-102	18
poly(di-*n*-propylsiloxane)	**-109**	22
poly(thiodifluoromethylene)	-118	20
poly(methyl-*n*-propylsiloxane)	**-120**	19
polydimethylsiloxane	**-123**	18
polyethylene[c]	-125	18
poly(methylethylsiloxane)	**-135**	19
poly(diethylsiloxane)	**-139**	22

[a] Various methods of measurement gave different results ranging within the indicated limits. [b] Conflicting data, values range from -115 to -40 °C.[18] [c] Conflicting interpretations of data; branch point at -21 °C.[18]

flexible chains known, and its highly pronounced inherent conformational flexibility is apparent both at the segmental and at the molecular level. At the segmental level, polysiloxanes are able to change their spatial arrangements by relatively unrestricted rotation around the skeletal Si–O bonds, for which the energy barriers are unusually low, only of the order of several hundred calories per mole,[23] while at the molecular level, entire molecules can readily change shape and form random coils.[24]

The segmental, or dynamic, flexibility of the polysiloxanes has been shown to result from the following two important structural characteristics.[1,24] First, the Si–O skeletal bonds and the Si–C side linkages are both relatively long units, normally extending to about 1.64 Å[24,25] and to about 1.87–1.90 Å,[24,25] respectively.[26] These unusually long bonds provide for increased spatial separation of the neighboring side groups and result in significantly reduced steric interferences to relieve molecular congestions, which would otherwise occur between these groups. This effect is particularly important if the side groups are relatively large and bulky units, such as methyl or phenyl groups.

Second, the alternating arrangement of the relatively large silicon and considerably smaller oxygen atoms along the $-(SiO)_x-$ polymer chains results in a favorably alternating arrangement of the Si–O–Si and O–Si–O bond angles, of which the former can be described as unusually "soft", since in different siloxane compounds it was found to vary from about 104 to almost 180°.[27,28] Therefore, these units have a small barrier of linearization of about 0.3 kcal/mol,[29] and values between 140 and 150° are most often reported for linear polysiloxanes.[1,19,28] In contrast to this, the O–Si–O angle is considerably more rigid, and it is usually found between about 102 and about 112°,[27,28] depending on the nature of the pendant substituents on silicon.

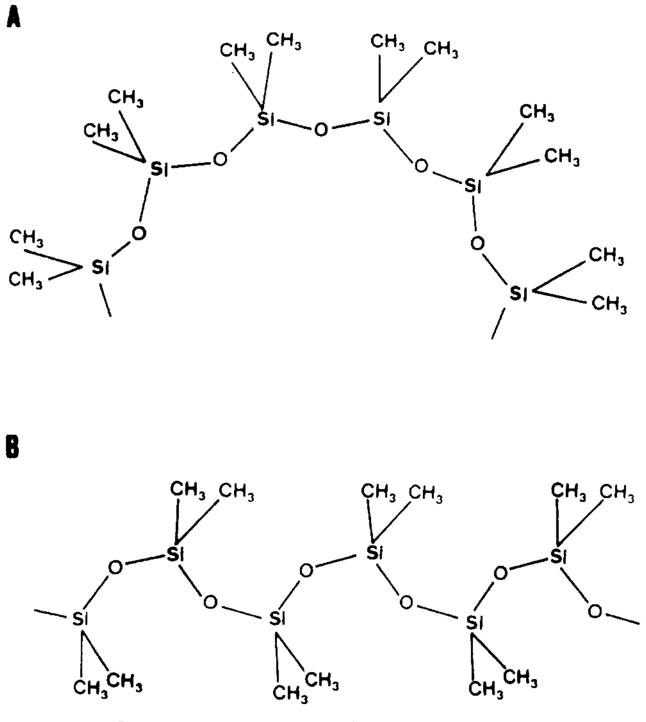


Figure 1. Conformations of poly(dimethylsiloxane) chains: (A) all-trans (according to ref 25); (B) trans–syn (according to ref 34).

The softness of the Si–O–Si bond angle permits considerable bending of the polysiloxane segments about their oxygen atoms, which allows the $-(SiO)_x-$ skeleton to assume shapes which would otherwise be either impossible or at least highly restricted from occurring. It has been suggested[28] that the "softness" of the Si–O–Si bond angle is a consequence of delocalization of the lone electron pairs of oxygen into the covalent bonding region between the Si and O atoms, so that the sp^3 hybridization is altered to widen the angle at oxygen.[30]

