Coherent Molecular Dynamics in Silarylene–Siloxane Polymers

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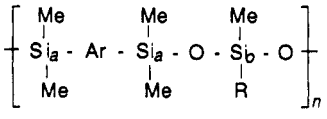
ABSTRACT: The molecular dynamics for seven silarylene–siloxane polymers, $Si_a(Me_2)ArSi_a(Me_2)OSi_o(Me)(R)_n$ (SSP), have been investigated by NMR, where Ar = *p*-phenylene (P), oxabis(*p*-phenylene) (PO), and *p,p'*-biphenylene (BP) and R = phenyl (Ph), vinyl (V), *n*-propyl (Pr), and methyl (Me). ^{29}Si spin–lattice relaxation times (T_1) were determined over a wide temperature range for Si_a and Si_o nuclei of the silarylene and siloxane, respectively. The two silicon nuclei in SSP having R = Pr share the same T_1 from low temperature to the temperature for $T_{1,min}$ ($\tau_c \approx \omega_o$); that is they move in unison in this regime. At higher temperatures their motions became decoupled. The SSP with R = Me exhibit coherent dynamics only at very low temperatures, which was disrupted at temperatures well below that for $T_{1,min}$. The Si_a and Si_o nuclei in SSP with R = V or Ph have different T_1 values at all temperatures, indicating that all the Si nuclei moved independently. T_1 measurements at different applied fields and frequencies suggested that the dipole–dipole interaction is the dominant relaxation mechanism.

Introduction

Poly(siloxanes) are important elastomers. Their superior low-temperature physical properties have been attributed to "crankshaft" motions in the backbone[2] with three or more repeating units undergoing displacement as one dynamic unit. However, the molecular structural requirements for the model are not known. Solid NMR[3] can measure the molecular motion of individual nuclei. ^{29}Si has 4.7% natural abundance, nuclear spin of $^1/_2$ and chemical shifts spanning more than 550 ppm, but Si has a negative gyromagnetic ratio and long spin–lattice relaxation time (T_1). Even though Si NMR has been used[4-6] to determine the structures of poly(silanes) and poly(siloxanes), the technique has yet to be applied to investigate their molecular motions.

Silarylene–siloxane polymers (SSP), such as the ones studied in this work, have the general structure



where Ar is an aromatic moiety, and subscripts a and o denote silicon atoms of the silarylene and siloxane repeating units, respectively. These SS polymers also possess excellent physicomechanical properties over a wide range of temperatures because of their unique combination of high thermal stability and low-temperature flexibility. These properties are influenced by the subsituents on the polymer backbone, which affect its mobility and determines its application. Many available techniques, such as dynamic mechanical thermal analysis (DMTA), dielectric relaxation, and several others, have been used to obtain knowledge about the mobility of such macromolecules.

The Si_a and Si_o nuclei in SSP have different chemical shift values, which makes it possible to monitor the relaxation behaviors of the two types of Si nuclei individually. If they move in unison, such as by a crankshaft-type model encompassing both Si_a and Si_o atoms, then they will have identical nuclear relaxation rates. Otherwise, Si_a and Si_o will exhibit different relaxation rates. The principal purpose of this research was to measure the ^{29}Si nuclear magnetic relaxations as a function of temperature and to determine the correlation times for a series of SSPs differing in R groups and Ar moieties. The results should shed light on the effects of both the rigid Ar moieties in the backbone and the type of R substituent on the dynamics of the macromolecules. Measurements were also made at different magnetic fields to elucidate the mechanism of ^{29}Si relaxation processes.

Experimental Section

The SSPs were synthesized by the procedure of Dvornic and Lenz.[7] The structures, molecular weights (MW), and glass transition temperatures (T_g) of the SSPs are summarized in Table I. The designation of SSP includes first the abbreviations for the Ar moiety (P, *p*-phenylene; PO, oxabis(*p*-phenylene); BP, *p,p'*-biphenylene) followed by the abbreviations for the R group (V, vinyl; Pr, *n*-propyl; Ph, phenyl; Me, methyl). The SSPs were purified by reprecipitating three times from chloroform solution with methanol.

