

Motion of the Mesogenic Unit in Liquid-Crystalline Polyesters

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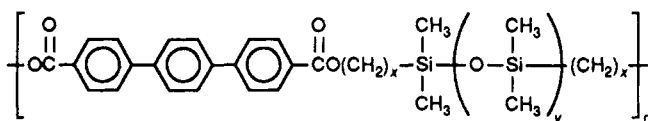
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ABSTRACT: ^{13}C MAS-NMR spectra were obtained for several polyesters of the type $[\text{OCO}(\text{C}_6\text{H}_4)_3\text{COO}(\text{CH}_2)_x\text{Si}(\text{CH}_3)_2[\text{OSi}(\text{CH}_3)_2]_y(\text{CH}_2)_z]_n$ at various temperatures in the solid and liquid-crystalline states. The results of a spinning sideband analysis show that in all polyesters investigated a motion of each of the three rings in the terphenyl moiety within the mesogenic unit sets in at a temperature 5–10 °C below the transition point into the liquid-crystalline state. The experimental results suggest that we are dealing with a flip of the aromatic rings over 45–50°. An attempt was made to correlate these spectroscopic results with theoretical results obtained with MMP2 force field calculations. Comparison of the NMR data with the theoretical results leads to the conclusion that not intramolecular but rather intermolecular forces determine the observed motional process.

Introduction

Thermotropic liquid-crystalline polymers are of commercial and academic interest. Their unique properties, e.g., mechanical strength, thermal stability, etc., let them play an important role in polymer applications. From a more fundamental point of view, one is interested in the structure and dynamics of these systems in the solid and mesomorphic phase.

Solid-state NMR spectroscopy turned out to be a powerful tool to give insight into these features. In this respect, NMR line-shape analysis of ^2H -labeled materials was highly successful.^{1,2} When dealing with unlabeled materials, high-resolution ^{13}C solid-state NMR, a combination of cross-polarization (CP), high-power decoupling and magic angle spinning (MAS), can often provide similar information. Here we report results concerning the dynamics of the mesogenic unit of a series of polyesters with the general formula³



Experimental Section

Synthesis of the polyesters is described elsewhere.³

Spectra were obtained by using a Bruker AM 500 spectrometer equipped with a solid-state accessory operating at 125 MHz for carbon-13. Standard CP and TOSS (total suppression of spinning sidebands) pulse sequences were used with a $\pi/2$ pulse length of 6.5 μs . The MAS frequency in all experiments was approximately 4 kHz. Temperature was controlled by the B-VT 1000 unit supplied with the spectrometer; the accuracy is ± 3 °C. Spinning sideband analyses were performed by a least-squares minimization based on the tables by Herzfeld and Berger.⁴

Molecular mechanics calculations were performed with the MMP2 force field program. Standard force-field parameters were used. The program was run on a Convex 220. For the rotational

energy barrier calculation, the dihedral angle was increased in 10° steps and the resulting structure minimized.

Theory

^{13}C MAS spectra consist, if the spinning speed does not exceed the static line width, of resonances at the isotropic chemical shifts and spinning sidebands (SSB) separated from the centerband by multiples of the spinning frequency. From the relative intensities of these sidebands, one can derive the principal elements of the chemical shift (CS) tensor.⁴ If, in addition, the direction of the principal axes is known, the CS tensor is completely characterized.

In the case of six-membered aromatic ring carbons, single-crystal studies of various compounds have shown that the most shielded direction σ_{33} is perpendicular to the plane of the ring and the least shielded orientation σ_{11} is directed to the proton or group bonded to the carbon⁵ (Figure 1). When an atom is involved in a motion, the contribution of the CS tensor of its nuclear spin to the NMR spectrum can be affected by this dynamical process. In spectra of static samples, this is documented in changes of the line shape, whereas MAS spectra reveal this process is changed relative SSB intensities. How the NMR spectrum is affected by the dynamical process depends on the type and frequency of the motion.

