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Exactly Alternating Silarylene–Siloxane Polymers. 10. Synthesis and Characterization of Silphenylene–Siloxane Polymers Containing Fluoroalkyl and Hydrido Side Groups

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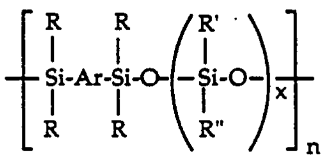
ABSTRACT: Six exactly alternating, silphenylene–siloxane polymers containing either 3,3,3-trifluoropropyl, tridecafluoro-1,1,2,2-tetrahydrooctyl, hydrido, methyl, or vinyl substituent groups on the siloxyl silicons were prepared by low-temperature, solution polycondensation reactions of 1,4-bis(dimethylhydroxysilyl)benzene, DMHSB, and the respective dichlorosilane monomers. All of the polymers prepared were characterized by ^{1}H and ^{13}C NMR spectroscopy, gel permeation chromatography and differential scanning calorimetry. The polymers with tridecafluoro-1,1,2,2-tetrahydrooctyl substituents showed two glass transition temperatures, and the higher transition at −37 °C was attributed to the mobility of the highly fluorinated substituents.

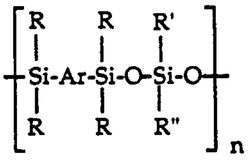
Introduction

Silarylene–siloxane polymers of the general structure I, and particularly the exactly alternating members of this family, II, are of interest for applications as high-temperature elastomers.[1]



$$\left[-\overset{R}{\underset{R}{\mathrm{Si}}}-\mathrm{Ar}-\overset{R}{\underset{R}{\mathrm{Si}}}-\mathrm{O}-\left(-\overset{R'}{\underset{R''}{\mathrm{Si}}}-\mathrm{O}-\right)_x-\right]_n$$

I



$$\left[-\overset{R}{\underset{R}{\mathrm{Si}}}-\mathrm{Ar}-\overset{R}{\underset{R}{\mathrm{Si}}}-\mathrm{O}-\overset{R'}{\underset{R''}{\mathrm{Si}}}-\mathrm{O}-\right]_n$$

II

The silarylene–siloxane polymers in which Ar in I and II is *p*-phenylene have attracted most of the attention because of their favorable combination of good properties and relative ease of preparation.[1] Within this group, numerous polymers with various substituents on the siloxyl silicons have been reported, including those with methyl, ethyl, vinyl, allyl, phenyl, cyanoethyl, cyanopropyl, and hydrido units, including copolymers which contained a combination of these groups.[2-14] However, few polymers of this type containing fluoroalkyl groups have been reported. In this report we describe the synthesis and characterization of four new fluoroalkyl-substituted, exactly alternating silphenylene–siloxane polymers, including polymers containing trifluoropropyl (TFP) and tridecafluoro-1,1,2,2-tetrahydrooctyl (TDFO) substituent groups, R′, in combination with methyl, hydrido, and vinyl groups, R″. The thermal stabilities and degradation behavior of these polymers have been described elsewhere.[1,10]

Experimental Section

Monomers and Solvents. 1,4-Bis(dimethylhydroxysilyl)benzene, DMHSB, and methyl(tridecafluoro-1,1,2,2-tetrahydrooctyl)dichlorosilane, MTDFOS, were purchased from Petrarch Systems Silanes and Silicones and used in the polymerization reactions without further purification. (3,3,3-Trifluoropropyl)dichlorosilane, TFPS, methylvinyldichlorosilane, MVS, dimethyldichlorosilane, DMS, and methyldichlorosilane, MS (all purchased from Petrarch) were purified prior to use by distillations in dry nitrogen. The fractions which distilled at 120–121, 92, 70, and 41 °C, respectively, were used in the polymerization reactions. Tetrahydrofuran, THF, was dried by repeated refluxing from a sodium–benzophenone solution under dry nitrogen, followed by distillation bp = 66 °C. Toluene was refluxed over calcium hydride and distilled under nitrogen.

Table 1. Compositions and Molecular Weights of Exactly Alternating Silphenylene–Siloxane Polymers, II, Ar = *p*-C$_6$H$_4$

polymer	R′	R″	$\bar{M}_w$[a]	$\bar{M}_n$[a]	$\bar{M}_w/\bar{M}_n$
1	CH$_3$	CH$_3$			
2	CH$_3$	0.85H + 0.15CH═CH$_2$	40 000	21 500	1.86
3[b]	0.85 H + 0.15 CH$_3$	0.85R$_f$ + 0.15CH═CH$_2$	39 500	20 000	1.98
4[b]	H	R$_f$[b]	42 000	22 000	1.91
5[c]	CH$_3$	R′$_f$[c]	62 000	33 500	1.85
6[c]	CH$_3$	0.85R′$_f$ + 0.15CH═CH$_2$	58 500	30 100	1.94

[a] $\bar{M}_w$, weight average, and $\bar{M}_n$, number average, molecular weights, determined by GPC relative to polystyrene standards. [b] R$_f$ = (CH$_2$)$_2$CF$_3$. [c] R′$_f$ = (CH$_2$)$_2$(CF$_2$)$_5$CF$_3$.