The exceptional inherent conformational flexibility of these polymers, however, not only is characteristic of the polysiloxane segments but also extends to entire macromolecules[24,25,27] which can form rather specific shapes and compact their random coils in size.[24] Thus, it was found that the value of the unperturbed, mean-square end-to-end distance, $|r^2|_0$, of the poly(dimethylsiloxane) (PDMS) macromolecule is very close to that calculated by assuming a freely rotating chain; so that the ratio $|r^2|_0/|r^2|_{0,\text{free rot.}}$ was only about 1.4.[1,31] This indicates a relatively unrestricted rotation about the main-chain bonds and highly pronounced molecular flexibility which approaches that of an ideal freely rotating chain. In addition to this, theoretical calculations showed that the preferred conformations of the same polymer, as shown in Figure 1, are quite unusual as compared to most of the other known macromolecules. Thus, the so-called FCM model, which was based on the rotational isomeric state theory, predicted a surprising all-trans conformation[32] (A in Figure 1) from which the flexibility of PDMS can be explained as being due to the increase in the number of gauche states upon stretching.[25,33] In contrast, a more recent model, which was deduced from the calculations of the *intra*molecular rotational potential energy surfaces based on a self-consistent-field molecular orbital ab initio theory, proposed a trans–syn conformation[34] (B in Figure 1), which seems to be able to explain why such flexible chains as the polysiloxanes do not tend to close upon themselves into oligomeric macrocyclic ring structures. Of course, with the increase in size of the pendant groups, steric effects between the neighboring substituents of the main polysiloxane chains can become important, and these unusual conformations cease to be preferable for poly(diethylsiloxane) and poly(di-*n*-propylsiloxane), the chain dimensions of which increase relative to those of PDMS.[25]

From the preceding discussion it follows that the unusually pronounced inherent flexibility of the polysiloxane $-(\mathrm{SiO})_x-$ chains is a direct consequence of their high degree of freedom of reorientational motions, both in the rotational (rotation around the Si–O bonds) and in the bending sense (bending about the oxygen atoms), and this property is caused by the following fundamental structural features of the alternating arrangement of the silicon and oxygen atoms: (1) the relatively large difference in size of these atoms; (2) the relatively long Si–O main-chain bonds and Si–C side-chain linkages; and (3) the unusually soft Si–O–Si bond angles at oxygen.

Intermolecular Interactions in Polysiloxanes. Various rheological investigations have shown that activation energies for viscous flow, ΔE_{visc}, of the polysiloxanes are generally very small and rarely above approximately 10 kcal/mol, indicating that only small frictional forces are associated with the translational flow of these polymers. For example, the values found range from only 3.4 kcal/mol for PDMS to about 12 kcal/mol for poly(methylphenylsiloxane), while those for polymers with methylpropyl and methyl-3,3,3-trifluoropropyl groups were 4.3 and 7.9 kcal/mol,[35,36] respectively. It should be noted that this order is identical to the order of the size of the side groups.[1]

Also, when subjected to a shearing stress the flow patterns of the polysiloxanes depend on the nature of their organic substituent groups, and non-Newtonian flow is more prominent for the polymers which contain bulkier pendant units.[1] Most interesting in this respect is the well-known, surprisingly Newtonian behavior of PDMS and its characteristically small viscosity–temperature coefficient (viscosity of this polymer typically decreases by no more than a factor of 2 over the temperature range from 40 to 100 °C[27]).

This behavior can be rationalized as a consequence of the regularly coiled 6_1 helical conformation of the PDMS molecules, which is not only characteristic for its crystalline state[37] but should also be largely retained at low temperatures in the melt.[1,38] If so, the more or less intact helices project their methyl side groups outward and generate only relatively low viscosity because of both weak interactions between the side groups of the neighboring segments and very little interpenetration of the chains. The latter property is caused by effective shielding of the polar $-(\mathrm{SiO})_x-$ main-chain backbones by the pendant side groups, which not only are bulky units but also undergo considerably unrestricted so-called "umbrella type" rotational motions around their Si–C bonds. These motions are very pronounced even well below the crystallization temperature[39] and enable side groups to occupy a larger space than their actual volume and to thereby create a larger free volume between the neighboring segments and/or molecules.

On the basis of these considerations, it follows that the structural features of polysiloxanes which are responsible for their low *inter*molecular interactions are generally as follows: (1) the polymer forms regularly coiled helical structures at lower temperatures, (2) the polymer has a relatively free rotation of the substituents around the Si–C bond, which facilitates the shielding of the main-chain backbone by these pendant side groups, and (3) the polymer has a relatively large free volume between the neighboring chain segments.

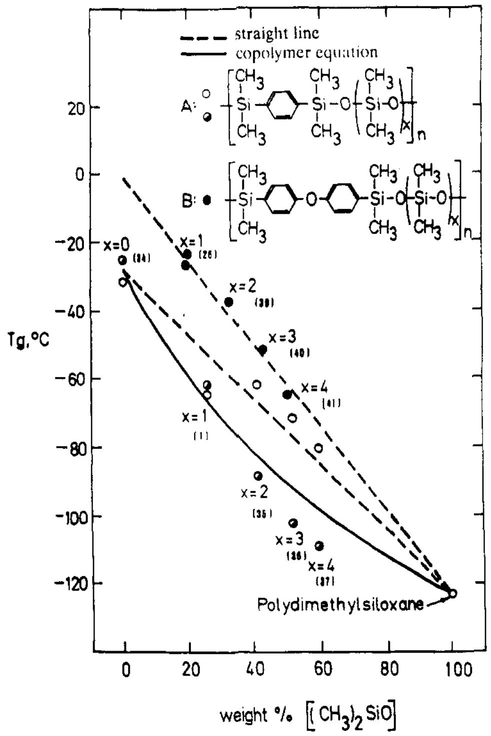


Figure 2. Effect of the siloxane segment length on the glass transition temperature of *p*-phenylene (A) and *p*,*p*′-diphenyl ether (B) containing silarylene–siloxane polymers of structure I. For A: (○) by differential scanning calorimetry, DSC; (◐) by torsional braid analysis, TBA. For B: (●) by DSC. See Tables I and III for the polymer numbering system.