^{29}Si solid-state NMR measurement was performed on a IBM 200-AF spectrometer (4.7-T magnetic field, ^{29}Si frequency 39.7 MHz) equipped with IBM Instruments solid accessories and a Doty Scientific multinuclear magic-angle spinning probe. A Bruker VT B-1000 temperature control unit was used to regulate the spinner gas and sample temperature to ±2 °C. The SSP sample was packed into a sapphire rotor fitted with axial-screw Vespel end caps. A 5.0-μs 90° pulse was used. The spinning rate was around 1 kHz. Measurements at higher frequency were made with a Varian 300-XL spectrometer (7-T magnetic field, ^{29}Si frequency 59.2 MHz), using a 16-μs 90° pulse on neat SSP packed in 10-mm sample tube. The pulse sequence for the spin–lattice relaxation measurement was an inversion–recovery method (180°–τ–90°). The relaxation time was obtained by fitting the data to a single exponential. The fitting results were in good agreement with the slope of ln $(1 - M(\tau)/M(\infty))$ versus τ plots. The chemical shifts are referenced to sodium 2,2-dimethyl-2-silapentane-5-sulfonate.

To ascertain that the SSP samples were sufficiently pure to give reliable spin–lattice relaxation times, the T_1 values of SSP-II(P, Pr) before and after reprecipitation were measured at room temperature and at 40 °C. The T_1 values are given in Table II. The room-temperature results had a ~10% fluctuation because the temperature control unit did not operate well near ambient temperature. In contrast, the data at 40 °C showed good reproducibility, indicating good sample quality. SSP-V(PO, V) was evacuated for 6 h then spun with N_2 gas. The spin–lattice relaxation times obtained before and after evacuation are also given in Table II. The results showed that oxygen did not affect the ^{29}Si relaxations in the SSP.

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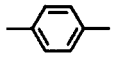
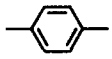
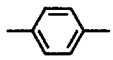
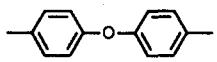
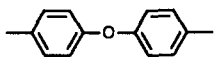
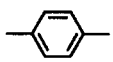
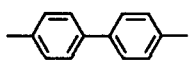
Table I
Physical Properties of Silarylene–Siloxane Polymers

designation	Ar	R	MW	T_g, °C
I(P, V)		$CH_2{=}CH_2$	140 000	−69
II(P, Pr)		n-C_3H_7	142 000	−65
III(P, Me)		CH_3	12 000	−62
IV(PO, Pr)		n-C_3H_7	60 000	−51
V(PO, V)		$CH{=}CH_2$	80 000	−34
VI(P, Ph)		C_6H_5	14 500	−32
VII(BP, Me)		CH_3	10 000	NA[a]

[a] NA, not available.

Table II
Effect of Sample Quality on Spin-Lattice Relaxation Rates

		T_1, s			
		Si_o		Si_a	
SSP	temp, °C	before	after	before	after
II(P, Pr)[a]	28	6.0	7.0	5.0	6.0
II(P, Pr)[a]	40	8.8	8.2	7.5	7.3
V(PO, V)[b]	28	10.3	10.2	6.9	7.3

[a] Before and after two reprecipitations from chloroform solution with methanol. [b] Before and after evacuation.

Table III
Chemical Shift Values for SSP

	chemical shift, ppm			chemical shift, ppm	
SSP	Si_o	Si_a	SSP	Si_o	Si_a
I(P, V)	−36.8	−4.9	V(PO, V)	−36.8	−4.9
II(P, Pr)	−23.95	−6.1	VI(P, Ph)	−35.6	−4.9
III(P, Me)	−22.7	−5.5	VII(BP, Me)	−22.7	−5.5
IV(PO, Pr)	−22.7	−4.9			

