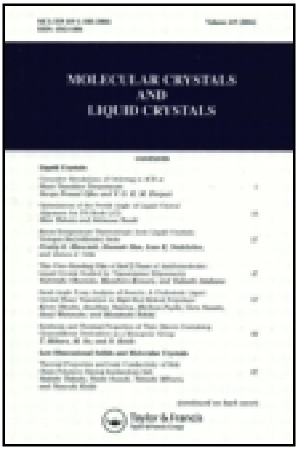

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^{19}F Multipulse NMR Study of Some Amphiphilic Liquid Crystals

A. Jasinski [a] [b] , P. G. Morris [a] & P. Mansfield [a]
[a] Department of Physics, University of Nottingham, Nottingham, England
[b] Institute of Nuclear Physics, Krakow, Poland

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^{19}F Multipulse NMR Study of Some Amphiphilic Liquid Crystals

A. JASINSKI†, P. G. MORRIS and P. MANSFIELD

Department of Physics, University of Nottingham, Nottingham, England.

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Multipulse NMR techniques have been used to investigate the dynamic properties of cesium perfluoro-octanoate (CsPFO) and ammonium perfluoro-octanoate (APFO) + water systems, which are liquid crystals over a wide range of temperature and concentration.

Axially symmetric fluorine chemical shift tensors have been measured for the CF_2 and CF_3 groups, with respect to a C_6F_6 internal reference, by performing a rotation study of an aligned sample (50% CsPFO: 50% D_2O) at room temperature. By fitting experimental spectra the order parameter S_r relative to 50% CsPFO: 50% D_2O at room temperature, has been determined for 70% APFO: 30% D_2O and 72.2% CsPFO: 27.8% D_2O in the lamellar mesophase over a temperature range 20°C–85°C. A model is assumed in which wagging motion of the molecular chain leads to scaling of the shift anisotropy.

The order parameter S has been estimated using known values of the ^{19}F chemical shift tensor elements for CF_2 groups in teflon at liquid nitrogen temperature.

1 INTRODUCTION

Nuclear magnetic resonance (NMR) has been successfully applied to the study of both thermotropic and amphiphilic liquid crystals.[1–3] Most of the work was concentrated on measurements of broad line and high resolution spectra, the determination of relaxation times and investigations using small probe molecules. However, long range dipolar interactions, not averaged out in the liquid crystalline phase, made interpretation of the spectra very difficult and led to some erroneous conclusions.[3,4] Nuclear quadrupole resonance of per-deuterated samples overcomes this problem to some extent,[5] allowing separate signals to be observed from the chemically inequivalent nuclei.

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† On leave of absence from the Institute of Nuclear Physics, Krakow, Poland.

However, there is still the problem of separating the effects of varying electric field gradients from those due to variations in order parameter. Also of great interest are the recent experiments of Pines *et al*,[6,7] who have measured relative order parameters in a number of nematic liquid crystals, using the ^{13}C proton double-resonance technique. This takes advantage of the very small dipolar interaction between low abundance ^{13}C nuclei.

Recently developed multipulse NMR techniques[8,9] for removing the dipolar interaction, offer new possibilities for studying liquid crystals.[10] The multiple pulse technique operates by switching the Hamiltonian among suitably chosen states by means of resonant r.f. pulses, leading to an "average Hamiltonian" in which the dipolar part vanishes. The spectrum is then determined by the chemical shift tensor, which is simply scaled by the multipulse sequence. Chemical shift tensor components are readily extracted, and in favourable cases, information concerning the motion can be obtained.[11] However, the problem of untangling changes in the shift tensor due to motion from those caused by variations in the electronic environment, remains and cannot be readily resolved by this NMR technique.

The multipulse NMR technique is applied to the study of the lamellar mesophases formed by solutions of cesium and ammonium perfluorooctanoate (CsPFO and APFO) in D_2O[12]. Little is known about the ordering of molecules in amphiphilic liquid crystals and, to the best of the authors' knowledge, there is no theory describing the lamellar mesophase. The APFO + water system has been extensively studied by Tiddy using optical microscopy, low angle X-ray diffraction[13] and NMR relaxation time measurements.[14,15] ^{19}F relaxation time (T_1) measurements in 75% APFO: 25% D_2O have suggested[14] that the long chain APFO molecules revolve rapidly about their long axes and are more rigid than their hydrocarbon counterparts. A lamellar mesophase is also formed by CsPFO and water systems. However, little is known about its properties.