Polymerization Reactions. All polymer preparations were performed by using the "silane-deficient" polymerization method,[2,3,5,11] in which the silanol end groups on the growing polymers were combined during the final stages of the polymerization reactions with the silane comonomer by the continuous addition of the latter, and the increase in the growing polymer molecular weight was monitored by gel permeation chromatography to determine the amount of the silane comonomer to be added.[5] A typical procedure is described below for the preparation of polymer 4 of Table 1 from DMHSB and TFPS.

A 100 mL, three-neck, round bottom flask, equipped with a Teflon-coated stirring bar, inlet and outlet for inert gas, and a dropping funnel capped with a rubber septum, was assembled while still hot from the oven, flamed several times under vacuum and thoroughly flushed with nitrogen, which was prepurified by passing through a series of columns that contained H$_2$SO$_4$, KOH, and P$_2$O$_5$. After the inert atmosphere had been established, the reactor was cooled to between −15 and −10 °C, 11.09 g (49.06 mmol) of DMHSB monomer was transferred to the flask under a strong stream of purge nitrogen, and 40 mL of THF was siphoned in from a storage flask. Stirring was started, and the disilanol was allowed to dissolve completely. From a gastight syringe, 9.5 g (48.22 mmol) of TFPS was transferred through a serum cap

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into a dropping funnel and diluted with another 40 mL of THF, and the solution was added to the disilanol solution. The molar ratio of the reacting monomers thus obtained, *r* = [dichlorosilane]/[disilanol], was 0.983. After 1 h, the reaction mixture was allowed to warm to room temperature, 0.5 mL of the reaction mixture was taken for GPC analysis and diluted with 15 mL of THF, the solution was filtered, and a 0.5 mL aliquot of the filtrate was analyzed. The chromatogram obtained showed two peaks: one, corresponding to the polymer product, at 50.4 mL and the other, corresponding to the HCl byproduct, at 56.3 mL on the elution volume scale. Another 0.2 g (1.02 mmol) of TFPS monomer was slowly added to increase the molar ratio, *r*, to 1.004. The GPC chromatogram obtained after the adjustment showed peaks at 43 and 56.2 mL. Consecutive additions of the dichlorosilane were continued until the GPC peak, which appeared at the smaller elution volumes and thus corresponded to the growing polymer molecules, ceased to shift any further and remained at 39.6 mL, when the molar ratio of the reacting monomers was 1.04. At this point, a small amount of the disilanol was added to readjust the molar ratio back to 1.00, stirring was stopped, and THF was allowed to evaporate during the next 24 h. The viscous, oily polymer obtained was redissolved in 40 mL of THF, the solution was filtered through a sintered glass funnel, and the polymer was reprecipitated into 300 mL of well-stirred methanol. The polymer was isolated after decantation of the liquid and dried in a vacuum oven at 25 °C for 48 h. The molecular weight of the product as determined by GPC was found to agree with that measured at the end point of the polymerization within less than 10%.

Analytical Methods. Gel Permeation Chromatography, GPC. A Waters GPC Model 501 was used with five in-line Styragel (cross-linked polystyrene) columns with pore sizes of 500, 10^3, 10^4, 10^5, and 10^6 Å. THF was used as solvent and 1–2% (w/v) solutions were carefully filtered before injection. The samples were run at 25 °C at a flow rate of 1.5 mL/min. Molecular weights were determined on the basis of the universal calibration with monodisperse polystyrene standards.

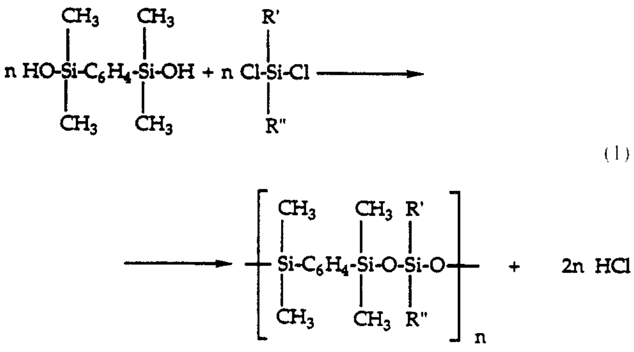
NMR Spectroscopy. ^{1}H and ^{13}C NMR spectra were obtained on a Varian XL-300 NMR spectrometer. Chemical shifts are given relative to tetramethylsilane, TMS, but they were determined with deuterated chloroform as the internal standard at 7.27 ppm for ^{1}H and 76.91 ppm for ^{13}C spectra. Sample concentrations ranged from 0.3 to 0.5 g of polymer/2 mL of solvent. For ^{1}H measurements a spectral width of 4000 Hz was covered and 17 500 acquisitions were taken in each case. For ^{13}C measurements the spectral width covered was 11 062 Hz with 13 700 acquisitions taken for each sample. Acquisition times of 2.0 and 1.446 s/pulse were used for ^{1}H and ^{13}C recordings, respectively, with 0 and 1.0 s delays between pulses.