Silarylene–Siloxane Polymers. Siloxane Segment Length Effect. From the preceding discussion it is to be expected that structural modifications of the polysiloxane main-chain backbone, which would result in disrupting the alternating arrangement of the silicon and oxygen atoms, should generally yield polymers with reduced low-temperature elasticity relative to that of the parent polysiloxanes because of the lower degree of conformational flexibility of the resulting polymer chains. Therefore, if such modifications of the polysiloxanes are required to increase thermal stability but low-temperature elasticity is still desired, the extent of such modifications should be kept to a minimum in order to retain as many Si–O–Si units in the resulting polymer structures as possible, because the key contributor for polysiloxane conformational mobility is apparently the low-energy bending of the Si–O–Si bonds and the free rotation around these bonds which increase intersegmental free volume.

If these assumptions are correct, then replacement of a fraction of the oxygen atoms in the polysiloxane main-chain backbones by rigid aromatic groups to form silarylene–siloxane polymers, such as I or IX, should increase the T_g of such polymers. The results obtained in the study of T_g values of the silarylene–siloxane polymers, which contained *p*-phenylene and *p*,*p*′-diphenyl ether units and methyl substituent groups at R_1 through R_4 in structure I, clearly confirmed this expectation, as shown by the data presented in Figure 2 and Table III.

It can be seen from these data that while the effect of introducing arylene units between the dimethylsiloxane chain segments was in all cases to stiffen the silarylene–siloxane main chains with respect to the flexibility of poly-

Table III
Effect of the Siloxanylene Segment Length on the Glass Transition Temperature of the *p*-Phenylene and *p,p'*-Diphenyl Ether Containing Silarylene–Siloxane Polymers of Structure I[a]

polym no.	aromatic group	x	T_g, °C
34	p-C_6H_4	0	−23,[b] −25,[c] −31[d]
1		1	−61,[c] −62,[e] −63,[f] −64,[g] −65[h]
35		2	−62,[i] −88[c]
36		3	−72,[i] −102[c]
37		4	−80,[i] −109[j]
38	p,p'-$C_6H_4OC_6H_4$	0	
26		1	−24,[e] −26[g]
39		2	−37[i]
40		3	−52[i]
41		4	−65[i]
poly(dimethylsiloxane)			−123[k]

[a] $R_1 = R_2 = R_3 = R_4 = CH_3$. [b] Reference 45; determination method and heating rates not reported. [c] Reference 7; by torsional braid analysis. [d] Reference 44; determination method and heating rates not reported. [e] This work; by differential scanning calorimetry at a heating rate of 20 °C/min. [f] Reference 6; by differential scanning calorimetry, no heating rate reported. [g] This work; by differential scanning calorimetry at a heating rate of 5 °C/min. [h] Reference 7; by differential scanning calorimetry at a heating rate of 4 °C/min. [i] Reference 43; by differential thermal analysis with no heating rate reported. [j] Reference 7; determination method and heating rates not specified. [k] Reference 18.

(dimethylsiloxane), and the glass transition temperatures of such polymers were always higher than the T_g of PDMS, the magnitude of that increase was not too great. The T_g, as expected, depended on the particular aromatic group involved, and, also as expected, the increase was always greater for the polymers with the shorter siloxane segments; that is, for smaller values of x. Thus, if these polymers are viewed as derivatives of poly(dimethylsiloxane) in which fractions of the siloxane oxygens are regularly replaced by arylene units, as shown by the generalized formula I, it can be concluded that, as the extent of this replacement was larger and the length of the siloxane segments in the silarylene–siloxane repeating units, x, was shorter, the polysiloxane-like character of the resulting polymers was reduced because the inherent conformational flexibility of the silarylene–siloxane main-chain backbones was diminished. Nevertheless, from the data of Table III, it can be concluded that the polysiloxane-like character of the silarylene–siloxane polymers prevailed above a value of x of 4.

As shown in Figure 2, the variation of T_g of the silarylene–siloxane polymers followed very closely the predictions of the so-called copolymer equation

$$1/T_g = w_1/T_{g1} + w_2/T_{g2}$$

in which w_1 is the weight fraction of the structures corresponding to the repeating units of the silarylene–siloxane parent polymers (polymers 34 or 38 of Table III), w_2 is the weight fraction of the dimethylsiloxane segments, and T_g, T_{g1}, and T_{g2} are the glass transition temperatures of the silarylene–siloxane polymer examined, polymer 34 or 38, and poly(dimethylsiloxane), respectively.