In this paper 50% CsPFO: 50% D_2O, 72.2% CsPFO: 27.8% D_2O and 70% APFO: 30% D_2O systems were studied in the lamellar mesophase. Single pulse and multipulse ^{19}F spectra were recorded for non-aligned and aligned[16] 50% CsPFO: 50% D_2O samples at different temperatures. The chemical shift tensor elements for CF_2 and CF_3 groups in the lamellar mesophase of 50% CsPFO: 50% D_2O were determined at 22°C by studying the line positions in an aligned sample as a function of its inclination to the magnetic field. The relative order parameter S_r for 72.2% CsPFO: 27.8% D_2O and 70% APFO: 30% D_2O has been obtained over a temperature range 20°C–85°C by recording and fitting the multipulse spectra, assuming a model in which there is wagging motion of the molecular chains. Values of the order parameter S were also estimated.

2 THEORETICAL

The truncated interaction Hamiltonian for ^{19}F nuclei in a magnetic field B_0 is[17]

$$\hbar H_{\mathrm{INT}} = \hbar H_D + \hbar H_\sigma \tag{1}$$

where: $\hbar H_D$ and $\hbar H_\sigma$ are the truncated dipolar and chemical shift interaction Hamiltonians respectively. At the magnetic field of about 2.25 kG used here, $|H_D| \gg |H_\sigma|$ and the single pulse spectra are characterized mainly by the dipolar interaction. The multipulse line shapes on the other hand, are determined by the chemical shift anisotropy interaction since the dipolar interaction is averaged to zero.

A crystallite in the lamellar mesophase consists of parallel bilayers of amphiphilic molecules, with their hydrophilic heads pointing towards the intervening water layers.[18] Molecules reorient around their long axes fast compared with the corresponding width of the spectrum. To describe the ordering of molecules in the lamellar mesophase let us introduce the lamellar reference frame (LAM) with the z_L axis parallel to the director of the lamellar plane, oriented with respect to the laboratory frame (LAB) at Euler angles $\Omega_L = (0, \theta_L, 0)$. The molecular reference frame (MOL) with the z_M axis parallel to the long molecular axis, oriented with respect to the LAM frame with time dependent Euler angles $\Omega_M(t) = (\alpha(t), \beta(t), \gamma(t))$, is introduced to take into account the molecular motion. Then the dipolar interaction Hamiltonian is[4]

$$H_D = d_{00}^{(2)}(\theta_L) \sum_{j>k} \langle D_{00}^{(2)}(\Omega_M(t)) F_{20}(\mathbf{r}_{jk}^M)\rangle_{\mathrm{av}} A_{20}(I_j, I_k) \tag{2}$$

with

$$F_{20}(\mathbf{r}_{jk}^M) = -2\lambda^2 \hbar r_{jk}^{-3} D_{00}^{(2)}(\Omega_{jk}^M) \tag{3}$$

and

$$A_{20}(I_j, I_k) = \tfrac{1}{2}(I_j^{+1} I_k^{-1} + 2 I_j^0 I_k^0 + I_j^{-1} I_k^{+1}) \tag{4}$$

where $I^{\pm 1}$, I^0 are the spherical spin operators,[19] γ is the magnetogyric ratio, $\mathbf{r}_{jk}^M$ is the vector joining nuclei j and k in the MOL frame, Ω_{jk}^M the Euler angle of $\mathbf{r}_{jk}^M$ in the MOL frame, $d_{00}^{(2)}$ and $D_{00}^{(2)}$ are Wigner rotation matrices,[19] and $\langle\ \rangle_{\mathrm{av}}$ is the average over the motion.

