^{13}C NMR Investigation of Local Dynamics in Nonoriented Mesomorphic Polysiloxanes

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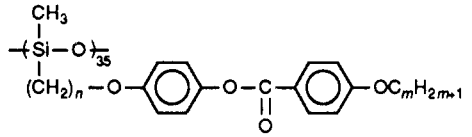
ABSTRACT: High-resolution solid-state ^{13}C NMR spectroscopy has been used to investigate the local dynamics of two side-chain liquid crystal polysiloxanes, one amorphous and one semicrystalline, both exhibiting a smectic A phase. Selective pulse sequences have been employed to accentuate the behavior of either the amorphous or the crystalline phases. From the line-shape study of the aromatic part of the ^{13}C NMR spectra recorded over a large temperature range, the rotation of the phenyl rings of the mesogenic core has been observed and characterized. There does not appear to be any difference in their dynamics in either the amorphous or crystalline phase, indicating that, in the crystalline regions, they undergo very localized motions that do not modify the organization of the centers of gravity of the phenyl rings. The motions of the methylene units of the spacer have been studied by determining the contact time necessary to obtain half of the maximum magnetization in cross-polarization experiments, $t_{1/2}$. These measurements have demonstrated that, for both polymers, the glass transition observed by DSC involves the polysiloxane backbone as well as the nearest spacer carbons. With regard to the glassy smectic A phase made by the mesogenic groups, its glass transition is not observed by DSC but is reflected by the increase in mobility of the methylene carbon atom adjacent to the mesogenic unit.

High-resolution solid-state ^{13}C NMR spectroscopy has become a powerful tool for studying molecular order and dynamics in mesomorphic polymers. Results obtained by using proton dipolar decoupling on static samples of liquid crystal polysiloxanes ($P_{n,m}$) of general formula



have been reported in a previous paper.[1] The ^{13}C chemical shift dependence on temperature observed in the mesophases has clearly shown that, when slowly cooled from the isotropic phase, static samples of the $P_{n,m}$ polysiloxanes orient in the magnetic field. The apparent variations of the order parameter along the side chains have demonstrated the existence of several motional processes occurring in the oriented mesophases. Among them are the trans–gauche conformational changes in the spacer, the internal rotation of the phenyl rings about their symmetry axis, the motion of the COO plane associated with the β_2 transition of polysiloxanes, and the overall rotation of the whole side group about its molecular axis.[1]

The subject of the present paper is the ^{13}C NMR investigation of local dynamics in nonoriented $P_{n,m}$ samples at temperatures below and above the glass transition temperature, T_g. For this purpose, samples were packed as nonoriented powders in rotors and studied by using the well-known techniques of proton dipolar decoupling and magic-angle spinning.[2] Among the number of NMR parameters that are sensitive to molecular motions, the line-shape modifications as a function of temperature and the intensities of the spinning sidebands[3,4] were chosen to follow the dynamics of the mesogenic cores, whereas the local motions of the spacer were studied by measuring the $t_{1/2}$ contact time necessary to obtain half of the maximum polarization in cross-polarization experiments using very short contact times.[5,6] The spectrum line shapes are very sensitive to site-exchange phenomena such as ring flips.[7] The spinning sidebands result from the part of the chemical shift anisotropy that is not averaged by the spinning of the sample or by the existing molecular processes. The $t_{1/2}$ contact time technique permits one to determine the strength of individual ^1H–^{13}C dipolar couplings, whose values depend on the averaging effect of molecular motions.

The mesomorphic polysiloxanes chosen for this study are the $P_{3,1}$ polymer, which shows only a glassy smectic A phase below T_g, and the $P_{5,1}$ polymer, which is a semicrystalline material and has both crystalline and glassy smectic A regions at temperatures below T_g.[8] For the latter polymer, use of NMR selective pulse sequences will allow us to accentuate either the more mobile amorphous regions or the rigid crystalline parts.[9–11] Comparison of results obtained from these two polysiloxanes should provide a deeper insight of the motional processes occurring in the different phases as a function of temperature.

Experimental Section

4-Butoxyphenyl 4-methoxybenzoate was obtained by classical reaction between 4-methoxybenzoyl chloride and 4-butoxyphenol in dry pyridine. The product was purified by chromatography on silica gel with ether (3)/hexane (7) as eluent.

The polysiloxanes $P_{n,m}$ were synthetized at C.R.P.P.[8] The number of monomer units per chain is 35. Samples were used as nonoriented powders. The $P_{3,1}$ sample is amorphous. The $P_{5,1}$ sample is semicrystalline. DSC traces of the $P_{5,1}$ sample show a small base shift corresponding to the glass transition phenomenon and a high enthalpy of melting (8 J/g), independent of the thermal history of the sample. In these semicrystalline side-chain liquid crystal polymers, it is generally recognized[12] that there is a segregation of the polysiloxane main chain and of the mesogenic groups, the polysiloxane main chain belonging to the amorphous phase and the mesogenic groups yielding the organized regions. Therefore, DSC results obtained from the $P_{5,1}$ polymer suggest that the majority of the mesogenic groups

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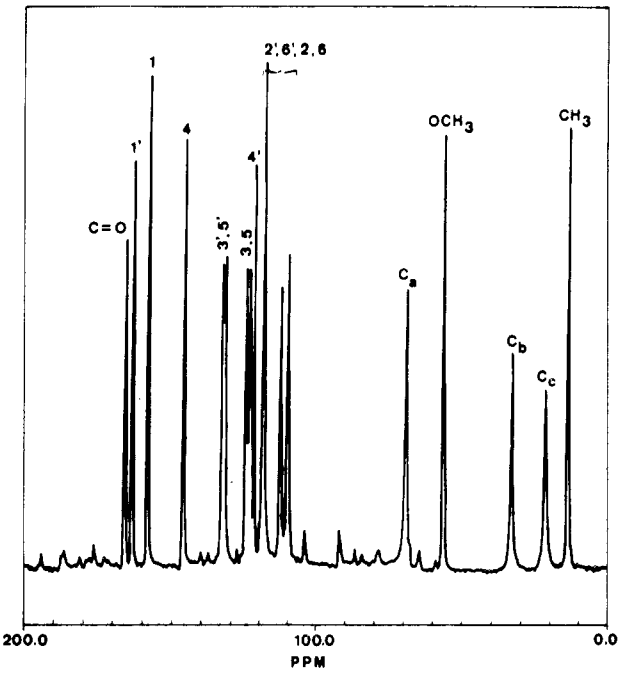


Figure 1. MAS/CP/DD ^{13}C NMR spectrum of the (4,1) molecule recorded at room temperature by using the TOSS[15] sequence and a contact duration of 1 ms.

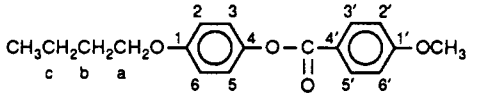
are involved in the crystalline phase.

High-resolution solid-state ^{13}C NMR experiments using proton dipolar decoupling (DD) and magic-angle spinning (MAS) were conducted at 75 MHz with a Bruker CXP 300 spectrometer, with quadrature detection and a single rf coil, which was double-tuned for both ^{13}C and ^{1}H. Experiments were performed on magic-angle spinning samples contained in Al_2O_3 rotors. The spinning speed was of the order of 4 kHz. The pulse sequences consisted either of a single carbon pulse followed by proton dipolar decoupling or of a cross-polarization (CP) proton dipolar decoupling sequence. The matched spin-lock cross-polarization transfers were carried out with ^{13}C and ^{1}H magnetic field strengths of 64 kHz. Spin-temperature inversion techniques allowed the minimization of baseline noise and roll.[13] Flip-back[14] was also used to shorten the delay between two successive pulse sequences.