Arylene Group Effect. For a given length, x, of the siloxane segment in the silarylene–siloxane repeating unit, the nature of the arylene group would be expected to exert an important influence on the polymer flexibility. In agreement with this, it was found that T_g values of the polymers, which had all structural variables the same (the value of x and the substituent groups R_1 through R_4) depended considerably on the type of aromatic groups present, as shown in Tables IV and V.

Table IV
Effect of the Aromatic Group Structure on the Glass Transition Temperature of Silarylene–Siloxane Polymers of Structure I[a]

polym no.	aromatic group	x	R_3	R_4	T_g, °C
34	p-C_6H_4	0			−23 to −31[b]
1		1	CH_3	CH_3	−61 to −65[c]
36		3	CH_3	CH_3	−72,[d] −102[e]
42	m-C_6H_4	3	CH_3	CH_3	−75[f]
26	p,p'-$C_6H_4OC_6H_4$	1	CH_3	CH_3	−24, −26[g]
40		3	CH_3	CH_3	−52[f]
30	0.5 p-C_6H_4 + 0.5 p,p'-$C_6H_4OC_6H_4$	1	CH_3	CH_3	−42,[h] −43[i]
43	5,5'-$C_5H_4FeC_5H_4$	1	C_6H_5	C_6H_5	37[j]
44	0.5 5,5'-$C_5H_4FeC_5H_4$ + 0.5 p,p'-$C_6H_4C_6H_4$	0			7[j]
45	0.5 5,5'-$C_5H_4FeC_5H_4$ + 0.5 p-C_6H_4	0			−2[j]
46	p,p'-$C_6H_4(CF_2)_3C_6H_4$	0			−12[k]
47	0.5 p,p'-$C_6H_4(CF_2)_3C_6H_4$ + 0.5 m,m'-$C_6H_4(CF_2)_6C_6H_4$	0			−34[k]

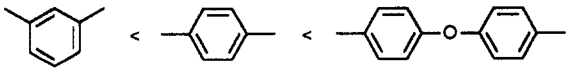
[a] $R_1 = R_2 = CH_3$. [b] See footnotes *b–d* of Table III. [c] See footnotes *c–h* of Table III. [d] See footnote *d* of Table III. [e] See footnote *c* of Table III. [f] See footnote *i* of Table III. [g] See footnotes *e–g* of Table III. [h] See footnote *e* of Table III. [i] See footnote *g* of Table III. [j] See footnote *h* of Table III. [k] Reference 46; by differential scanning calorimetry with no heating rate reported.

Table V
Effect of the Aromatic Group Structure on the Glass Transition Temperature of Methyl/Vinyl Substituted Polymers of Structure IX[a,b]

polym no.	aromatic group	R_4	T_g, °C
1	p-C_6H_4	CH_3	−61 to −65[c]
9		$0.95\ CH_3 + 0.05\ CH{=}CH_2$	−63 to −65
10		$0.925\ CH_3 + 0.075\ CH{=}CH_2$	−63 to −66
12		$CH{=}CH_2$	−69, −72, −76
30	0.5 p-C_6H_4 + 0.5 p,p'-$C_6H_4OC_6H_4$	CH_3	−42, −43
31		$0.95\ CH_3 + 0.05\ CH{=}CH_2$	−43, −44
32		$0.925\ CH_3 + 0.075\ CH{=}CH_2$	−44, −47
33		$CH{=}CH_2$	−51, −53
26	p,p'-$C_6H_4OC_6H_4$	CH_3	−24, −26
27		$0.95\ CH_3 + 0.05\ CH{=}CH_2$	−25, −26
28		$0.925\ CH_3 + 0.075\ CH{=}CH_2$	−25, −26
29		$CH{=}CH_2$	−27

[a] $R_3 = CH_3$. [b] All T_g values were determined by differential scanning calorimetry unless otherwise noted. Lower values correspond to heating rates of 20 °C/min and higher values to 5 °C/min. [c] See footnotes *c–h* of Table III.

For example, a comparison of the T_g values obtained for the polymers which contained three dimethylsiloxy groups (x = 3) and either a p,p'-diphenyl ether or a p- and m-phenylene nucleus in the repeating unit (polymers 40, 36, and 42 of Table IV), reveals that the chain rigidity, as indicated by an increase in T_g, decreased in the following order:

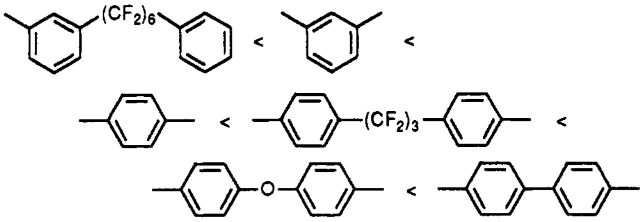


The same conclusion can be made by a comparison of the T_g values determined for the exactly alternating silarylene–siloxane polymers, x = 1, in which the main-chain arylene units were either p-phenylene or p,p'-diphenyl ether groups (or their combinations), while the types of the pendant groups were kept constant with R_1, R_2, and R_3 as methyl groups and R_4 as various combinations of methyl and vinyl groups, as shown in Table V.