Here we want to calculate the effect of a rotation of an aromatic ring between two orientations, which can be expected to be the relevant motional process for the *p*-terphenyl moiety. We assume the rotational axis or the flip axis to be coincident with the principal axis σ_{11} of the CS tensor of the quaternary carbons. Then, in an axis system x,y,z defined in such a way that the σ_{11} axis is parallel to x , due to the rotation, the σ_{22} axis of the CS tensor of the quaternary carbons moves in the yz plane from initial position A to final position B (Figure 1). In its principal

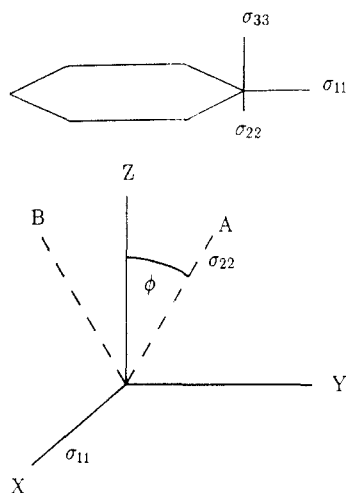


Figure 1. Direction of the CS principal axes of aromatic carbons in six-membered rings and the spatial relation between the CS principal axis system and an axis system x, y, z . A and B are the initial and final positions of σ_{22} due to the motional process.

axes system, the CS tensor is diagonal and given by

$$\begin{bmatrix} \sigma_{11} & 0 & 0 \\ 0 & \sigma_{22} & 0 \\ 0 & 0 & \sigma_{33} \end{bmatrix}$$

Thus, the CS tensor of site A expressed in the reference axis system x, y, z is

$CS_A =$

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos \phi & \sin \phi \\ 0 & -\sin \phi & \cos \phi \end{bmatrix} \begin{bmatrix} \sigma_{11} & 0 & 0 \\ 0 & \sigma_{22} & 0 \\ 0 & 0 & \sigma_{33} \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos \phi & -\sin \phi \\ 0 & \sin \phi & \cos \phi \end{bmatrix} \quad (1)$$

$CS_A =$

$$\begin{bmatrix} \sigma_{11} & 0 & 0 \\ 0 & \sigma_{22} \cos^2 \phi + \sigma_{33} \sin^2 \phi & \frac{1}{2}(\sigma_{33} - \sigma_{22}) \sin 2\phi \\ 0 & \frac{1}{2}(\sigma_{33} - \sigma_{22}) \sin 2\phi & \sigma_{22} \sin^2 \phi + \sigma_{33} \cos^2 \phi \end{bmatrix} \quad (2)$$

To get the CS tensor of a quaternary carbon at site B in the axis system x, y, z , we replace ϕ by $-\phi$:

$CS_B =$

$$\begin{bmatrix} \sigma_{11} & 0 & 0 \\ 0 & \sigma_{22} \cos^2 \phi + \sigma_{33} \sin^2 \phi & \frac{1}{2}(\sigma_{33} - \sigma_{22}) \sin 2\phi \\ 0 & \frac{1}{2}(\sigma_{22} - \sigma_{33}) \sin 2\phi & \sigma_{22} \sin^2 \phi + \sigma_{33} \cos^2 \phi \end{bmatrix} \quad (3)$$

We now distinguish two motional processes: a rotational jump between orientations A and B and a rotation between A and B.

Jump between Two Sites. In a rotational jump process, it is assumed that the molecule or part of it rotates between orientations A and B in an infinitely short time, while the residence time in each orientation is relatively long. When the jump frequency is high on the NMR time scale (i.e., the chemical shift differences between A and B), then the resulting CS tensor is the average of the CS tensors of the two orientations A and B, expressed in the reference axis system x, y, z . The average, $CS_{\text{jump}}(2\phi)$,

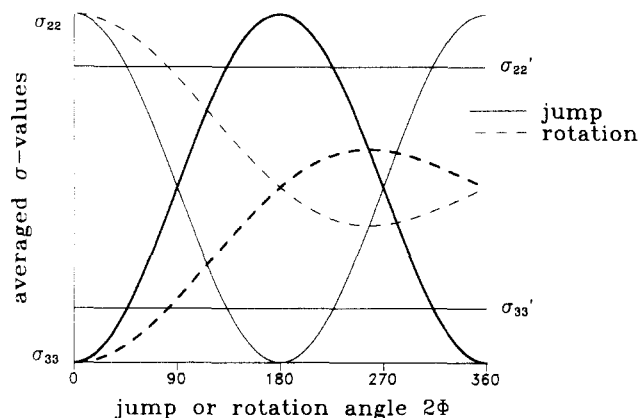


Figure 2. σ_{22} and σ_{33} chemical shift principal elements of a quaternary carbon in a phenyl ring for a rotation or a jump around an σ_{11} axis over 2ϕ . The horizontal lines show the experimental values σ_{22}' and σ_{33}' for carbon C4 at 70 °C.