Results

Solid-state ^{29}Si NMR spectra were acquired by the cross-polarization mode at temperatures below the T_1 minimum ($T_{1,min}$). At higher temperatures the signal-to-noise ratios of cross-polarization spectra were poor; simple direct polarization spectra were recorded instead by using $\pi/2$ pulses. The two ^{29}Si resonances were well resolved with the Si_o resonating at higher field than Si_a. Above T_g, the NMR line width was narrow (~100 Hz) and independent of spinning rate. The result indicates that rapid tumbling of Si nuclei occurred with complete averaging of chemical shift anisotropy and dipole–dipole interactions. The ^{29}Si chemical shift values for the SSPs are given in Table III. The relaxation times were measured over a broad temperature range depending on the T_g of the SSP, always spanning both higher and lower temperatures than the T_1 minimum. The plots of T_1 versus temperature are given in Figures 1–7 for SSP-I to -VII. Table IV summarizes the temperature for $T_{1,min}$ and the values of $T_{1,min}$.

The relaxation times for SSP-I(P, V) were determined at two magnetic fields of 4.70 and 7.05 T. The data are plotted for both in Figure 1.

Discussion

Spin–Lattice Relaxation. NMR relaxation is caused by the fluctuation of local magnetic fields in the sample due to molecular motion. The local fields are modulated at various frequencies corresponding to motions of different molecular components. That motional component having a frequency close to the Larmor frequency of the magnetic nucleus under observation is most effective in relaxing it. The relaxation rate for isotropic motion is given by the following equations:[3]

$$T_1^{-1} = \alpha(\tau_c/1 + \omega_0^2\tau_c^2) \quad (1)$$

$$\tau_c = \tau_0 \exp(-E_a/kT) \quad (2)$$

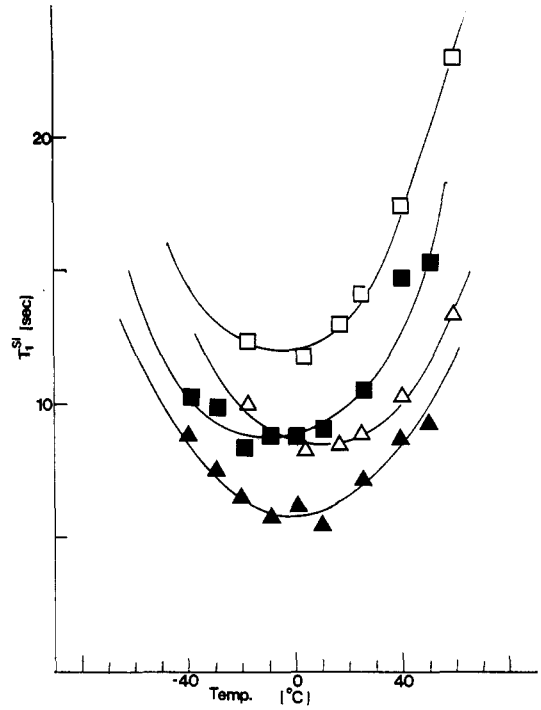


Figure 1. Plot of T_1 versus temperature for SSP-I(P, V). (□) Si_o; (△) Si_a; open symbols for 7.05 T and filled symbols for 4.7-T field.

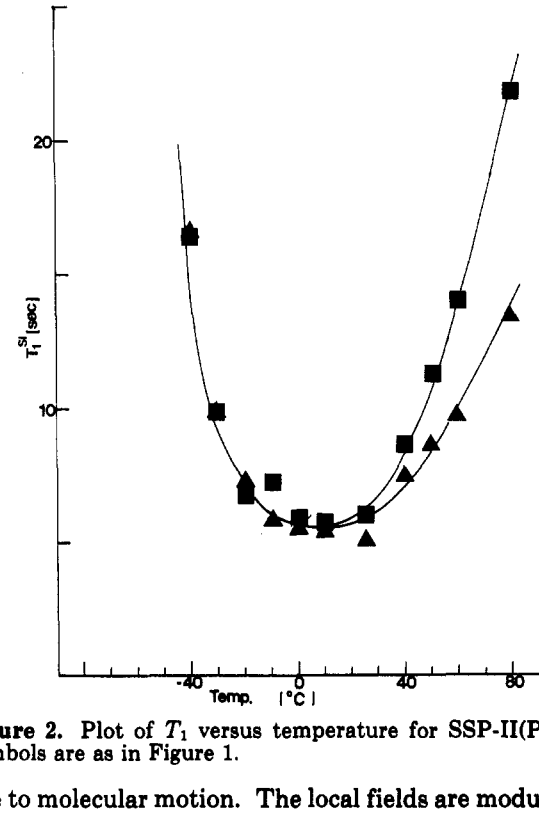


Figure 2. Plot of T_1 versus temperature for SSP-II(P, Pr). Symbols are as in Figure 1.