It is seen from these data that, in all comparable cases, for the polymers which had same combinations of methyl and vinyl groups at the R_4 positions (compare polymers 1, 30, and 26; 9, 31, and 27; 10, 32, and 28; 12, 33, and 29 of Table V), the p,p'-diphenyl ether polymers (polymers

26–29) always had higher T_g values than their *p*-phenylene homologs (polymers 1 and 9, 10 and 12). As expected, the glass transition temperatures of copolymers, which contained equal molar concentrations of the two arylene groups (polymers 30–33), had intermediate values, which again agreed very well with the values calculated from the copolymer equation, as shown in Figure 3.

Several other relationships between polymer structure and T_g can also be deduced from the data of Table IV. First, from the T_g values for polymers 44 and 45 (−7 and −2 °C, respectively), it can be concluded that the *p,p'*-biphenylene unit stiffened the silarylene–siloxane chains much more than the *p*-phenylene group. Second, if the linear relationship between the siloxane content, *x*, and T_g holds for the silarylene–siloxane polymers containing *p,p'*-diphenyl ether groups, as indicated by the data shown in Figure 2, then by extrapolating that plot to $x = 0$ the T_g of that homopolymer (which has not been reported in the literature) should be about 0 °C. Third, by comparing the data for polymers 46 and 47 of Table IV (−12 and −34 °C, respectively) with the calculated value for the corresponding *p,p'*-diphenyl ether silarylene–siloxane polymer with $x = 0$ (about 0 °C), it follows that the T_g of the latter polymer should be considerably higher than the T_g values of the two fluorinated silarylene–siloxane polymers considered. Therefore, the following general order for the stiffening effect of aromatic units should hold for the silarylene–siloxane polymers of any specific length of the siloxane groups, *x*:



Exactly Alternating Silarylene–Siloxane Polymers. Side Groups Effect. The third important structural factor which exerts a considerable influence on T_g of the silarylene–siloxane polymers is the type of substituent groups. An excellent model for studying these effects is the family of exactly alternating silphenylene–siloxane polymers which have Ar = *p*-C_6H_4, $R_1 = R_2 = CH_3$, and $x = 1$, while R_3 and/or R_4 is either methyl, phenyl, vinyl, *n*-propyl, allyl, fluoroalkyl, or cyanoalkyl groups as shown in Table VI.

It can be seen from the data in this table that, with the exception of the diphenylsiloxanyl polymer (polymer 49), all other silphenylene–siloxane polymer homologs showed T_g values below −30 °C. All of these polymers, therefore, are good candidates for useful elastomers in applications at temperatures of approximately −10 °C, or above. In addition, the following important relationships between polymer structure and T_g can be deduced from these data.

(1) Phenyl and Other Bulky Substituent Groups Effects. First, in the series of methyl-substituted polymers, the first nine polymers of Table VI, in which R_3 was CH_3 and R_4 varied, but with the clear exceptions of those members of this series in which R_4 was either *n*-propyl (polymer 2) or vinyl or allyl groups (polymers 12 and 13), the replacement of methyl groups in the R_4 position of polymer 1 by larger and bulky groups, such as phenyl, cyanoalkyl, or fluoroalkyl groups, always led to an increase in T_g (compare polymers 48 and 3–6 with polymer 1). The same conclusion can also be drawn from the comparison of T_g values obtained for the polymers in Table VII as well as for polymers 1, 48, and 49, 12 and 21, 13 and 22, 3 and 23 of Table VI, in which this substitution was also in R_3 as well as in R_4.

The largest increase in the T_g values of these polymers resulted from the replacement of methyl groups by the phenyl groups (compare polymers 1, 48, and 49 of Table VI), a somewhat smaller increase with the 2-cyanoethyl groups (polymers 1, 3, and 23 of the same table), and a still smaller increase with the fluoroalkyl units (polymer 1, 5,

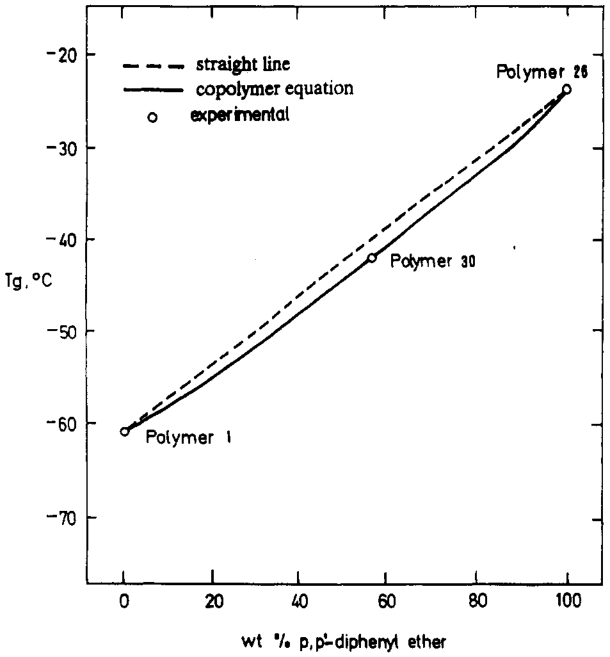


Figure 3. Effect of the type of aromatic group on the glass transition temperature of exactly alternating silarylene–siloxane polymers of structure IX. See Table I for the polymer numbering system.