corresponds to $1/2(CS_A + CS_B)$

$CS_{\text{jump}}(2\phi) =$

$$\begin{bmatrix} \sigma_{11} & 0 & 0 \\ 0 & \sigma_{22} \cos^2 \phi + \sigma_{33} \sin^2 \phi & 0 \\ 0 & 0 & \sigma_{22} \sin^2 \phi + \sigma_{33} \cos^2 \phi \end{bmatrix} \quad (4)$$

From eq 4 it is immediately clear that a π flip of the ring between $\phi = -90^\circ$ and $\phi = 90^\circ$ will not give an observable change of the CS tensors of the quaternary carbons.

Rotation. In the case of a rotation, we assume that the reorientation itself is much slower than in the case of a jump, but still fast compared to the inverse of the line width. Thus, the averaged tensor is derived by integration over the whole rotational path:

$CS_{\text{rot}}(2\phi) = \frac{1}{2\phi} \times$

$$\int_{-\phi}^{\phi} \begin{bmatrix} \sigma_{11} & 0 & 0 \\ 0 & \sigma_{22} \cos^2 \alpha + \sigma_{33} \sin^2 \alpha & \frac{1}{2}(\sigma_{33} - \sigma_{22}) \sin 2\alpha \\ 0 & \frac{1}{2}(\sigma_{22} - \sigma_{33}) \sin 2\alpha & \sigma_{22} \sin^2 \alpha + \sigma_{33} \cos^2 \alpha \end{bmatrix} d\alpha \quad (5)$$

$CS_{\text{rot}}(2\phi) =$

$$\begin{bmatrix} \sigma_{11} & 0 & 0 \\ 0 & (\sigma_{22} - \sigma_{33})(\sin 2\phi/4\phi) + \frac{1}{2}(\sigma_{22} + \sigma_{33}) & 0 \\ 0 & 0 & (\sigma_{33} - \sigma_{22})(\sin 2\phi/4\phi) + \frac{1}{2}(\sigma_{22} + \sigma_{33}) \end{bmatrix} \quad (6)$$

A rotation over $2\phi = n \times 180^\circ$ ($n = \text{integer}$) results in an axially symmetric tensor, as one should expect. The effect of a jump or a rotation over 2ϕ of the aromatic rings around the σ_{11} axis, as described by eqs 4 and 6, is depicted in Figure 2. The dashed lines indicate the functional behavior of σ_{22} and σ_{33} on rotation, and the solid curved lines represent the result for a jump. The graphs clearly show that the effect on σ_{22} and σ_{33} of a jump over 2ϕ is a periodic phenomenon, while rotation gives a genuine averaging.

Results and Discussion

Several polyesters were investigated, which, depending on x and y (see formula), show a different thermodynamic behavior.³ The phase transition temperatures are summarized in Table I.

Table I
Phase Transition Temperatures of the Investigated Polyesters^a

x	y	phase transition points, ^a °C				temp where ring motion set in, °C
		C	S	I		
3	1	C 78	S 177	I		70
4	1	C 102	S 164	I		95
5	1	C 106	S 168	I		101
6	1	C 108	S ₁ 160	S ₂ 172	I	98
11	1	C 109	S ₁ 134	S ₂ 157	I	105
3	2	C 51	S ₁ 126	S ₂ 140	I	45

^a C = crystalline, S₁ and S₂ = smectic, I = isotropic.