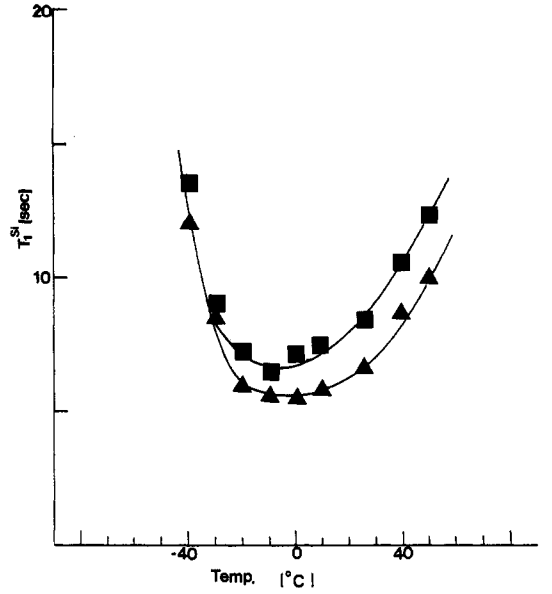


Figure 3. Plot of T_1 versus temperature for SSP-III(P, Me). Symbols are as in Figure 1.

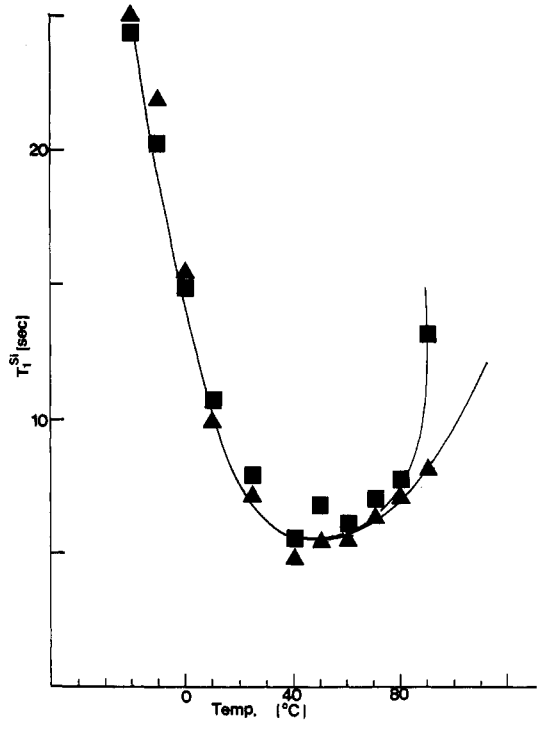


Figure 4. Plot of T_1 versus temperature for SSP-IV(PO, Pr). Symbols are as in Figure 1.

where α is the prefactor depending on the relaxation mechanism, ω_0 is the frequency of the applied field, τ_c is the correlation time, and E is the activation energy.

Parabolic curves are expected for plots of the relaxation time versus either τ_c or $1/T$. At the minimum, $\omega_0\tau_c = 1$, the molecule is moving at the same frequency as the applied field. The position of this minimum depends on the molecular size and applied field. Large molecules or high applied fields will shift the $T_{1,min}$ to a higher temperature as compared to smaller molecules or lower applied fields. The prefactor α affects the value of the relaxation time but not the position of its minimum. Because ω_0 is ~40 MHz, the kinds of motions that are effective in causing nuclear relaxations are torsion, rotation, and libration.