Table VI
Effect of the Substituent Groups on the Glass Transition Temperature of Polymers of Structure IX

polym no.	R_3	R_4	T_g, °C
48	CH_3	C_6H_5	−25,[a] −32[b]
3	CH_3	$(CH_2)_2CN$	−37
4	CH_3	$(CH_2)_3CN$	−37
5	CH_3	$(CH_2)_2CF_3$	−51
6	CH_3	$(CH_2)_2(CF_2)_5CF_3$	−55
1	CH_3	CH_3	−61 to −65[c]
2	CH_3	$(CH_2)_2CH_3$	−65
13	CH_3	$CH_2CH{=}CH_2$	−66
12	CH_3	$CH{=}CH_2$	−69,[d] −75
49	C_6H_5	C_6H_5	1,[a] −4[b]
21	C_6H_5	$CH{=}CH_2$	−31
22	C_6H_5	$CH_2CH{=}CH_2$	−38
23	$(CH_2)_3CN$	$(CH_2)_3CN$	−30
24	H	$(CH_2)_2CF_3$	−37

[a] See footnote *c* of Table III. [b] See footnote *h* of Table III. [c] See footnotes *c*–*h* of Table III. [d] By differential scanning calorimetry at a heating rate of 5 °C/min.

Table VII
Effect of the Content of the Phenyl Groups on the Glass Transition Temperature of Phenyl/Methyl/Vinyl-Substituted Polymers of Structure IX[a]

polym no.	R_3	R_4	T_g, °C
8	CH_3	$0.99\,CH_3 + 0.01\,CH{=}CH_2$	−65
14	CH_3	$0.66\,CH_3 + 0.33\,C_6H_5 + 0.01\,CH{=}CH_2$	−60
15	CH_3	$0.33\,CH_3 + 0.66\,C_6H_5 + 0.01\,CH{=}CH_2$	−44
16	CH_3	$0.99\,C_6H_5 + 0.01\,CH{=}CH_2$	−32

[a] By differential scanning calorimetry at a heating rate of 20 °C/min.

and 6). For the phenyl and 2-cyanoethyl substituents, it is evident, as expected for the copolymer effect, that the magnitude of this increase in T_g was proportional to the extent of CH_3 substitution, so that it was largest when all of the methyl groups at both R_3 and R_4 positions were replaced (polymers 49 and 23 of Table VI).

A similar effect was also found for the polymers which had a small but constant content of vinyl side groups (1 mol %) but varying amounts of CH_3 and C_6H_5 units in the R_4 position. This effect can be seen from the data of Table VII, in which the polymer with R_4 containing 0.99 C_6H_5 and 0.01 $CH{=}CH_2$ mole fractions of the respective groups (polymer 16) had a T_g of −32 °C, while the corresponding all-methyl-containing polymer (polymer 8) had this transition at −65 °C. As expected, polymers in which R_4 was of intermediate compositions (polymer 14 with 0.66 C_6H_5, 0.33 CH_3, and 0.01 $CH{=}CH_2$ mole fractions and polymer 15 with 0.33 C_6H_5, 0.66 CH_3, and 0.01 $CH{=}CH_2$ mole fractions) had T_g values between the former two, at −44 and −60 °C, respectively.

In agreement with these observations, it was reported earlier that the replacement of methyl groups by phenyl groups led to a comparable increase in T_g values for the polymers in which this substitution was made at the silarylene silicon atoms, the R_1 and R_2 positions, as well as for those in which the *p*-phenylene groups were replaced by the *m*-phenylene units.[43]

These substituent effects can be rationalized on the basis of the free-volume theory of glass transition through the effect of the bulkier side groups on reducing *inter*segmental free volume and, consequently, decreasing the freedom of rotation of the polymer chain segments, thereby increasing T_g. On the basis of these data, the order of effectiveness of the substituent groups on increasing T_g in exactly alternating silphenylene–siloxane polymers is as follows:

$$CH_3 < (CH_2)_2(CF_2)_5CF_3 < (CH_2)_2CF_3 < (CH_2)_3CN < C_6H_5$$

(2) Vinyl and Allyl Groups Effect. In clear contrast to the previous effects, a comparison of the data for polymers 1, 13, and 12 or 49, 21, and 22 of Table VI reveals that the inclusion of unsaturated vinyl and allyl side groups in these silarylene–siloxane polymers led to an unexpected decrease in T_g. This observation is also supported by the T_g values in Figure 4 and Tables VIII and IX.