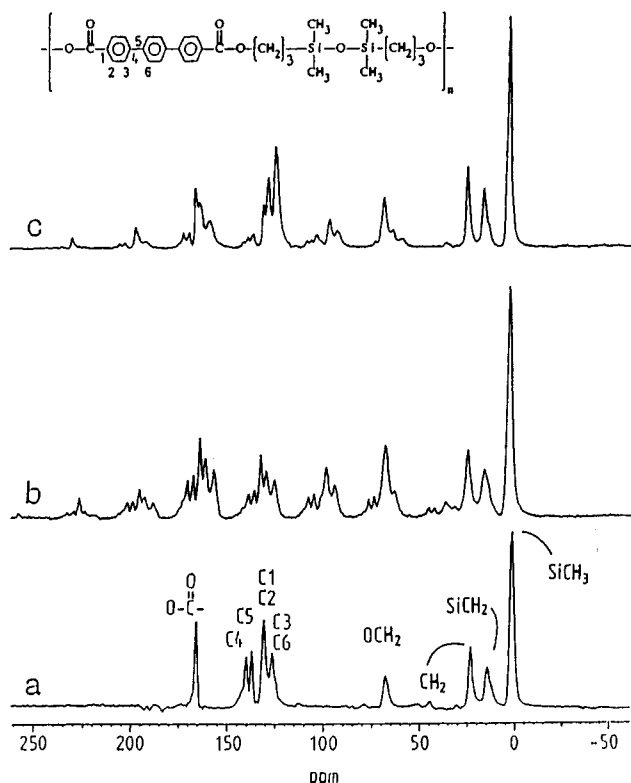


Figure 3. ¹³C NMR spectra of the sample with $x = 3$ and $y = 1$: (a) room temperature TOSS spectrum; (b) room temperature MAS spectrum; (c) MAS spectrum obtained at 70 °C.

Figure 3a shows the room temperature ¹³C CP-TOSS spectrum of the sample with $x = 3$ and $y = 1$. Assignment of the aromatic resonances was done by the aid of non-quaternary suppression techniques^{6,7} and ¹³C addition rules. For the aromatic carbons, only four signals are found in the spectrum. Resonances of the quaternary carbons C4 and C5 and the carbonyl carbons are well resolved.

Without suppression of spinning sidebands, the room temperature spectrum shown in Figure 3b is obtained. At the MAS frequency chosen, the chemical shift anisotropy of the aromatic and carbonyl carbons is not completely averaged, which gives rise to significant SSBs up to the third order. The principal elements of the CS tensors derived from the relative sideband intensities are summarized in Table II. An increase in the temperature in steps of 10 °C caused the observed spectrum to remain unchanged up to 60 °C. At 70 °C, however, the relative intensities of the SSB change significantly (Figure 3c). Renewed evaluation of the CS principal elements (σ_{11}' , σ_{22}' , σ_{33}') led to the values given in Table II in parentheses. Comparing these values with those derived from the room temperature spectrum shows that the CS tensor of the carbonyl carbon remains unchanged, as do the downfield elements σ_{11} of the C4 and C5 carbons. On the other hand, σ_{22} and σ_{33} of both aromatic carbons change at higher temperatures.

Table II
Chemical Shift Tensor Principal Elements (ppm) at Room Temperature of the Quaternary Carbons C4 and C5 and the Carbonyl Carbon of the Sample^a

	σ_{11}	σ_{22}	σ_{33}	σ_i
C4	234 (232)	164 (142)	22 (44)	140
C5	236 (233)	159 (135)	17 (42)	137
C=O	250 (252)	137 (135)	110 (110)	166

^a With $x = 3$ and $y = 1$. Values in parentheses are derived at 70 °C.

In all these cases, no variation of the SSB width with MAS frequency and temperature was observed; thus, the motional frequency is fast compared to the MAS frequency. In addition, the same results of the sideband analyses were obtained when the temperature was increased further. This led us to the conclusion that the partial averaging of the chemical shift tensor by the motion is complete, and thus an interpretation of the results of the sideband analysis in terms of eq 4 or 6 is valid.

These results are understood, within the limitations of our model, by assuming a hindered ring rotational motion with its symmetry axis coincident with σ_{11} . The unchanged CS values of the carbonyl carbon suggest that this group is not involved in any motional process, which affects its spectrum. On the basis of eqs 4 and 6 or the graphs of Figure 2, we see that the experimental values for σ_{22}' and σ_{33}' for carbons C4 and C5, summarized in Table II, do not give a unique solution for the motion of the aromatic rings. The experimental values of σ_{22}' and σ_{33}' for carbon C4 are represented in Figure 2 by the two horizontal lines, and they cross the calculated curves at various angles. Clearly, we can explain the experimental chemical shift values as the result of a rotation of the ring around σ_{11} over 80–90° or of a jump over $n \times 180^\circ \pm (45-50^\circ)$. We observe the same motion for C4 in the outer rings and for C5 in the inner ring. Thus, all three aromatic rings of the *p*-terphenyl moiety perform the same motion. As mentioned above, the carboxyl group seems not to cooperate in this motional process.