Differential Scanning Calorimetry, DSC. Transition temperatures were determined using a Perkin-Elmer DSC-2, at a heating rate of 20 °C/min with liquid helium as the cooling fluid. In all cases, the temperature interval from −110 to +120 °C was scanned, with samples which ranged from 5 to 13 mg in weight.

Results and Discussion

Polymerization Reactions. Six different, exactly alternating, silphenylene–siloxane polymers, II, of the structures shown in Table 1, were prepared by step-growth polymerization reactions of 1,4-bis(dimethylhydroxysilyl)-benzene, DMHSB, and a series of dichlorosilane monomers, including mixtures of the latter, as shown by eq 1.

All polymerization reactions were carried out in THF at temperatures between −15 and +25 °C in order to minimize the extent of the undesired silanol coupling reactions.[5] The HCl byproduct was removed by a continuous nitrogen purge.[7,11] As described in Experimental Section, the "silane-deficient" polymerization procedure was used with monitoring of the polymerizations by GPC,[4,5,11] in order to prepare polymers of the highest possible molecular weights.[4,5,7,11]



$$n\,\mathrm{HO{-}}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{Si}}}\mathrm{{-}C_6H_4{-}}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{Si}}}\mathrm{{-}OH} + n\,\mathrm{Cl{-}}\overset{\mathrm{R'}}{\underset{\mathrm{R''}}{\mathrm{Si}}}\mathrm{{-}Cl} \longrightarrow \left[\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{Si}}}\mathrm{{-}C_6H_4{-}}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{Si}}}\mathrm{{-}O{-}}\overset{\mathrm{R'}}{\underset{\mathrm{R''}}{\mathrm{Si}}}\mathrm{{-}O}\right]_n + 2n\,\mathrm{HCl} \tag{1}$$

II

The polymers thus obtained had various types and contents of siloxyl substituent groups, as listed in Table 1 together with the polymer containing only methyl substituent groups, which is considered to be the parent polymer of the exactly alternating silphenylene–siloxane family.[1] The degrees of polymerization of the polymers in Table 1 ranged from about 90 to about 150. Our previous studies have shown[5,7,10] that above a degree of polymerization of about 100, the physical properties of silarylene–siloxane polymers are not affected by the changes in molecular weights.

NMR Characterization of Polymers. All of the polymers of Table 1 were characterized by ^{1}H and ^{13}C NMR spectroscopy. Selected examples of ^{1}H and ^{13}C spectra obtained are shown in Figures 1 and 2. It can be seen from these figures that a general feature of all these spectra was a noticeably pronounced sharpness of the characteristic absorption peaks. This result was expected because similar silarylene–siloxane polymers, as well as the closely related polysiloxanes, have been reported to show the same type of behavior,[6,7,16,17] presumably because of high inherent chain flexibility of these polymers.

^{1}H NMR peak assignments of the polymers of Table 1 and their corresponding chemical shifts relative to tetramethylsilane are listed in Table 2. Most of the characteristic ^{1}H NMR peaks, except the phenylene singlets (9 in Table 2) and, to some extent, the vinyl group quartets and Si—***H*** singlets (7 and 8 in Table 2, respectively), were found at essentially identical spectral positions independent of polymer structures. Thus, the silphenylene methyl protons, Ph—Si—C***H***$_3$ (3 in Table 2), of all of the polymers in the series, gave sharp and intensive singlets at δ 0.35 ppm. This result was also observed in our earlier examination of almost 20 other closely related exactly alternating silphenylene–siloxane polymers.[6,7] Also, as with other previously reported exactly alternating silarylene–siloxane polymers,[6,7,13–16] the absorptions of the C***H***$_3$ protons in the methyl/vinyl and methyl/tridecafluoro-1,1,2,2-tetrahydrooctyl siloxyl units of polymers 2, 3, 5, and 6 (2 and 1 in Table 2) were all found at about 0.1 ppm, while the methylene protons of the fluoroalkyl groups of polymers 5 and 6 (5 and 6 in Table 2) appeared at 0.75 and at 2 ppm, respectively. However, the methyl protons in the methyl/*n*-propyl substituted silphenylene–siloxane polymer[13] appeared at 0.01 ppm compared to 0.14 ppm for the all-methyl homologue.[7] In contrast, the absorption of the methyl group in the C***H***$_3$—Si—H polymer (4 in Table 2) occurred at 0.37 ppm. These results may represent meaningful shifts resulting from changes in the methyl groups environments, while the 0.37 ppm shift found for the (C***H***$_3$)—Si—H singlet might indicate a stronger-deshielding effect of the electron rich hydride units.