$t_{1/2}$ values have been obtained from the variation of the intensities $S(t)$ of the spacer carbon lines in cross-polarization experiments as a function of the contact duration t. At room temperature, the whole curve $S(t) = f(t)$ has been determined, including a precise evaluation of the maximum magnetization, S_{max}, that can be gained from cross-polarization. For the other temperatures under investigation, in order to limit the number of experiments, we have assumed that spectra obtained with a 1-ms contact time are representative of the maximum magnetization, S_{max}, that can be gained from cross-polarization and $t_{1/2}$ values have been deduced from intensity ratios, $S(t)/S(1ms)$. However, when the mobility of the spacer is going from near rigid to some form of motionally averaged second moment, the spectral density of motions in the midkilohertz region can become appreciable. In that case, variations in proton spin–lattice relaxation times in the rotating frame $T_{1\rho}$ can modify the cross-polarization dynamics and the 1-ms cross-polarization amplitude may be somewhat less than the maximum magnetization, S_{max}, that can be gained from cross-polarization. Then, the $t_{1/2}$ values as determined from intensity ratios $S(t)/S(1ms)$ are an underestimation of the true $t_{1/2}$ values. Since they are underestimated, when starting from the rigid-lattice behavior and increasing temperature, any increase in the $t_{1/2}$ values determined from intensity ratios $S(t)/S(1ms)$ is all the more indicative of an onset or an increase in the spacer mobility, which is the information one is looking for in the $t_{1/2}$ experiments. Besides, the kind of relative error involved in these $t_{1/2}$ measurements has been estimated to less than 5% from proton $T_{1\rho}$ determinations on both polysiloxanes in the temperature range 25–60 °C. It is independent of the spacer carbon under consideration since there is no noticeable proton $T_{1\rho}$ variation along the spacer.

Results and Discussion

I. The (4,1) Molecule. The molecule (4,1) with the following formula



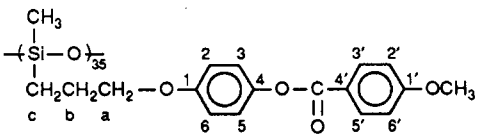
has the following phase transition temperatures:

$$\text{crystal} \overset{74\,^\circ\text{C}}{\leftrightarrow} \text{nematic} \overset{81\,^\circ\text{C}}{\leftrightarrow} \text{isotropic}$$

In the crystalline state, the chemical shifts of its aromatic carbons should be quite close to those of the corresponding carbons of the $P_{n,m}$ polysiloxanes in the absence of molecular motions.

The high-resolution solid-state ^{13}C NMR spectrum of the (4,1) molecule was recorded at room temperature by using the techniques of proton dipolar decoupling, magic-angle sample spinning, and cross-polarization as well as the TOSS sequence, which leads to the suppression of spinning sidebands.[15] The spectrum and line assignments are shown in Figure 1. For carbons 2, 6, 2′, and 6′, they are based on data obtained on *p*-dimethoxy- and *p*-diethoxybenzene by Hohener.[16] These chemical shifts and line assignments are in general agreement with those reported for $P_{n,m}$ polysiloxanes in the isotropic phase.[1] However, for each carbon pair in the ortho position with respect to phenyl substituents, the spectrum of the crystalline (4,1) molecule presents two peaks, whereas in the isotropic phase of the polymer only one peak is observed. For example, there is only one line for carbons 3′ and 5′ in the isotropic phase of polysiloxanes and there are two lines in the spectrum of the crystalline (4,1) molecule. The same pattern is observed for the 2,6, 2′,6′, and 3,5 carbon pairs, each of them yielding two lines in the spectrum of the (4,1) molecule. The splittings of the 2,6 and 2′,6′ are such that one resonance of each pair is found near 118 ppm in Figure 1, whereas the other resonances of these pairs are found near 110 and 113 ppm. This difference in the behavior of the isotropic and crystalline phases can be easily interpreted in terms of differences in the mobility of the aromatic rings. In the crystalline phase of the (4,1) molecule, phenyl rings have a rigid-lattice behavior and carbons in the ortho position with respect to the ring substituents, which have distinct environments, are magnetically inequivalent: they yield two lines on the spectrum. On the other hand, in the isotropic state, the aromatic rings of the polymer are freely rotating about their para axis and the ortho carbons are rendered equivalent by the motion. This free rotation results in the observation of only one peak for each pair of ortho carbons for correlation times of the phenyl rotation much shorter than $1/\delta\omega$, where $\delta\omega$ is the separation in frequency units of the two lines in the rigid-lattice spectrum.

II. The $P_{3,1}$ Polysiloxane. The $P_{3,1}$ polysiloxane



has the following phase transition temperatures:[8]

$$T_g = 15\ ^\circ\text{C};\ \text{smectic A} \overset{T = 119\,^\circ\text{C}}{\leftrightarrow} \text{isotropic}$$

This polysiloxane does not show any melting phenomenon. Therefore, below the glass-transition temperature,

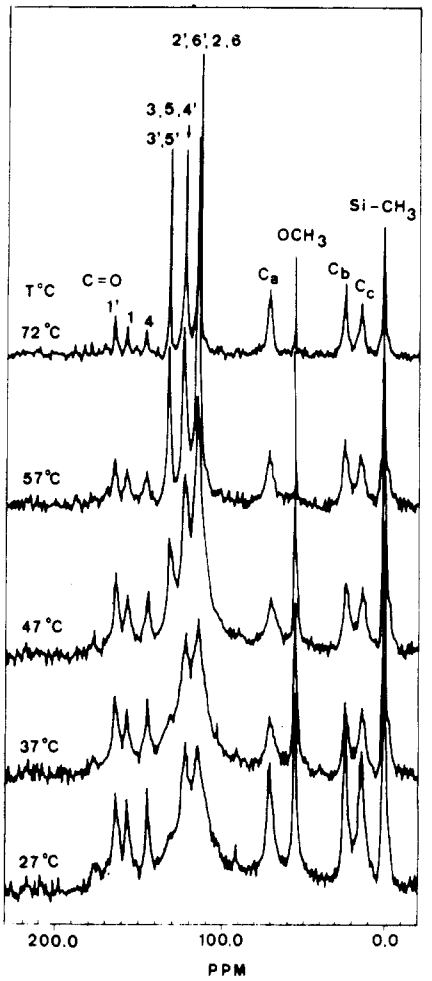


Figure 2. Variable-temperature MAS/CP/DD ^{13}C NMR spectra of the $P_{3,1}$ polysiloxane (contact duration, 1 ms).

T_g, its behavior is characteristic of a glassy smectic A polymer.