To decide with NMR which of the two types of motion takes place is not straightforward, since C4 and C5 are the only well-resolved signals of the terphenyl group. A rotor-synchronized 2D-exchange experiment⁸ with a suitable mixing time performed at lower temperatures to get to the slow exchange limit perhaps could solve this problem. An independent check on the interpretation can also be obtained in principle from C–H dipolar interaction measurements along the lines of the work by Munowitz et al.⁹ and Schaefer et al.¹⁰ To distinguish between a correlated or noncorrelated motion is even more complicated. For this purpose, an interaction which relates the inner ring with the outer ones, e.g., the dipolar interaction between a spin of the inner ring and a spin of the outer rings, would have to be utilized. Further work regarding these subjects is in progress.

In order to put our experimental results in a broader perspective, we decided to perform theoretical calculations

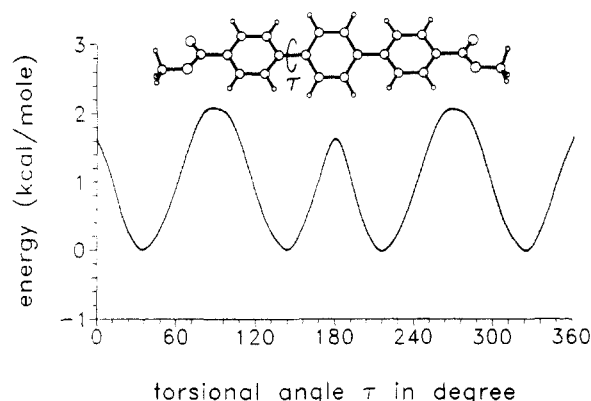
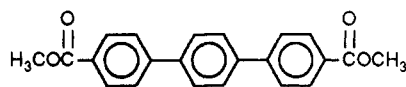


Figure 4. Conformational energy shown as a function of torsional angle τ . The ball-stick plot shows a low-energy conformation (aromatic rings twisted 35° to each other) of the partial structure used for MMP2 calculations.

with the MMP2 force field program. The calculations were restricted to the fragment shown below which is best suited



to represent the mesogenic unit. As a first result, we found that the global energy minimum is found for those conformations where the phenyl rings are twisted 35° to each other (Figure 4), which is in good agreement with other theoretical¹¹ and experimental¹² results. The next step was to calculate the conformational energy profile as a function of the dihedral angle τ (Figure 4). The immediate conclusion is that the height of the rotational barrier is too low to explain the relatively high temperature (70°C) where the motion observed by NMR sets in. Also, the rotational angles of the energy minima of Figure 4 do not agree with the values obtained from the NMR results. Therefore, our conclusion has to be that the intramolecular energy barrier does not determine the detected motional process but rather the intermolecular interactions play a dominant role. Unfortunately, we are not able to calculate these intermolecular forces.

As mentioned above, several polyesters were investigated. In all systems, the same ring motion set in $5\text{--}10^\circ\text{C}$ (see Table I) below the transition temperature into the liquid-crystalline phase. Thus, the alkyl chain length and the number of siloxane fragments do influence the melting points of the samples and the temperature where the detected motion sets in. However, the type of motion

seems to be independent of these structural parameters. Also, for all systems listed in Table I no change of the spectra was observed above the temperature where the motion had started, up to 110°C . That means that even for the polyesters with $x = 3$ and $y = 1$ or 2 far in the liquid-crystalline state no new or enhanced motions have been detected. Since the spectra did not change, also no orientational ordering of the polymers took place in the mesomorphic phase in the magnetic field.

The rather sudden onset of motion and no visible further change at higher temperatures favors the above-mentioned motional model of a jump over $45\text{--}50^\circ$ (the flip). For a rotation, one would expect an increase of amplitude with temperature and consequently a gradual change of the spectrum with temperature.

The results reported above let us conclude that we detect the onset of a motion of each of the rings of the mesogenic unit at a temperature $5\text{--}10^\circ\text{C}$ below the melting point for each polyester. It may well be that the slow, large amplitude motion of the polyesters that characterizes the melting lowers the intermolecular barrier and induces this ring motion or that the ring motion induces the melting.

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