The most surprising deviations from normal spectral positions were encountered for the vinyl quartets (7 in Table 2), which appeared at δ 3.66 ppm for polymer 2 and

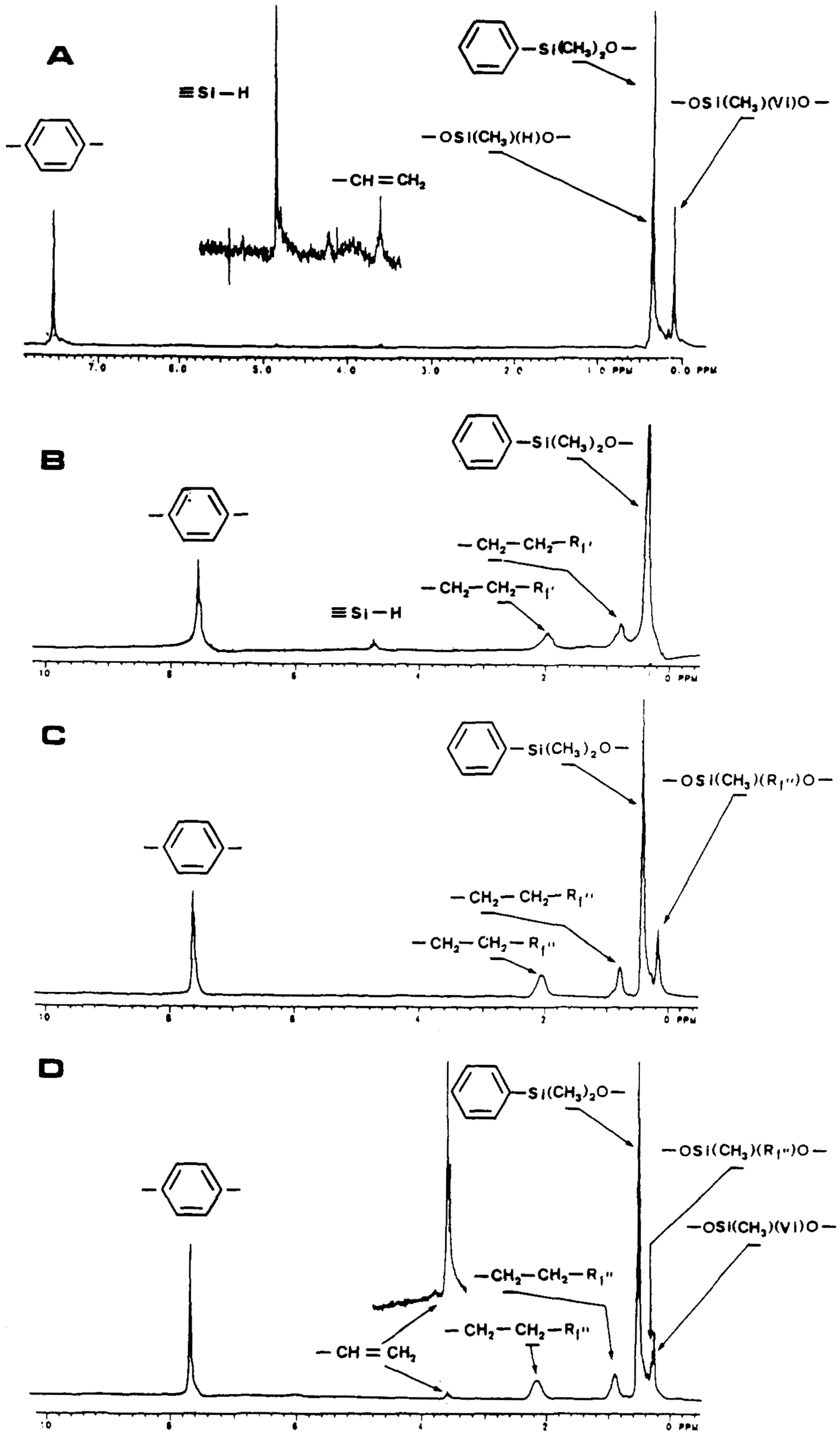


Figure 1. ^1H NMR spectra of selected polymers from Table 1: (A) polymer 2; (B) polymer 4; (C) polymer 5; (D) polymer 6.