II.1. Line Shape of the Aromatic Carbon Spectra. The high-resolution solid-state ^{13}C NMR spectra of the nonoriented $P_{3,1}$ polymer, recorded at different temperatures in the range 27–72 °C by using the techniques of proton dipolar decoupling, magic-angle sample spinning, and cross-polarization (t_{cp} = 1 ms), are shown in Figure 2. In the range of temperature investigated, peaks corresponding to aromatic carbons do not show any visible splitting: to each pair of ortho carbons (2,6; 2',6'; 3,5; 3',5') corresponds only one line whose chemical shift does not vary with increasing temperature. Lines are relatively broad at temperatures in the range 27–47 °C and more narrow at temperatures higher than 47 °C. Spectra recorded at 67 and 72 °C have a resolution sufficient to separate the line for carbons 2 and 6 from that for carbons 2' and 6'. Spectra given in Figure 3 show that the chemical shift of each of these peaks is the half-sum of the chemical shifts of the individual corresponding lines observed in the crystalline (4,1) molecule spectrum. These line shapes as well as their dependence on temperature are typical of an exchange of the ortho carbons between their two equilibrium positions. Motions responsible for that exchange consist either of jumps of the phenyl rings covering 180° angles about the para axis or of rotational diffusion. Therefore the whole set of spectra can be interpreted in terms of phenyl ring motion: at temperatures in the range 27–47 °C, the phenyl rings are involved in a motion that becomes faster at higher temperature. This result can be analyzed in a more detailed way by means of chemical exchange theories.[7,17]

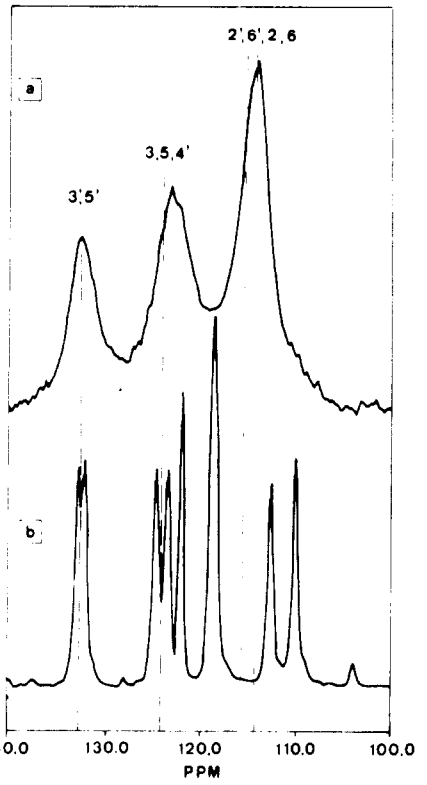


Figure 3. MAS/CP/DD ^{13}C NMR spectra of the aromatic carbons of (a) the $P_{3,1}$ polysiloxane at 52 °C and (b) the (4,1) molecule at room temperature.

The precise line-shape simulation of exchange phenomena in polymers in a large temperature range is a difficult task. Calculations have been performed by Garroway et al. for the phenyl flip motion of epoxy resins under the following simplifying assumptions: (i) line broadenings due to residual ^1H–^{13}C dipolar interactions or to chemical shift anisotropies, which are not fully averaged by the spinning of the sample, are negligible under the conditions of the experiments; (ii) a Lorentzian description of the line shape is appropriate; (iii) elementary motions of each phenyl ring are assumed to be 180° ring flips about the para axis.[7] As regard the ring flip process, these authors have used different motional models, including a single correlation time model, and a homogeneous distribution of correlation times as well as an inhomogeneous one. For the liquid crystalline polymers under study, most of these assumptions are obviously oversimplifications at low temperatures: line broadenings arising from residual tensorial interactions may no longer be negligible. There may exist a large distribution of chemical shifts of static origin. Besides, as suggested by the line shape and broad base of the aromatic carbon lines at low temperature, there most probably exist a wide inhomogeneous distribution of correlation times, which also implies that the Lorentzian description of the individual lines is inappropriate. However, at temperatures higher than 47 °C, the lines are much more narrow and well-resolved, and their shape can be reasonably approximated by a Lorentzian. These results indicate that the line broadenings arising from a large static distribution of isotropic chemical shifts, residual tensorial interactions, and inhomogeneous distribution of correlation times are strongly reduced at temperatures higher than 47 °C. Therefore, we have determined the correlation times for the ring motion only at temperatures higher than 47 °C, and we have used the simplifying assumptions (i–iii) listed above. Besides, in the absence of information from other techniques, we have assumed that the phenyl ring flips

Table I
Exchange Parameters Used in the Line-Shape Simulations

carbon	$\delta\omega/2\pi$, Hz	T_{2A}, ms	T_{2B}, ms
C2′,6′	481	6.4	7.5
C2,6	642	7.4	8.4

are described by a single correlation time. Although still oversimplified, in the temperature range investigated, these simulations have proved relevant to represent the major part of the line corresponding to carbons 2, 6, 2′, and 6′, which have the highest chemical shift difference in the rigid-lattice behavior and thus are the most precise. Besides, they allow the comparison of our data with results obtained by other authors or on different polymers under the same assumptions.

Under the above assumptions, for an exchange between two sites, A and B, with equal populations but with unequal relaxation times, T_{2A} and T_{2B}, the line shape is given by the following equation:[7,17]

$$M(\omega) = \frac{-2\omega Y + (\xi^{-1} + \tau_c^{-1})X}{X^2 + Y^2} \quad (1)$$

where

$$X = (\delta\omega/2)^2 - \omega^2 + (2\tau_c\xi)^{-1} + (T_{2A}T_{2B})^{-1}$$

$$Y = (\delta\omega/2)(T_{2B}^{-1} - T_{2A}^{-1}) - \omega(\xi^{-1} + \tau_c^{-1})$$

and

$$\xi^{-1} = T_{2A}^{-1} + T_{2B}^{-1}$$

$\delta\omega$ is the isotropic chemical shift difference, and resonance offset ω is measured from the center of the two lines A and B. The lifetime of each site, τ_c, is equal to the correlation time for 180° flips of the phenyl ring. As assumed above, the motion of each ring is described by only one correlation time.

Values of $\delta\omega$, ω, T_{2A}, and T_{2B} have been deduced from the spectrum of the model molecule (4,1) shown in Figure 1. They are listed in Table I and have been assumed to be independent of temperature. The constancy of both $\delta\omega$ and ω in the temperature range under investigation is corroborated by the fact that line shapes in the fast-exchange limit are well represented by a Lorentzian with a relaxation time 2ξ.

The temperature dependence of the correlation times τ_c in $P_{3,1}$ as determined by the simulations is shown in Figure 4. An approximate value of the activation energy of the ring motion, E_a, has been estimated from the correlation time dependence in the temperature range investigated. It is equal to 75 ± 10 kJ/mol, of the same order of magnitude as the activation energy calculated by Garroway et al.[7] (E_a = 50 kJ/mol) for the ring motion in epoxy resins under the same assumptions.

II.2. Spinning Sideband Intensities. The spinning speed used for obtaining the high-resolution solid-state ^{13}C NMR spectra shown in Figure 2 is of the order of 4000 Hz. Small spinning sidebands are observed for all the protonated aromatic carbons. The signal-to-noise ratio is not sufficient to detect the spinning sidebands associated with the unprotonated aromatic carbons. As an example, variation as a function of temperature of the intensity ratio of the spinning sideband of order +1 with respect to the corresponding main line, I_{+1}/I_0, is shown for the 3, 5, and 4′ carbon line in Figure 5. This ratio is a decreasing function of temperature. From a qualitative point of view, this result is consistent with a more and more efficient motional modulation of the chemical shift anisotropy by phenyl ring flips. At the highest temperatures under investigation the I_{+1}/I_0 ratio approaches the theoretical limit (≈0.025), which can be calculated for carbons 3 and 5 for fast flips of the phenyl rings by using the chemical shift anisotropies listed in ref 1 and plots calculated in ref 4.