Let us consider a model of molecular ordering in which we assume that molecular chains vibrate in a wagging motion which is fast compared with the corresponding width of the NMR spectrum. Fast reorientation about the long molecular axis averages out the inter-molecular dipolar interaction[4] and allows separation of Eq. (2) to give

$$H_D = d^{(2)}_{00}(\theta_L) S \sum_{j<k} (-2\lambda^2 \hbar r_{jk}^{-3} \langle D^{(2)}_{00}(\Omega^M_{jk})\rangle_{\mathrm{INTRA}}) A_{20}(I_j, I_k) \tag{5}$$

with

$$S = \langle D^{(2)}_{00}(\Omega_M(t))\rangle_{\mathrm{av}} \tag{6}$$

where S is the order parameter[19] of the long molecular axis with respect to the lamellar director and $\langle\ \rangle_{\mathrm{INTRA}}$ is the average over internal motion in the amphiphilic molecule. The second moment M_2 for an aligned sample is

$$M_2(\theta_L) = (d^{(2)}_{00}(\theta_L))^2 [S^2 M_2(0)]. \tag{7}$$

Calculation of $M_2(0)$ requires detailed knowledge of the internal motion in the molecule making the measurement of the order parameter S based on the use of the single pulse spectra and Eq. (7) rather impractical.[20]

The chemical shift anisotropy interaction is written as

$$H_\sigma = -\omega_0 \sum_{p,q} \{\sigma^p(q) + T_{20}(\sigma^p_{\alpha,\beta}(q))\} I^0_k \tag{8}$$

where ω_0 is the resonance frequency, p and q number groups of nonequivalent and equivalent nuclei respectively, $\sigma^p(q) = \frac{1}{3} Tr \sigma^p_{\alpha\beta}(q)$ is the isotropic average of the chemical shift tensor $\sigma^p_{\alpha\beta}(q)$ for nuclei q belonging to the group p, $T_{20}(\sigma^p_{\alpha\beta}(q))$ is the 0th component of the 2nd rank spherical tensor $T_{2M}(\sigma^p_{\alpha\beta}(q))$ in the LAB[21] frame and

$$T_{20}(\sigma^p_{\alpha,\beta}(q)) = \tfrac{1}{3}[2\sigma^p_{zz}(q) - \sigma^p_{xx}(q) - \sigma^p_{yy}(q)] \tag{9}$$

where $\sigma^p_{\alpha\alpha}(q)$ are diagonal elements of the chemical shift tensor. It is well known that fast rotation around one axis averages out the full chemical shift tensor making it axially symmetric.[22] Taking this into account and expressing $T_{20}(\sigma^p_{\alpha\beta}(q))$ in the MOL frame using the transformation properties of spherical tensors[19] the line position for the group of nuclei p, in the shift scale relative to the resonance frequency ω_r of the reference is

$$\delta^p = \frac{\omega_r - \omega^p_0}{\omega_r} = \sigma^p + \sum_M \langle D^{(2)}_{M0}(\Omega_L) D^{(2)}_{0M}(\Omega_M(t)\rangle_{\mathrm{av}} T^M_{20}(\sigma^p) \tag{10}$$

Averaging it over the motion according to the model gives

$$\delta^p(\theta_L) = \sigma^p + \tfrac{2}{3} d^{(2)}_{00}(\theta_L) S(\sigma^p_\parallel - \sigma^p_\perp) \tag{11}$$

For a perfectly ordered sample $S = 1$. One can introduce the scaled chemical shift tensor components $\sigma^p_{s\parallel}$, $\sigma^p_{s\perp}$. These components are given by

$$\sigma^p_{s\parallel} = \tfrac{1}{3}(1 + 2S)\sigma^p_{\parallel} + \tfrac{2}{3}(1 - S)\sigma^p_{\perp} \tag{12a}$$

$$\sigma^p_{s\perp} = \tfrac{1}{3}(1 - S)\sigma^p_{\parallel} + \tfrac{1}{3}(2 + S)\sigma^p_{\perp} \tag{12b}$$

which for $S = 1$ reduce to the unscaled values. For an aligned sample the line position is given by Eq. (11), while for a non-aligned sample Eq. (11) must be averaged over all θ_L, leading to the well known lineshape formula[23]

$$f(\delta) = \sum_p A_p(\delta - \sigma^p_{s\perp})^{-1/2}(\sigma^p_{s\parallel} - \sigma^p_{s\perp})^{-1/2} \tag{13}$$

where the sum is over all groups of non-equivalent nuclei and A_p is the normalization factor.