at δ 3.43 ppm for polymer 6. This observation was in clear contrast with the results obtained from several previously examined silarylene–siloxane polymers, where these groups gave ^1H NMR absorption peaks that were considerably shifted downfield to between δ 5.65 and 6.05 ppm.[6,7,13]

The ^{13}C NMR peak assignments for the selected polymers of Table 1 and their corresponding chemical shifts are listed in Table 3. The carbon atom numbering system used in this table is shown in Figure 3. It can be seen from the data in Table 3 that, for all polymers examined, the chemical shifts of the phenylene carbons C_1 and C_2, and of the vinyl groups C_6 and C_7, were found at practically the same spectral positions, regardless of variations in polymer structures. This result indicated that these carbon atoms are not significantly influenced by the type of substituents on the siloxanylene silicons,

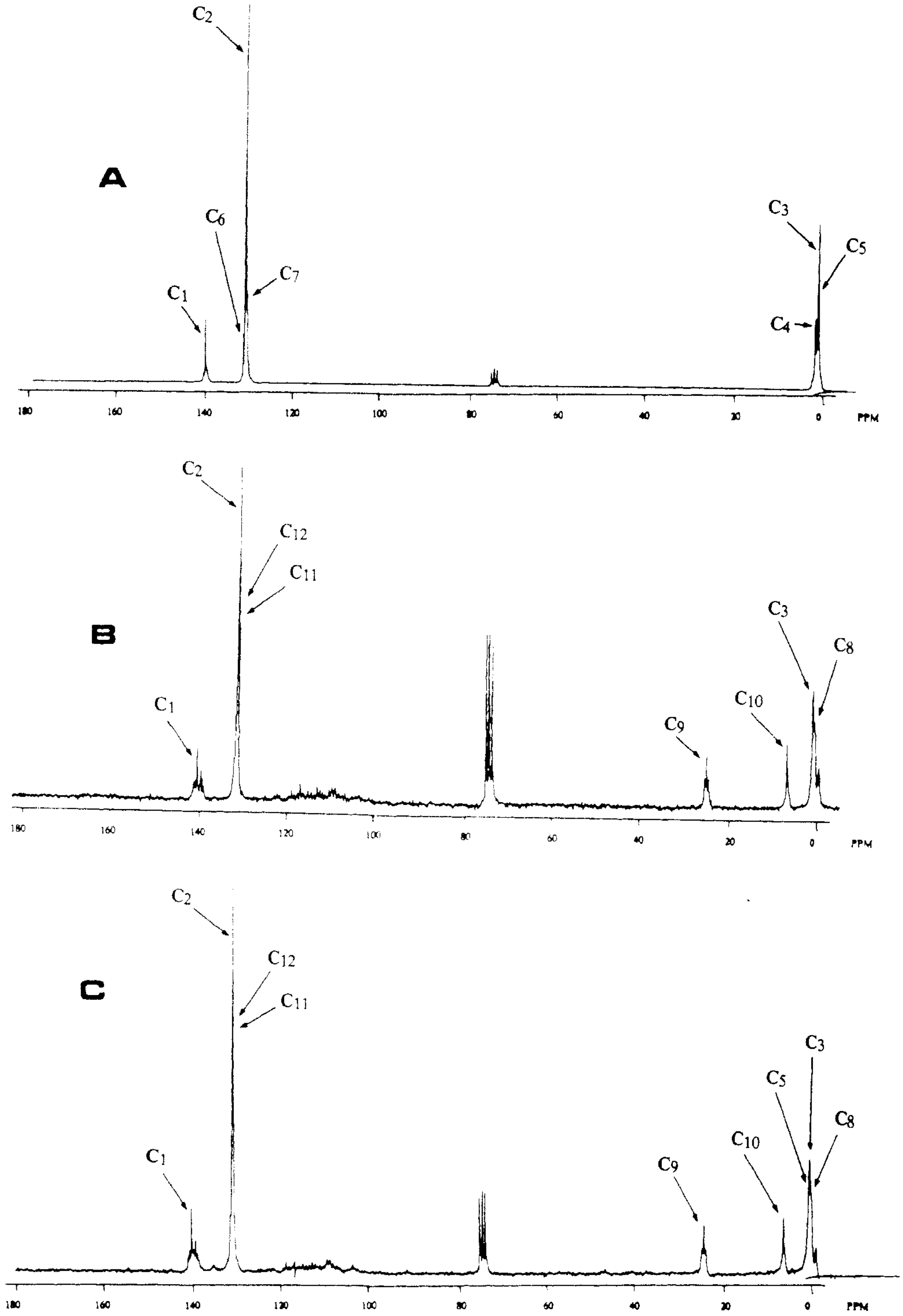


Figure 2. ^{13}C NMR spectra of selected polymers from Table 1: (A) polymer 2; (B) polymer 5; (C) polymer 6.