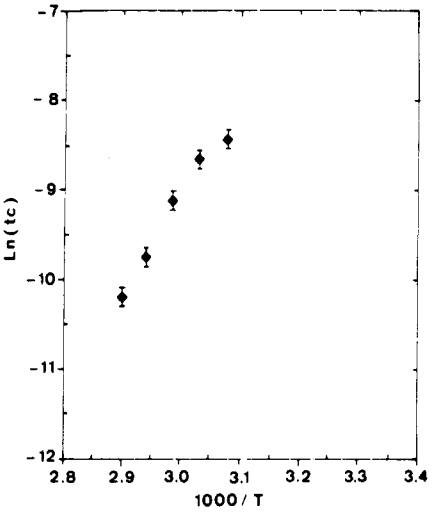


Figure 4. Temperature dependence of the correlation times τ_c of the ring motion determined from the line-shape analysis of the $P_{3,1}$ polysiloxane.

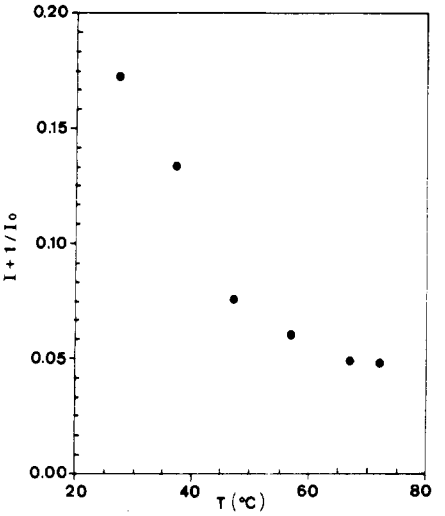


Figure 5. Temperature dependence of the intensity ratios I_{+1}/I_0 determined from the 3, 5, and 4′ carbon line of the $P_{3,1}$ polysiloxane.

II.3. Aliphatic Carbon Lines. The line assigned to the CH_3Si carbon shows a wide and complex structure in the 27 °C spectrum given in Figure 2. At temperatures above 27 °C, a narrower but still complex pattern is observed whose shape does not vary on increasing temperature. This line shape most likely corresponds to configurational dispersion arising from main-chain tacticity effects. The atactic nature of the $P_{n,m}$ polymers has been checked by solution ^{29}Si NMR measurements.[18]

In the temperature range under study, the OCH_3 group at the extremity of the $P_{3,1}$ side chain has a narrow line at 55.5 ppm with respect to the TMS resonance. The width of this peak is smaller than the width of the other aliphatic lines, which precludes the existence of conformational isomers of the C–O–C bonds frozen at the temperatures of the study. Moreover, the rapid rotation of the CH_3 group about its symmetry axis should have a frequency much higher than the frequencies that induce a strong motional line broadening ($\sim 10^6$ Hz).

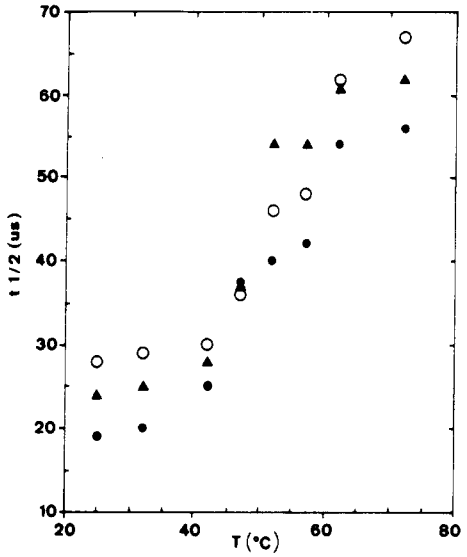


Figure 6. Temperature dependence of the $t_{1/2}$ contact times of the CH_2 (a) (●), CH_2 (b) (▲), and CH_2(c) (○) carbons of the $P_{3,1}$ spacer.

At 27 °C, the lines of the methylene carbons of the spacer are relatively intense. At temperatures above 27 °C, these resonances become weaker and wider. Both observations reflect the increasing mobility of the spacer, which decreases the cross-polarization efficiency and simultaneously induces a linebroadening arising from motional modulation of the ^1H-^{13}C dipolar interaction.

II.4. Local Dynamics of the Spacer. For carbons strongly coupled to protons, local motions can be investigated by means of cross-polarization experiments using very short contact times.[5,6] Such experiments lead to the determination of the square of the ^1H–^{13}C dipolar interaction, $\langle b^2 \rangle$, which is related to the contact time, $t_{1/2}$, necessary to obtain half of the equilibrium magnetization:

$$\langle b^2 \rangle^{1/2} = \pi / n^{1/2} t_{1/2} \qquad (2)$$

where n is the number of protons directly bound to the carbon of interest. Assuming that the C–H bond length is 1.09 Å, calculated $t_{1/2}$ values for a rigid lattice are equal to 28 and 20 μs for a CH and a CH_2 carbon, respectively. Experimental $t_{1/2}$ values longer than the rigid-lattice values are a clear indication of motional modulation of the ^1H–^{13}C dipolar interaction by motions with frequencies higher than 10^5 Hz.

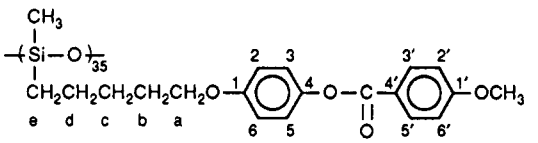
The $t_{1/2}$ variations as a function of temperature are shown in Figure 6 for the different CH_2 carbons of the $P_{3,1}$ spacer. At room temperature, the CH_2(a) carbon, which is adjacent to the mesogenic group, has a 19-μs $t_{1/2}$ value, equal to the rigid-lattice CH_2 $t_{1/2}$: therefore, this carbon does not undergo any molecular motion in the $t_{1/2}$ frequency domain at room temperature. On the other hand, CH_2(b) and CH_2(c) carbons have longer $t_{1/2}$ values of 24 and 28 μs, respectively, which indicate the existence of molecular motions involving the ^{13}C–^1H internuclear vectors. Moreover, for this three-carbon spacer, as indicated by the longer $t_{1/2}$ value, the CH_2(c) group adjacent to the polysiloxane main chain undergoes motions of amplitude larger than those of the CH_2(b) unit.

On increasing temperature, the increase in $t_{1/2}$ is first observed at 40 °C, indicating an increase in the amplitude and/or frequency of molecular motions. $t_{1/2}$ then increases progressively in the temperature range under investigation. Whatever the temperature, the CH_2(a) carbon, next to the mesogenic core, is the least mobile carbon in the spacer. On the other hand, CH_2(b) and CH_2(c) carbons show similar $t_{1/2}$ behavior on increasing temperature.

In order to interpret these results in terms of local motions, a model based on conformational jumps between trans and gauche± positions has been considered. In the limit of fast isolated conformational jumps between trans, gauche+, and gauche– positions on the valence cone, the ratio of the motionally averaged second moment to the second moment under rigid-lattice conditions is equal to 1/3.[19] For the methylene carbons of the polysiloxanes under study, if all the carbons of the species considered are involved in such conformational jumps, then the calculated $t_{1/2}$ values will be of the order of 33–35 μs. Comparison between calculated values and experimental ones (Figure 6) shows that at temperatures below 40 °C, the CH_2(a) group, next to the mesogenic core, displays rigid-lattice behavior. In this temperature domain, the CH_2(b) and CH_2(c) units have a reduced mobility consistent with either librations or isolated conformational jumps of only a small number of bonds in the sample. Above 45 °C, the motional amplitude of the different groups is significantly increased. Experimental $t_{1/2}$ values can then be interpreted in terms of larger amplitude modes, such as correlated conformational jumps, that progressively spread over the whole sample.