The observed decrease in T_g was clearly dependent on the relative amounts of unsaturated groups, so that, in the methyl/vinyl series of the silphenylene–siloxane polymers, the first seven polymers of Table VIII, the magnitude of the effect increased with increasing amounts of vinyl units in the copolymers to 10 or 15 °C for the complete replacement of CH_3 groups in R_4 by $CH{=}CH_2$ groups. In the *p,p′*-diphenyl ether series (polymers 26–29 of the same table), however, this effect was not as pronounced as with the silphenylene–siloxanes, and it amounted to only about a 3 °C decrease, but in the polymers which contained a combination of 50 mol % of the *p*-phenylene and 50 mol % of the *p,p′*-diphenyl ether aromatic units (polymers 30–33 of Table VIII), the effect clearly reappeared to reach about 10 °C. This result may indicate that the effect of the vinyl groups in decreasing T_g is a cooperative one, and by replacing *p*-phenylene groups with more extended *p,p′*-diphenyl ether groups, the effect is weakened because of increased separation of the vinyl groups.

The decrease in T_g caused by introduction of the vinyl groups was also observed for the polymers which contained other substituent groups. Thus, as shown in Table IX, for the polymers which had phenyl groups at R_4, the first five polymers of that table, the effect of the replacement of C_6H_5 by vinyl units was extraordinarily large and reached approximately 50 °C at complete substitution (compare polymers 48 and 12). A similar effect was also observed for the polymers which contained $(CH_2)_2(CF_2)_5CF_3$ fluoroalkyl groups, for which the insertion of only about 15 mol % of the vinyl groups at the R_4 position resulted in a T_g decrease of more than 20 °C (polymers 6 and 20 of Table IX).

For the polymers which contained $(CH_2)_2CF_3$ groups (polymers 5 and 25 of the same table), it was considerably

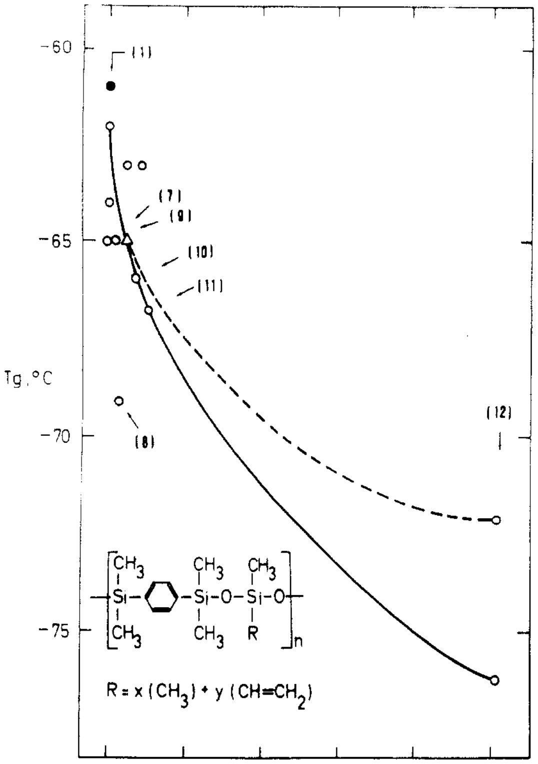


Figure 4. Effect of the vinyl group content on the glass transition temperature of exactly alternating silphenylene–siloxane polymers of structure IX: (○) by differential scanning calorimetry, DSC; (●) by torsional braid analysis. Solid line: more probable relationship. See Table I for the polymer numbering system.

Table VIII
Effect of the Vinyl Group Content on the Glass Transition Temperature of Polymers of Structure IX[a]

polym no.	aromatic group	R_4: CH_3	R_4: $CH{=}CH_2$	T_g, °C
1	*p*-C_6H_4	1	0	−61 to −65[b]
7		0.99	0.01	−65
8		0.97	0.03	−69
9		0.95	0.05	−63, −65
10		0.925	0.075	−63, −66
11		0.9	0.1	−67
12		0	1	−69, −72, −76
30	0.5 *p*-C_6H_4 + 0.5 *p,p′*-$C_6H_4OC_6H_4$	1	0	−42, −43
31		0.95	0.05	−43, −44
32		0.925	0.75	−44, −47
33		0	1	−51, −53
26	*p,p′*-$C_6H_4OC_6H_4$	1	0	−24, −26
27		0.95	0.05	−25, −26
28		0.925	0.075	−25, −26
29		0	1	−27

[a] All T_g values were determined by differential scanning calorimetry. Lower values correspond to heating rates of 20 °C/min and higher values to 5 °C/min. [b] See footnotes *c*–*h* of Table III.