which was in good agreement with the previously reported results for other silphenylene–siloxane polymers,[6,7,13,16,17] as well as with the values predicted for the chemical shifts of these carbons on the basis of accepted empirical equations.[6]

In contrast to this result, however, the absorption peaks which corresponded to the silphenylene methyl carbons, Ar—Si—$\mathit{C}H_3$, designated as C_3 in Figure 3 and Table 3, appeared to be influenced by the type of substituent on the siloxanylene silicons R′ and R″, so that these C_3 peaks shifted from δ 0.62 pm (for polymer 5) to δ 0.89 ppm (for polymer 6), when 15 mol % of the $(CH_2)_2(CF_2)_5CF_3$ groups was replaced by the $CH{=}CH_2$ units, and to $\delta = 1.31$ ppm (for polymer 2), when all of the $(CH_2)_2(CF_2)_5CF_3$ units of polymer 6 were replaced by H. This result might represent an order of increasing electronegativity of these substituent groups.

The four absorption peaks for C_9 to C_{12} were assigned to the carbon atoms of the $(CH_2)_2(CF_2)_5CF_3$ fluoroalkyl groups, as shown in Figure 3 and Table 3. It appeared from the spectra of polymers 5 and 6 that all five carbon atoms of the $—CF_2—$ units were equivalent between themselves (absorption at δ 131.84 ppm for polymer 5 and at δ 131.92 ppm for polymer 6), while CF_3 absorptions, C_{12} of Table 3, were found at about δ 132 ppm (compared with δ 127.48 ppm reported earlier for the closely related methyl/3,3,3-trifluoropropyl-substituted exactly alternating silphenylene–siloxane polymer[13]). The C_9 and C_{10} peaks of the methylene carbons from fluoroalkyl units of polymers 5 and 6 were found where expected (see Table 3 and

Table 2. ^{1}H NMR Chemical Shifts of Exactly Alternating Silphenylene–Siloxane Polymers of Table 1[a–c] (See Figure 1 for a Typical Spectrum)

		polymer (δ, ppm)[c]				
peak	assgnt[a,b]	1	2	4	5	6
1	—OSi(C$\boldsymbol{H}_3$)(R'_f)O— (s/s i)				0.09	0.12
2	—OSi(C$\boldsymbol{H}_3$)(Vi)O— (s/s i)		0.07			0.10
3	—PhSi(C$\boldsymbol{H}_3$)$_2$O— (sh s/h i)	0.35	0.35	0.35	0.35	0.35
4	—OSi(C$\boldsymbol{H}_3$)(H)O— (s/s i)		0.37			
5	—C$\boldsymbol{H}_2$—CH$_2$$R_f^*$ (b s/s i)			0.73	0.75	0.75
6	—CH$_2$—C$\boldsymbol{H}_2$—R_f^* (b s/s i)			1.96	2.01	2.01
7	—$\boldsymbol{CH{=}CH}_2$ (w q)		3.66			3.43
8	—Si($\boldsymbol{H}$)(R**)— (sh s/h i)		4.89	4.72		
9	—Si—$\boldsymbol{Ph}$—Si— (sh s/h i)	7.60	7.86	7.56	7.60	7.72

[a] R'_f = $(CH_2)_2(CF_2)_5CF_3$; Vi = CH═CH$_2$; Ph = p-C_6H_4; R_f^* = CF_3 for polymer 4 and $(CF_2)_5CF_3$ for polymers 5 and 6; R** = CH_3 for polymer 2 and $(CH_2)_2CF_3$ for polymer 4. [b] s = singlet; sh s = sharp singlet; b s = broad singlet; w q = week quartet; s i = small intensity; h i = high intensity. [c] For comparison: polymer 1, see ref 6; vinyl groups, see refs 6 and 7; Si—H, see ref 14; $(CH_2)_2CF_3$, see ref 13.

Table 3. ^{13}C NMR Chemical Shifts of Exactly Alternating Silphenylene–Siloxane Polymers of Table 1 (See Figure 2 for a Typical Spectrum)

	polymer (δ, ppm)[a,b]			
assgnt	ref	2	5	6
C_1	140.58[5]	140.80	140.69	140.75
C_2	132.15[5]	132.30	132.07	132.13
C_3	0.68[5]	1.31	0.62	0.89
C_4	1.57[14]	1.46		
C_5		0.82		0.90
C_6[a]	137.14[5]	132.63		132.46
C_7[a]	132.88[5]	131.99		131.92
C_8[b]	−0.69[13]		0.58	0.59
C_9[b]	27.65[13]		27.74	24.87
C_{10}[b]	9.12[13]		6.58	6.65
C_{11}[b]			131.84	131.92
C_{12}[b]	127.48[13]		131.99	132.01