The quantities of interest are the T_1 values as a function of temperature and the temperature at which T_1 is

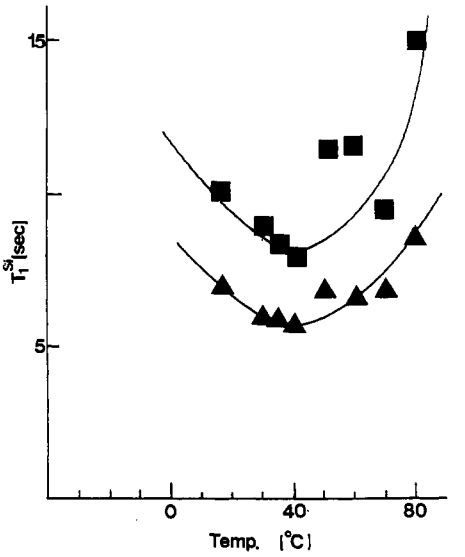


Figure 5. Plot of T_1 versus temperature for SSP-V(PO, V). Symbols are as in Figure 1.

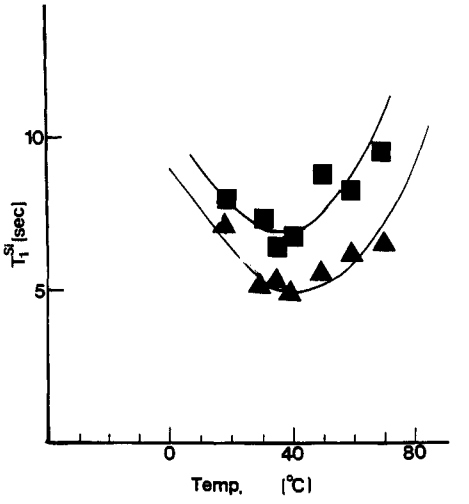


Figure 6. Plot of T_1 versus temperature for SSP-VI(P, Ph). Symbols are as in Figure 1.

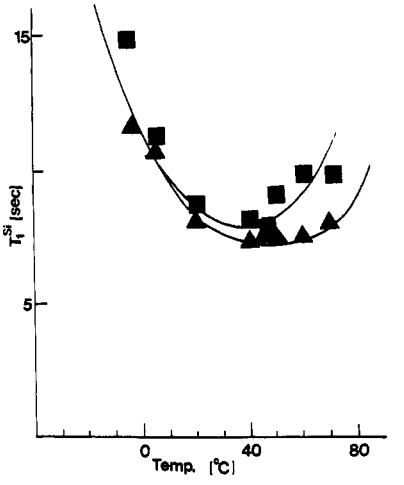


Figure 7. Plot of T_1 versus temperature for SSP-VII(BP, Me). Symbols are as in Figure 1.

minimum. Theoretical calculations of these parameters are still being developed and are model dependent. We are mainly interested in the relative values of these parameters for the two types of Si nuclei.

The T_1 versus temperature plots of the SSPs may be divided into two groups. In group A, the Si_o and Si_a atoms

Table IV
T_1 Data at Minimum

SSP	Si_o		Si_a	
	$T_{1,min}$, s	temp, °C	$T_{1,min}$, s	temp, °C
I(P, V)	8.9	−10	5.8	0
II(P, Pr)	5.6	10	5.5	10
III(P, Me)	7.1	0	5.5	5
IV(PO, Pr)	5.7	50	5.5	50
V(PO, V)	5.8	40	5.8	40
VI(P, Ph)	6.7	40	5.0	40
VII(BP, Me)	8.2	40	7.3	40

move in unison below a certain low temperature but move independently above that temperature. In group B, the motions of the two types of nuclei are not coupled at any temperature.

The group A behavior is best seen with Figure 4 for SSP-IV(PO, Pr). The T_1 values for Si_o and Si_a are the same up to approximately 60 °C then diverge above this temperature. Similarly, the plot for SSP-II(P, Pr) (Figure 2) indicates that this polymer has the same T_1 for Si_o and Si_a at temperatures below ~10 °C. At higher temperatures the Si_o has increasingly longer T_1 than Si_a.