Table IX
Effect of Bulky Groups on the Glass Transition Temperature of Polymers of Structure IX[a]

polym no.	R_3	R_4	T_g, °C
48	CH_3	C_6H_5	−25,[b] −32[c]
16	CH_3	$0.99\ C_6H_5 + 0.01\ CH{=}CH_2$	−32
17	CH_3	$0.97\ C_6H_5 + 0.03\ CH{=}CH_2$	−34
15	CH_3	$0.66\ C_6H_5 + 0.33\ CH_3 + 0.01\ CH{=}CH_2$	−44
14	CH_3	$0.33\ C_6H_5 + 0.66\ CH_3 + 0.01\ CH{=}CH_2$	−60
11	CH_3	$0.99\ CH_3 + 0.01\ CH{=}CH_2$	−65
12	CH_3	$CH{=}CH_2$	−69, −72, −76
18	CH_3	$0.9\ H + 0.1\ CH{=}CH_2$	−51
19	CH_3	$0.85\ H + 0.15\ CH{=}CH_2$	−53
6	CH_3	$(CH_2)_2(CF_2)_5CF_3$	−55
20	CH_3	$0.85\ (CH_2)_2(CF_2)_5CF_3 + 0.15\ CH{=}CH_2$	−76
5	H	$(CH_2)_2CF_3$	−37
25	$0.85\ H + 0.15\ CH_3$	$0.85\ (CH_2)_2CF_3 + 0.15\ CH{=}CH_2$	−48

[a] All T_g values were determined by differential scanning calorimetry at a heating rate of 20 °C, except the lowest value for polymer 12 which was determined at 5 °C/min. [b] See footnote *c* of Table III. [c] See footnote *h* of Table III.

more difficult to interpret the results because more than one structural change in the polymer occurred with the simultaneous substitution of H by CH_3 in the R_3 position and of $(CH_2)_2CF_3$ by $CH{=}CH_2$ at R_4. Nevertheless, in light of the preceding discussion, it seems likely that, aside from the replacement of about 15 mol % of the H atoms at the R_3 positions of polymer 25 by methyl groups, the introduction of $CH{=}CH_2$ units into the R_4 positions undoubtedly contributed to the observed decrease of about 11 °C of the T_g of that polymer relative to polymer 5. Less pronounced, but still detectable, was the effect of vinyl groups on T_g for the polymers which contained only hydrogen atoms and vinyl groups on the siloxane silicon atoms (polymers 18 and 19 of Table IX).

The effect of vinyl and allyl groups in decreasing T_g of these silphenylene–siloxane polymers was apparently also dependent on the type of other substituents on the siloxane silicon atoms at the R_3 position. Thus, as can be seen from the data in Table VI, when R_3 was a methyl group, the vinyl groups were more effective in decreasing T_g than the allyl groups (compare polymers 12 and 13 of that table), but, in contrast, when R_3 was a phenyl group, the effect was reversed, and allyl groups were more effective (compare polymers 22 and 21 of the same table). The reasons for these effects are not clear on the basis of the data now available.

It may be concluded from these comparisons that while unsaturated groups, either vinyl or allyl, can significantly decrease the T_g of exactly alternating silarylene–siloxane polymers, the extent of this decrease is strongly dependent on other structural features, especially the types of the main-chain aromatic groups and of the substituent side groups present. These effects are very important because, not only do such unsaturated groups decrease T_g, which are already low for silarylene–siloxane polymers, but these groups can also serve as highly desirable reactive centers for cross-linking reactions, either with vinyl-specific free-radical cross-linking agents or by hydrosilylation reactions, to prepare elastomers for low-temperature applications.

This effect of unsaturated side groups on T_g cannot be explained on the basis of the free volume theory of glass transition because both vinyl and allyl groups are large and bulky compared to methyl groups, so they should increase rather than decrease T_g. Perhaps, these relatively long, rodlike groups can undergo rotational motions about the Si–C bonds and create an additional free volume to lower T_g.

Table X
Effect of Three-Carbon Substituent Groups on the Glass Transition Temperature of Polymers of Structure IX

polym no.	R_3	R_4	T_g, °C
3	CH_3	$(CH_2)_2CN$	−37
5	CH_3	$(CH_2)_2CF_3$	−51
1	CH_3	CH_3	−61 to −65[a]
2	CH_3	$(CH_2)_2CH_3$	−65
13	CH_3	$CH_2CH{=}CH_2$	−66

[a] See footnotes *c*–*h* of Table III.

(3) Three Carbon Group Effects. The third important relationship between the polymer structure and T_g to be considered herein is the relative effect of the substituent groups of three carbons in length on T_g of exactly alternating silphenylene–siloxane polymers. This series includes polymers with the 2-cyanoethyl, 3,3,3-trifluoropropyl, *n*-propyl, and allyl groups at R_4 (polymers 3, 5, 2, and 13 of Table X). It can be seen from the data in this table that T_g of these polymers increased from −66 °C for the allyl-substituted polymer to −37 °C for the 2-cyanoethyl group homolog, with T_g values for the *n*-propyl and 3,3,3-trifluoropropyl group polymers in between these two, to give the following order of effectivness of these groups in increasing T_g:

$$CH_2CH{=}CH_2 < (CH_2)_2CH_3 < (CH_2)_2CF_3) < (CH_2)_2CN$$

This order can be rationalized as the expected effect of the size of the substituent groups on polymer T_g in accordance with the free volume theory of glass transition. An exception to this rationale, however, is the effect of the 2-cyanoethyl group, probably because of its polarizability, which would reduce segmental mobility in the polymer by increasing interchain interactions and, thereby, increase the T_g (compare polymers 4 and 23 of Table VI).

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