[a] Reference 5 gives δ values for the all-methyl exactly alternating silphenylene–siloxane polymer (polymer 1 of Table 1) and for the methyl–vinyl-substituted homologues with various vinyl contents. [b] Reference 13 gives δ values for exactly alternating silphenylene–siloxane polymers in which substituents on the siloxanylene silicons were CH_3 and $(CH_2)_2CF_3$ groups. Other fluoroalkyl-substituted homologues have not been reported yet.

compare with ref 13), with the exception that the C_{10} absorption was somewhat shifted upfield relative to that reported for the methyl/3,3,3-trifluoropropyl-substituted silphenylene–siloxane homologue.[13] This result was probably caused by a strong influence of the more fluorinated $(CF_2)_5CF_3$ unit on that C_{10} carbon atom.

Polymer Transition Temperatures. The transition temperatures of all of the polymers prepared, as determined by differential scanning calorimetry, DSC, are listed in Table 4. As indicated by the data in this table, all of the exactly alternating silphenylene–siloxane polymers examined had glass transition temperatures between −76 and −37 °C. With the exception of highly fluorinated polymer 6, these values are all higher than that of the parent, all-methyl-substituted polymer 1. This result is, presumably, attributable to the effects of the larger substituents in most of the polymers of this series on T_g (except for the hydrido-substituted polymers).

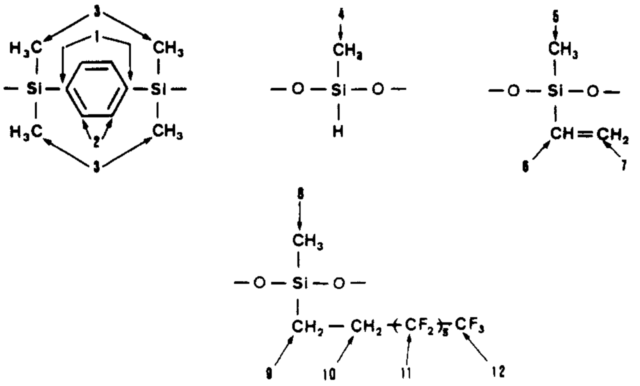


Figure 3. Numbering of carbon atoms in repeating units for the ^{13}C NMR shifts of the polymers in Figure 2 and Table 3.

Table 4. Transition Temperatures of Exactly Alternating Silphenylene–Siloxane Polymers of Table 1

polymer	T_g, °C	T_g(sc),[a] °C	T_m, °C[b]	ΔH_m, cal/g[b]
1	−62			
2	−54		45	1.06
3	−48		26	0.68
4	−37		33	1.57
5	−55	−36	39	0.85
6	−76	−38	91	n.d.

[a] Glass transition temperatures of the —$(CH_2)_2(CF_2)_5CF_3$ side chains. [b] Temperature, T_m, and enthalpy, ΔH_m, of melting, as determined by DSC.

The effect of hydrido substitution can clearly be seen by a comparison of the T_g values of polymers 4 and 5, in which a replacement of H and $(CH_2)_2CF_3$ groups of polymer 4 by considerably larger CH_3 and $(CH_2)_2(CF_2)_5CF_3$ units in polymer 5, resulted in an almost 20 deg decrease in the observed T_g value of the latter, which dropped from −37 °C for polymer 4 to −55 °C for polymer 5. However, it was somewhat more difficult to evaluate the effect of the hydrido groups on the T_g of other silphenylene–siloxane polymers examined. For example, compare the T_g of polymer 2 with that of other all-methyl polymers. The replacement of almost one-half of the methyl groups from the latter polymer by H units in polymer 2 (see Table 4) increased the T_g of polymer 2 by almost 10 deg with respect to the T_g of its methyl homologue. This result may again be taken as indicating that the replacement of larger side groups (methyl) by smaller hydrido units consistently leads to an increase in T_g.

As seen by the data in Table 4, the replacement of 85 mol % of the CH_3 groups of polymer 2 by the larger $(CH_2)_2CF_3$ groups in the silphenylene–siloxane polymer 3, caused an increase in the T_g value of the latter from −54 °C for polymer 2 to −48 °C for polymer 3. Surprisingly, a further increase in T_g resulted from complete replacement of all of the methyl and vinyl groups of polymer 3 by hydrido and trifluoropropyl units in polymer 4, so that T_g of the latter reached a value as high as −37 °C. One possible explanation for the effect of hydrido groups on T_g is that these substituents may be able to form hydrogen-bonded secondary networks with other polymer side groups, resulting in a decreased segmental mobility of these polymers and consequent increase in their T_g values.

With the possible exception of the 3,3,3-trifluoropropyl/hydrido-substituted silphenylene–siloxane polymer, polymer 4, the introduction of the fluoroalkyl side groups in the silarylene–siloxane polymers resulted in acceptably low glass transition temperatures for useful elastomers. Particularly noteworthy in that respect was the T_g of polymer 6 which was found to be as low as −76 °C.