The data for the other two group A SSPs, which have methyl groups for R, are shown in Figures 3 and 7, for SSP-III(P, Me) and SSP-VII(BP, Me), respectively. Both Si nuclei in the former have the same T_1 values only at tmperatures below −30 °C, while the $T_{1,min}$ of this SSP occurs at 0 °C. The latter polymer appears to have the same T_1 values for both Si at temperatures below ~5 °C; the $T_{1,min}$ of this SSP lies between 40 and 50 °C. The coherent motions of the Si_o and Si_a nuclei in these two SSPs are decoupled at temperatures well below $T_{1,min}$.

The other three SSPs, I, II, and VI, exhibit group B behaviors as shown in Figures 1, 5, and 6, respectively. These polymers, which contain either a phenyl or a vinyl R group, have T_1 values for Si_a that are significantly smaller than the T_1 values for Si_o nuclei over the entire temperature range. There is no evidence for any coherent dynamic entity involving more than one Si atoms.

Relaxation Mechanisms. The mechanism for ^{29}Si relaxation may involve dipolar–dipolar (DD), spin–rotational (SR), and chemical shift anisotropy (CSA) processes.[3-6] In some instances, the CSA contribution to T_1 has been estimated to be ~15% from the data of relaxation measurements at different magnetic fields.[6b] But in the case of silicate solution,[6c] no significant change of the spin–lattice relaxation was seen with increased magnetic field. The contribution of CSA to spin–lattice relaxation was investigated for SSP-I. The CSA contribution should be detectable through its dependence on B_o^2 (magnetic field). It is expected that the ^{29}Si relaxation rate will increase when B_o is increased from 4.70 to 7.05 T. Figure 1 shows that instead the relaxation rate was reduced slightly by the increase of B_o. This result suggests that CSA does not contribute significantly to T_1 in the case of SSP-I.

The SR component of T_1 is directly proportional to τ_c, and this mechanism is favored for small Si-containing molecules or Si-containing end groups in low molecular weight polymers, both at elevated temperatures. For instance, the relaxation of the silicon nuclei at the chain end of linear oligomeric poly(dimethylsiloxane)[6b,8] is dominated by the SR mechanism because of the free rotation of the trimethylsiloxyl group about its 3-fold axis. The silicon nuclei in the middle of the linear oligomeric poly(dimethylsiloxane) chain are relaxed primarily by the DD mechanism.[6b,8] The contribution of the DD processes to the overall relaxation can be obtained as previously described: $T_1(DD) = T_1(obsd)/\eta$, where η is the nuclear Overhauser enhancement factor, having a value of 2.53 for 100% ^{29}Si–H DD interaction. The same conclusions of SR and DD contributions to spin–lattice relaxations were reached in the study of poly(methylhydrosiloxane).[9]

The SSPs of this work have molecular weights of 10 000–145 000 (Table I). In these macromolecules the SR contribution to T_1 from the end group rotation is negligibly small. It has been shown[6b,8] previously for linear oligomeric poly(dimethylsiloxane) that the SR contribution became unimportant when the molecular weight exceeds 5000. In conclusion, the spin–relaxation mechanism of the SSPs is predominantly due to DD interactions. For this mechanism, the $T_{1,min}$ should shift to shorter conclusion times and higher temperatures when the frequency of the applied field was increased. Figure 1 showed that the $T_{1,min}$ of both Si_o and Si_a were shifted ~10 °C higher when the B_o was increased from 4.70 to 7.05 T, and the relaxation rates were reduced ~20% for both silicon nuclei.

Structure–Property Relationship. In the crankshaft model, several backbone atoms undergo translational displacement as one coherent dynamic entity. If the atoms are nuclear magnetic then those atoms in the same unit should relax at the same rate. Conversely, other atoms not belonging to this coherent dynamic unit would relax at different rates. The present SSPs offer ideal systems for the investigation of coherent molecular dynamics for reasons already given in the Introduction. Furthermore, the results presented above can shed light on the relationships between the structures of SSP and its molecular dynamics observed as T_1, $T_{1,min}$, and T_g.