It must be noticed that there is a 30° difference between the glass transition temperature as measured by DSC and the temperature for which the amplitude of local motions as observed by NMR begins to increase. This difference is due to the fact that $t_{1/2}$ values are sensitive to relatively high frequency modes (>10^5 Hz). By taking into account the temperature shift between T_g as measured by DSC and T_g as observed by NMR in the $t_{1/2}$ frequency domain, one is led to the conclusion that, for the amorphous $P_{3,1}$ polymer, the increase in the amplitude and/or frequency of the spacer motions at T_g + 30° can be assigned to the increase in mobility associated with the glass transition phenomena of the main chain.

III. The $P_{5,1}$ Polysiloxane. The chemical formula of the $P_{5,1}$ polysiloxane is



The phase transition temperatures are the following:[8]

$$T_g = 4\ °C;\ \text{crystal} \overset{T=71\ °C}{\leftrightarrow} S_A \overset{T=122\ °C}{\leftrightarrow} I$$

The $P_{5,1}$ polymer is a semicrystalline material that has both crystalline and glassy smectic A regions at temperatures below T_g. DSC traces strongly suggest that a high amount of the mesogenic groups belongs to the crystalline phase.

In order to investigate the local dynamics of this semicrystalline polymer in the nonoriented state at temperatures between T_g and the melting point (71 °C) we have used high-resolution solid-state ^{13}C NMR spectra obtained either from the cross-polarization technique or from a single ^{13}C pulse followed by proton dipolar decoupling.[9-11] In the former experiment, the more mobile parts of the sample are discriminated against; i.e., the more organized regions are preferentially observed. This effect is still stronger for very short contact times in the range 20–50 μs. On the other hand, in the second series of experiments, when the delay between two pulse sequences is short enough, carbons with a short T_1, i.e., carbons belonging to

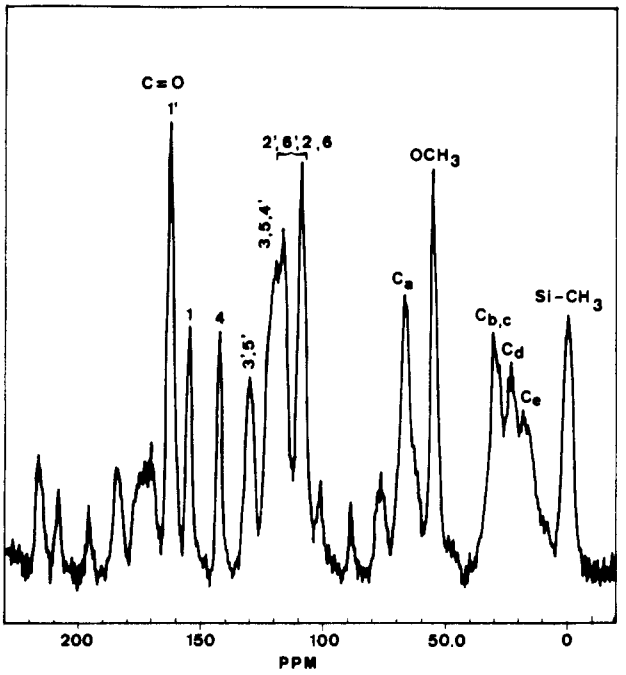


Figure 7. MAS/CP/DD ^{13}C NMR spectrum of the $P_{5,1}$ polysiloxane at −98 °C (contact duration, 1 ms).

the more mobile and thus less ordered regions of the sample, are accentuated in the spectra.

III.1. Line Shape of the Aromatic Carbon Spectra. The high-resolution solid-state ^{13}C NMR spectra of the nonoriented $P_{5,1}$ polymer, recorded at −98 °C, by using the techniques of proton dipolar decoupling, magic-angle sample spinning, and cross-polarization (t_{cp} = 1 ms), are shown in Figure 7. The line assignments are summarized in this figure. Lines are broader than those observed for the crystalline (4,1) molecule. However, the observed chemical shifts are quite similar, and in the poorly resolved regions, the polymer spectrum may be considered to be the envelope of spectrum of the (4,1) molecule. The pattern corresponding to carbons 3′ and 5′ is broad and its line shape suggests that these two carbons are not rendered equivalent by the phenyl ring motion. The same result is observed for carbons 3 and 5. On the other hand, carbons 2′ and 6′ clearly yield two lines, which is also the case for carbons 2 and 6, whose lines overlap with those of carbons 2′ and 6′. The similarity of the polymer chemical shifts with those of the model molecule, as well as the splitting of the lines for the ortho carbons, indicate that, in the $P_{5,1}$ polymer, the phenyl ring motion about the para axis either does not occur or is very slow at low temperatures.

Variable-temperature, high-resolution solid-state ^{13}C NMR spectra of nonoriented $P_{5,1}$, obtained by using a 1-ms contact time, are shown in Figure 8. At 27 and 37 °C, lines corresponding to carbons 3,5 and 3′,5′ are relatively broad. The carbon 2, 6, 2′, and 6′ pattern is no longer composed of two lines but appears as a single peak located at the center of the −98 °C spectrum lines. As discussed for the $P_{3,1}$ polysiloxane, these line shapes can be interpreted in terms of an exchange of the ortho carbons between their two equilibrium positions. At higher temperatures (47, 57, and 67 °C), the increase in the motional frequency induces the narrowing, at constant chemical shift, of the single peak corresponding to each pair of ortho aromatic carbons. At 67 °C, the resolution is sufficient to separate the line of carbons 2 and 6 from that of carbons 2′ and 6′ on the original spectrum.

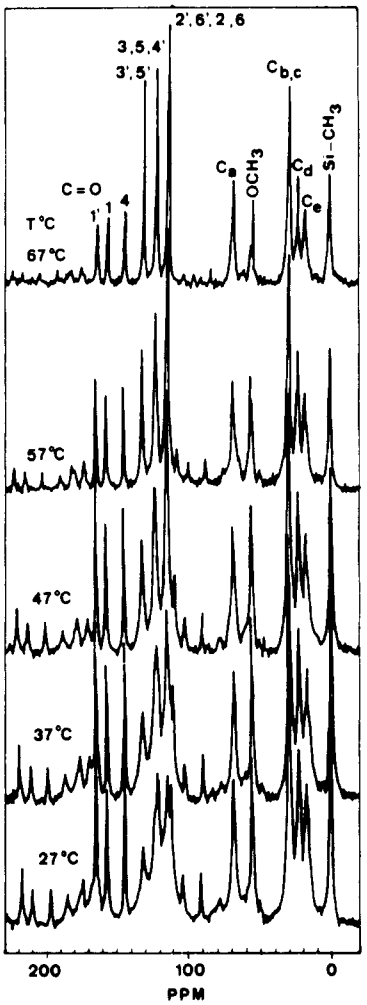


Figure 8. Variable-temperature MAS/CP/DD ^{13}C NMR spectra of the $P_{5,1}$ polysiloxane (contact duration, 1 ms).