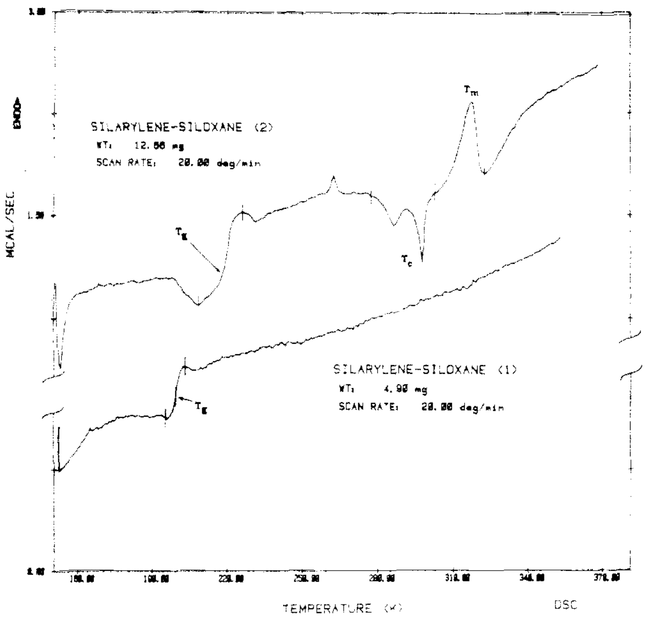


Figure 4. DSC thermograms of polymers 1 and 2 of Table 1.

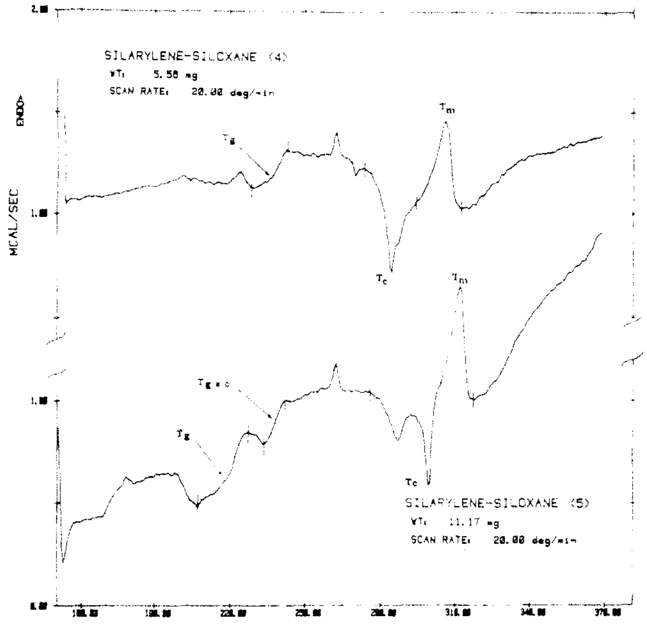


Figure 5. DSC thermograms of polymers 4 and 5 of Table 1.

As previously observed,[12] the vinyl groups also imparted a considerably lower T_g to their polymers.

As shown in the DSC thermogram in Figure 5, all of these polymers showed sharp and prominent endotherms at temperatures ranging from 26 to 91 °C. Endotherms of that type generally represent melting transitions, although in all cases, the amounts of thermal energy involved in these transitions were quite small, ranging from about 0.7 to about 1.6 cal/g. It would be very surprising if these polymers were capable of crystallizing because they are not expected to have stereoregular structures.

As seen from the data of Table 4, the endotherms in the thermograms of these polymers increased in temperature with the extent of fluorination, from 26 °C for the 3,3,3-trifluoropropyl-substituted polymer 3 to 33 °C for polymer 4. Further increases in the degree of fluorination associated with the placement of $(CH_2)_2(CF_2)_5CF_3$ groups in polymers 5 and 6 resulted in even more prominent endotherms, with a peak temperature as high as 91 °C for polymer 6. With the exception of the hydrido-containing polymer mentioned above, no other exactly alternating silarylene–siloxane polymer has been found to exhibit any tendency toward crystallization,[1,12] but no other explanation can be offered at this time to account for the observation of the endotherms.

In another unexpected observation, as seen in the data in Table 4 and Figure 5, polymers 5 and 6, which contained unusually long $(CH_2)_2(CF_2)_5CF_3$ units, also exhibited two glass transition temperatures, the second in both cases appearing at −37 °C. The transition may be attributed to a separate T_g of the extended tridecafluoro-1,1,2,2-tetrahydrooctyl substituents. If so, this would be the first report of a side chain T_g in a silarylene–siloxane polymer.[1,12]

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