Coherent dynamic units definitely exist in the group A SSPs, but they are absent in the group B SSPs. Since the coherent entity contains only a few repeat units, its formation should be independent of molecular weight. This is born out by the fact that the group A SSPs have molecular weights ranging from 10 000 to 142 000. The formation of coherent dynamic units is not strongly dependent on the nature of the Ar moiety, as evidenced by the fact that the group A polymers II–IV and VII contain P, PO, and BP in the silarylene units, respectively. Apparently these Ar groups are all sufficiently rigid to assist in motional correlation. However, the nature of the Ar group does strongly determine the length of the coherent dynamic unit at a given temperature and its temperature dependence, as well as the limiting temperature for the existence of the minimal unit comprising one silarylene–siloxane repeat unit. Above this limiting temperature, the T_1 values for the two types of Si atoms become different when all the bonds linking them are free to rotate. In the case of SSP-II and -IV, the complete decoupling of the motions of Si_o and Si_a occurs only at the temperature of $T_{1,min}$ when $\tau_c \approx \omega_o$. The coherent dynamic units in SSP-III and -VII are much weaker and more readily disrupted in comparison. The Si_o and Si_a nuclei began to move independently of each other at temperatures 30–40 °C below that for $T_{1,min}$. The differences may be associated with the steric bulk of the R group, which is a propyl in the case of SSP-II and -IV but is a methyl in the case of SSP-III and -VII.

The Si atoms exhibit no coupling of motions at all temperatures for the group B polymers SSP-II, -III, and -VI. Since the group A polymers can contain either P, PO, or BP as the Ar moiety, then the nature of the Ar moiety cannot be responsible for the absence of coherent dynamic entities in the group B polymers. It is probably the nature of the R group in the group B polymers (R = vinyl or phenyl) which makes them different from the group A

polymers (R = methyl or *n*-propyl). The chemical shift values in Table III are consistent with these structural differences. The Si_a nuclei in all the SSPs have nearly the same chemical shift values. On the other hand, the Si_o nuclei in the group A polymers are more shielded than they are in the group B polymers by ~13 ppm. This difference indicates that there is more donation of the lone-pair electrons on oxygen to the $d\pi$ orbital of Si_o in the group A polymers than in the group B polymers. This $p\pi$–$d\pi$ interaction can impart a rigidity to the polymer backbone to form coherent dynamic units. This effect is reduced in the cases of the group B polymers because of other electronic interactions between Si_o atom and the π system of the Ph or V group attached to it.

The $T_{1,min}$ occurs at 10 and 0 °C for SSP-II and -III, respectively. By laying Figure 2 on top of Figure 3, one can see that the data at the low-temperature regime are superimposable. The same is also true of Figures 4 and 7 for SSP-IV and -VII, which have temperatures for $T_{1,min}$ at 50 and 40 °C, respectively. The low-temperature relaxation data are most extensive for SSP-II and -IV. If one places Figure 2 above Figure 4 and shifts the temperature axis by 40 °C without shifting the T_1 axes, the data in the two plots are seen to be superimposable. These behaviors are consistent with the T_1–τ_c dependences for relaxation by DD interactions (eq 1). The observation of coherent dynamic units by NMR requires the structural entity to have stability comparable to the rotational correlation time of the macromolecule. The Ar group strongly influences τ_c of the SSP. The τ_c is much longer for Ar = PO or BP than it is for Ar = P as evidenced by the 30–40 °C higher temperatures for $T_{1,min}$ in the former SSP. A bulky R group also contributes toward a long τ_c as shown by the 40 °C higher temperature for $T_{1,min}$ of SSP-VI(P, Ph) than it is found for SSP-III(P, Me).

The SSPs have T_g values that are very different from the temperatures for $T_{1,min}$. When Si_a and Si_o have different minima, the $T_{1,min}$ values are higher than T_g by 79, 75, 63, 74, and 72 °C for SSP-I–III, -V, and -VI, respectively. In the case of SSP-IV(PO, Pr) the difference is 101 °C, probably because the Ar moiety is larger than for the other SSPs, which have P for Ar. The temperature differences are mainly attributable to the frequency of the motion, which is approximately 40 MHz for $\tau_c \approx \omega_o$, while the motions associated with T_g are of very low frequencies.

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