^{13}C NMR spectra of the $P_{5,1}$ sample in the range 27–67 °C, recorded by using very short contact times, are shown in Figure 9. Under these conditions, only protonated carbons can acquire some magnetization, whereas the lines assigned to aromatic quaternary carbons are not visible in the spectra. More interestingly, this experiment favors the observation of the more rigid regions. Therefore, in the case of the $P_{5,1}$ sample in which the mesogenic groups are predominantly in the crystalline phase, the observed line shapes in cross-polarization experiments with very short contact times are representative of the crystalline phase behavior. Besides, the line shapes of protonated aromatic carbons, which are very sensitive to site exchange, have very similar widths in the 1-ms contact time spectra and in the very short contact time spectra. Therefore, the 1-ms contact time spectra of the aromatic carbons can also be considered to be mainly representative of the behavior of the more ordered regions of this semicrystalline material. This conclusion could also have been expected from the high degree of crystallinity of the mesogenic groups in the $P_{5,1}$ sample.

^{13}C NMR spectra of the $P_{5,1}$ sample, obtained from the single ^{13}C pulse sequence by using a 2-s repetition time between two successive pulse sequences, are shown in Figure 10. They accentuate carbons with greater-than-average mobility, i.e., protonated carbons located in the less ordered regions. However, it must be noticed that although other carbons (quaternary carbons and crystalline carbons) have relaxation times T_1 too long to give rise to intense spectrum peaks, they may also contribute in some lesser extent to the spectra.

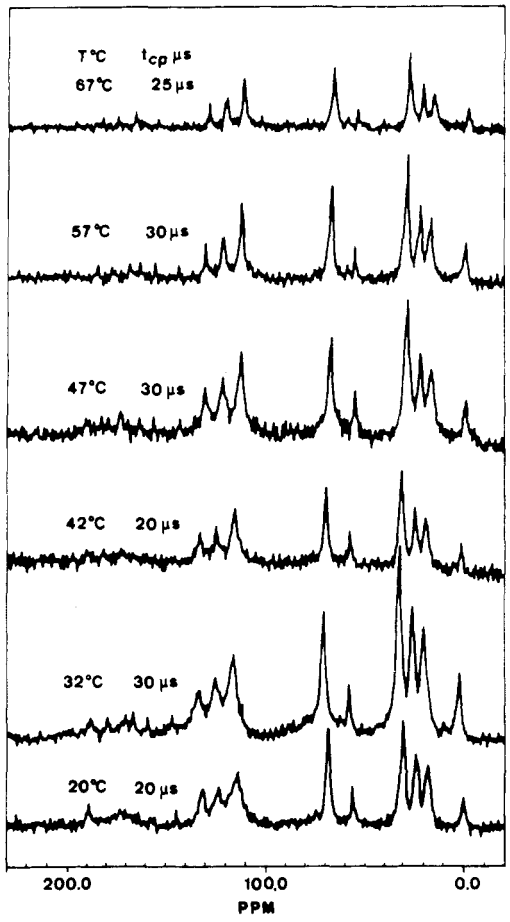


Figure 9. Variable-temperature MAS/CP/DD ^{13}C NMR spectra of the $P_{5,1}$ polysiloxane obtained by using very short contact durations.

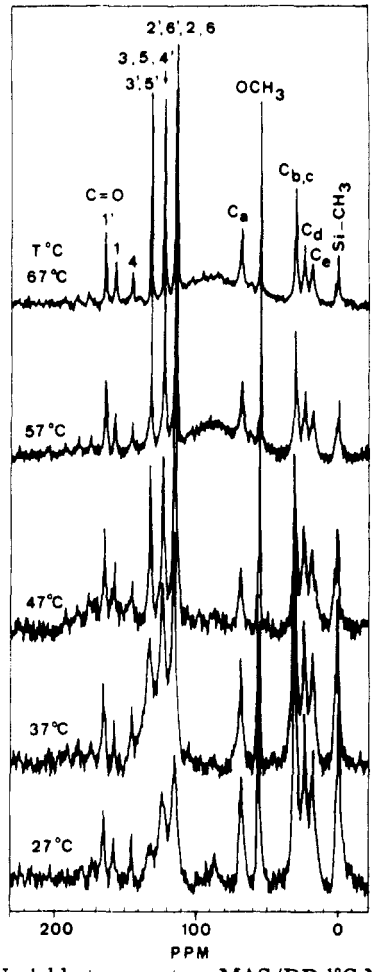


Figure 10. Variable-temperature MAS/DD ^{13}C NMR spectra of the $P_{5,1}$ polysiloxane obtained by using the single pulse sequence (repetition time, 2 s).

In the range from 37 to 67 °C, detailed comparison of the line shapes obtained for the aromatic carbons either by using the cross-polarization sequence with a 1-ms contact time or by using the single-pulse experiment is provided by the enlarged spectra displayed in Figure 11. All these line shapes are typical of a fast exchange of the ortho carbons and indicate that in this temperature range a phenyl ring motion about the para axis is observed even in the more ordered regions. Line narrowing occurs at least until 67 °C. The comparison of the widths of the lines associated with carbons 3 and 5 in the two series of spectra is not straightforward, since there is also a participation of the quaternary carbon 4' in the cross-polarized experiments. Carbons 2, 6, 2', and 6' have quite similar line shapes and line widths in the two series of spectra. Almost identical line widths are also observed for carbons 3' and 5'. Qualitatively, it implies that there is no significant difference in the frequencies of the 180° ring flips in the more ordered regions of the $P_{5,1}$ polysiloxane and in the less ordered ones. This result is supported by simulations of the aromatic 2, 6, 2', and 6' carbon spectra of $P_{5,1}$ carried out by using the procedure described for $P_{3,1}$ in the temperature range from 37 to 67 °C. Figure 12 shows the dependence on temperature of correlation times of the 180° ring flips as observed from the cross-polarization spectra accentuating the more ordered regions of $P_{5,1}$ and the single-pulse experiments with a delay time of 2 s between two successive pulse sequences accentuating the less ordered ones. These correlation times are equal within the accuracy of the measurements. They are characterized by an apparent activation energy of 70 ± 10 kJ/mol, similar to the activation energy determined for the $P_{3,1}$ polysiloxane.

III.2. Spinning Sideband Intensities. The ^{13}C NMR spectra of $P_{5,1}$, obtained by using a spinning speed of 4000 Hz, show spinning sidebands that do not overlap with the main band pattern. Such a situation is encountered for carbons 1; 4; 3' and 5'; 3, 5 and 4'; and 2, 6, 2', and 6' in the 1-ms contact time spectra reported in Figure 8. The temperature variation of the intensity ratio I_{+1}/I_0 determined for carbons 3, 5, and 4' is reported in Figure 13. In this figure are also given the intensity ratios I_{+1}/I_0 determined from the single-pulse spectra. In the latter case, only spinning sidebands associated to protonated carbons are observed, the signals arising from the quaternary carbons being too weak. Whatever the carbon under consideration and the pulse sequence used, these ratios are a decreasing function of temperature. As observed in $P_{3,1}$, this result is consistent with a more and more efficient motional modulation of the chemical shift anisotropy by phenyl ring flips.

Comparison of values reported in Figures 5 and 13 clearly shows that, at a given temperature, the relative intensities of the $P_{3,1}$ spinning sidebands are much weaker than those observed in the rigid parts of $P_{5,1}$. On the other hand, they are of about the same intensity as those measured in the less ordered regions. This similar behavior between amorphous $P_{3,1}$ and the more mobile parts of semicrystalline $P_{5,1}$ strongly supports the fact that the single-pulse experiment using a short delay between two successive pulse sequences mainly allows the observation of the less organized regions. In the particular case of the $P_{5,1}$ mesogenic cores, these regions are composed of smectic A that, as in $P_{3,1}$, is frozen below T_g. Moreover, whereas the

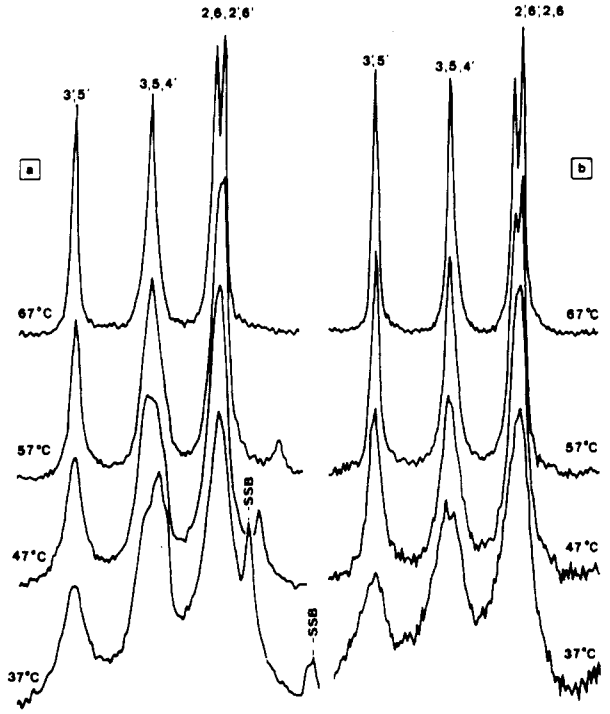


Figure 11. MAS/DD ^{13}C NMR spectra of the aromatic carbons of the $P_{5,1}$ polysiloxane obtained in the temperature range 37–67 °C by using (a) cross polarization with a contact duration of 1 ms and (b) the single pulse sequence (repetition time, 2 s).

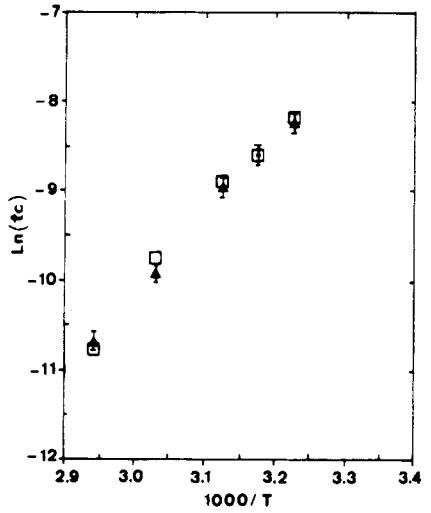


Figure 12. Temperature dependence of the correlation times τ_c of the ring motion determined from the line-shape analysis of the $P_{5,1}$ polysiloxane in the 1-ms CP spectra (□) and single pulse spectra (▲).

aromatic carbon line shape does not depend upon the pulse sequence in the temperature domain under study, the spinning sideband intensities are always weaker in the spectra obtained by using a single ^{13}C pulse than in those obtained from the cross-polarization technique. Therefore this difference in behavior, which, as shown in Figure 12, is not due to a difference in the ring flip motion about the para axis, may indicate the existence of an additional process involving the aromatic rings of amorphous $P_{5,1}$ and $P_{3,1}$. This motion could be a partial reorientation of the long axis of the mesogenic core that would be observed only in the less ordered parts of the material. In crystalline regions, the correlation distance between mesogenic cores may be long enough to prevent the motion of the long axis. In the domains where the smectic A is frozen, and not crystallized at low temperature, the correlation lengths

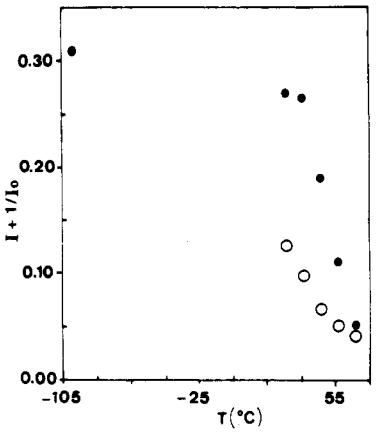


Figure 13. Temperature dependence of the intensity ratios I_{+1}/I_0 determined from the 3, 5, and 4′ carbon line of the $P_{5,1}$ polysiloxane in 1-ms CP spectra (●) and single pulse spectra (○).

are shorter, and the long axis of the mesogenic core has a certain degree of motional freedom.

III.3. Aliphatic Carbons. Comparison of spectra reported on Figures 8–10 shows that the chemical shifts of the spacer carbons are independent of both the temperature and the pulse sequence used within the accuracy of the experiments. At −98 °C, lines are broad. They are much more narrow at room temperature and their width is a decreasing function of temperature.

The CH_3Si carbon has a broad pattern at low temperature, which splits at higher temperatures. Peak proportions are independent of temperature. As in the $P_{3,1}$ polysiloxane, such a line shape has to be assigned to configurational effects resulting from units of different tacticities in the main chain.

Spectra reported in Figure 9, obtained from cross-polarization with very short contact times, show that, in the range 27–67 °C, the line corresponding to the OCH_3 carbon of the terminal side chain of $P_{5,1}$ is less intense than the other aliphatic lines. This result is a consequence of the rapid internal CH_3 group rotation, which partly averages the ^{13}C–^1H dipolar interaction and decreases the ability of this carbon to acquire magnetization by cross-polarization. In the 1-ms contact time spectra shown in Figure 8, which have a better signal-to-noise ratio, the line corresponding to this carbon is split at 47 °C; below this temperature, the peak is too wide for such a splitting to be observed. On increasing temperature, the proportions of the two components vary. Spectra obtained on $P_{5,1}$ by using the single pulse sequence (Figure 10) also show the same splitting at 27 °C and above, as well as a variation in the peak proportions on increasing temperature. At 67 °C, and unlike what is observed in the cross-polarization spectrum recorded at the same temperature (Figure 8), only one single line is observed for this carbon. All these results are likely due to a chemical shift difference of the methoxy carbons between the crystalline regions and the S_A phase. Intensity differences relate to changes in spin–lattice relaxation and cross-polarization efficiencies as a function of temperature. In contrast, in the $P_{3,1}$ polysiloxane, which has only a S_A phase and no crystalline parts, a single, narrow line is observed for the OCH_3 carbon over the whole range of temperature under study.

At the site of the first carbon of the spacer, comparison of spectra obtained either by cross-polarization or by the single pulse technique shows that, with respect to the lines assigned to the other spacer carbons, the peak corresponding to the OCH_2 carbon is much more intense in the cross-polarization spectra than in the single-pulse spectra. Therefore, this carbon has a reduced mobility as compared

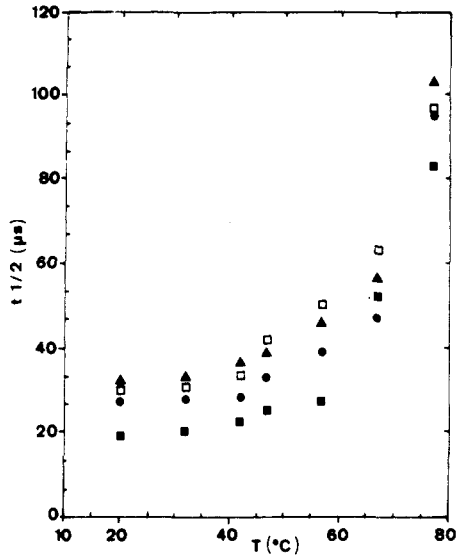


Figure 14. Temperature dependence of the $t_{1/2}$ contact times of the CH_2(a) (■), CH_2(b,c) (□), CH_2(d) (▲), and CH_2(e) (●) carbons of the $P_{5,1}$ spacer.

to the mobility of the other carbons of the spacer, which results in a higher amount of magnetization acquired by cross-polarization during a given contact duration. Therefore, this carbon most likely takes part in the crystallinity of the sample.

To describe the local spacer dynamics in $P_{5,1}$ in a more precise way, $t_{1/2}$ determinations by using cross-polarization experiments with very short contact times have been carried out. $t_{1/2}$ variations as a function of temperature for the spacer carbons of $P_{5,1}$ are shown in Figure 14.

At room temperature, the $t_{1/2}$ of the CH_2(a) carbon, next to the phenyl ring, is equal to 19 μs, which is the rigid-lattice value. The most mobile carbons are those located in the center of the spacer: CH_2(b,c) and CH_2(d), whose $t_{1/2}$ are 30 and 32 μs, respectively. The reduced mobility of the CH_2(e) group ($t_{1/2}$ = 27 μs) is likely to be due to constraints opposed by the main chain on the spacer extremity.

Between 25 and 32 °C there are no $t_{1/2}$ variations for the CH_2(a), CH_2(b,c), and CH_2(d) carbons. With further increase in temperature, $t_{1/2}$ increases first slightly and then more strikingly at temperatures in the range 60–70 °C. For the CH_2(e) carbon, no variation in $t_{1/2}$ can be detected at temperatures below 47 °C.

As observed in $P_{3,1}$, $t_{1/2}$ values for the different spacer carbons of $P_{5,1}$ reflect rigid-lattice behavior at low temperature for the CH_2(a) carbon and motions of low amplitude (librations or isolated conformational jumps involving a very small amount of bonds) for the CH_2(b,c,d,e) groups. With an increase in temperature, results observed for carbons CH_2(b,c,d,e) can be interpreted in terms of isolated, then correlated, conformational jumps that progressively spread over the whole sample. In the neighborhood of the melting point, $t_{1/2}$ values are much higher than 60 μs for all the spacer carbons: the spacer is thus likely involved not only in conformational jumps but also in large-amplitude modes.

IV. Comparison of the $P_{3,1}$ and $P_{5,1}$ Behaviors. The $P_{5,1}$ polysiloxane is a semicrystalline polymer, whereas $P_{3,1}$ is amorphous. Therefore, in order to get a deeper understanding of the behavior of the different $P_{5,1}$ regions, one has to compare the local dynamics of the spacer in both compounds. It must be noticed first that the increase in mobility of the CH_2(e) carbon of the $P_{5,1}$ spacer occurs at the same temperature as the increase in mobility of the CH_2(c) carbon of $P_{3,1}$. With respect to these carbons, the main difference lies in the fact that, at a given temperature, the $t_{1/2}$ variation is weaker in $P_{5,1}$ than in $P_{3,1}$. The CH_2(e) carbon being next to the main chain, its local dynamics are expected to be governed mainly by the difference between the temperature of the experiment and the glass–rubber temperature of the polysiloxane main chain. Therefore, the obtained results are in agreement with the fact that, at the characteristic frequencies of the NMR experiments, the amorphous regions of $P_{5,1}$ have a glass transition temperature close to the glass transition temperature of $P_{3,1}$.

At low temperature, the description of the $P_{5,1}$ polysiloxane as a semicrystalline polymer as opposed to a three-dimensional ordered smectic phase[20] mostly relies on the fact that, at low temperature, the CH_2(a) group, next to the mesogenic core, displays rigid-lattice behavior. Indeed, for a three-dimensional ordered smectic phase at low temperature, an overall reorientation of the mesogenic core about its long axis is expected to occur. This conclusion is corroborated by the study of the spinning sideband intensities.

The increase in mobility of the CH_2(a) carbon next to the mesognic core occurs at the same temperature in $P_{3,1}$ and in $P_{5,1}$. For this carbon also, the only difference between the two polymers is the $t_{1/2}$ variation at a given temperature. This analogy with the local dynamics of amorphous $P_{3,1}$ indicates that the onset of motions in $P_{5,1}$ around 40 °C can be assigned to spacers located in a frozen smectic A phase of $P_{5,1}$. This phase shows the same behavior as the glassy smectic A phase of $P_{3,1}$. On the other hand, regions where the $P_{5,1}$ spacers are crystalline do not contribute to the $t_{1/2}$ increase at 40 °C, which results in a lower $t_{1/2}$ variation in the $P_{5,1}$ polysiloxane. These conclusions relative to the existence of a glassy smectic A phase at low temperature have to be compared with the conclusions resulting from the comparison of the spinning sideband intensities in $P_{3,1}$ and in the less ordered regions of $P_{5,1}$. However, it must be noted that motional modulation of the chemical shift anisotropy occurs for frequencies of the order of 10^4 Hz or higher, weaker than those required for the averaging of the ^{13}C–^1H dipolar interaction; therefore, the increase in mobility associated with the disappearance of the glassy state manifests itself at temperatures as low as 27 °C from the spinning sideband intensities. In this case, the observed motion is a reorientation of the long axis of the mesogenic core.

The large increase in mobility associated with the glass transition phenomenon also induces an increase in the signal-to-noise ratio of spectra obtained by the single-pulse technique at 45 °C and above. Spectra shown in Figure 10 are the result of 4000 scans at 27 and 37 °C and only 1500 scans at higher temperatures.

Finally, in the neighborhood of the melting point, all the carbons of the $P_{5,1}$ spacer have long $t_{1/2}$ values. Therefore, the $P_{5,1}$ spacer is not only involved in conformational jumps, but it also undergoes large-amplitude modes. Morever, the CH_2(a) carbons behave slightly differently from the other spacer carbons: a sharp increase in mobility is observed at 67 °C for the CH_2(a) carbon, whereas one has to reach 71 °C, i.e., the melting point, to observe similar behavior for the CH_2(b,c,d,e) groups. This temperature difference may be due to the fact that the CH_2(a) group is bound to the mesogenic core. Its high mobility at 67 °C most likely originates from premelting phenomena. These effects are also responsible for the decrease in the I_{+1}/I_0 ratio observed at 47 °C and above for carbons in the crystalline regions (Figure 13). As for

the motions associated with the glass transition phenomena, temperatures at which the premelting processes manifest themselves depend on the type of NMR measurement, since to each type of experiment corresponds a different frequency window.

For a relatively long spacer and a semicrystalline organization of the mesogenic cores at low temperature, it thus appears that one can separate the influence on the local dynamics of both the main chain and the mesogenic core. The whole set of results obtained on the $P_{5,1}$ polysiloxane is consistent with the fact that the glass-transition phenomena observed by DSC at 4 °C mainly involve the polymer main chain and the neighboring spacer carbons. On the other hand, its influence is weaker at the site of the mesogenic core. Indeed, at low temperature, the mesogenic groups are organized either in a crystalline phase, with a melting point of 71 °C, or in a glassy smectic A phase. It has to be pointed out that the glass transition associated to the latter phase is not observed in the DSC traces. Besides, there does not appear to be any difference in the dynamics of the phenyl rings of the mesogenic groups between the amorphous and the crystalline phases. Correlation times for the 180° ring flips are independent of the pulse sequence and, as a consequence, of the phase to which these rings belong. This implies that, in the crystalline regions, the aromatic rings undergo very localized motions that do not modify the organization of the centers of gravity of the phenyl groups.

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