This lineshape must then be convoluted by a broadening function to account for relaxation broadening and the residual dipolar interactions not fully reduced by the multipulse sequence. These effects, in principle quite complicated,[24] are approximated by a simple gaussian broadening so that the observed lineshape $g(\delta)$ is given by

$$g(\delta) = \int_{-\infty}^{\infty} \mathrm{d}\delta' f(\delta')\exp\left[-\frac{(\delta - \delta')^2}{2B^2}\right] \tag{14}$$

where the characteristic broadening width B, is to be determined experimentally.

If the chemical shift tensor is known, the order parameter S may be determined by fitting the multipulse spectra according to Eqs. (12a), (12b), (13) and (14).

3 EXPERIMENTAL

All data were taken on a computer controlled line-narrowing spectrometer operating at 9 MHz. The $[\![132; 1\tilde{3}2]\!][\![123; 1\tilde{2}3]\!]$ sequence[24] with $\tau = 6.4\ \mu$ sec was used to record multipulse spectra. This sequence consists of 256 cycles, each comprising sixteen 90° r.f. pulses applied along the $\pm x$ or $\pm y$ axes in the rotating frame. The signal, sampled once per cycle, is Fourier transformed to obtain the absorption spectrum. This sequence achieved a true linewidth of 70 Hz for ^{19}F in a single crystal of CaF_2, oriented along the [111] direction with respect to B_0, at an offset of 500 Hz.

Single pulse spectra were recorded by Fourier transforming the free induction decay following one 90° r.f. pulse. Usually from 128 to 1024 spectra were accumulated to increase the signal to noise ratio.

The sample temperature was regulated by blowing air through the probe and was monitored by a copper-constantan thermocouple. Temperature stability during experiments was estimated in most cases to be better than ±0.5°C.

If no attempt is made to control the temperature, rapid sample heating occurs. This can be as much as 30°C or so over the period of a typical multipulse experiment and is presumably the result of unusually large dielectric absorption and/or ionic conduction. Under similar conditions water samples gave no noticeable temperature rise.

The 50% CsPFO sample was aligned in the magnetic field by heating it up to 38°C maintaining it at this temperature from 10 to 30 min and then cooling it down to room temperature over a period of about 10 min. A heating cycle in which the sample was raised to 50°C, well above the lamellar to isotropic phase transition, and then cooled down in the magnetic field was also used. The sample preserved its alignment for a number of days without any noticeable change and could be rotated in the magnetic field without any trace of alignment relaxation. The details of sample preparation are given by Tiddy.[13]

The accuracy of angle setting when taking rotation spectra was better than 0.5°.

4 RESULTS AND DISCUSSION

Single pulse spectra

Single pulse ^{19}F spectra recorded for aligned and non-aligned 50% CsPFO: 50% D_2O samples in the lamellar mesophase at room temperature are shown in Figure 1. The spectrum of the non-aligned sample 1A is similar to spectra recorded by other authors[25] for this mesophase and its shape has been explained by Wennerstrom.[4] The double peak at the centre of the spectrum arises from the chemically shifted CF_2 and CF_3 groups in the CsPFO molecule.

The spectra of the aligned sample 1B, 1C, 1D vary considerably with its orientation with respect to the magnetic field. The height of the central peak in 1B and 1D was found to be dependent on the degree of sample alignment.

The second moment angular dependence for the aligned sample of 50% CsPFO: 50% D_2O is shown in Figure 2. It follows very closely the angular dependence predicted by Eq. (7), indicating good sample alignment. The least square fitted curve according to Eq. (7) gave the value of $[S^2M_2(0)] = 0.54\ G^2$. A simple powder average gives the second moment for the non-aligned sample as $\frac{2}{5}[S^2M_2(0)] = 0.216\ G^2$ in good agreement with

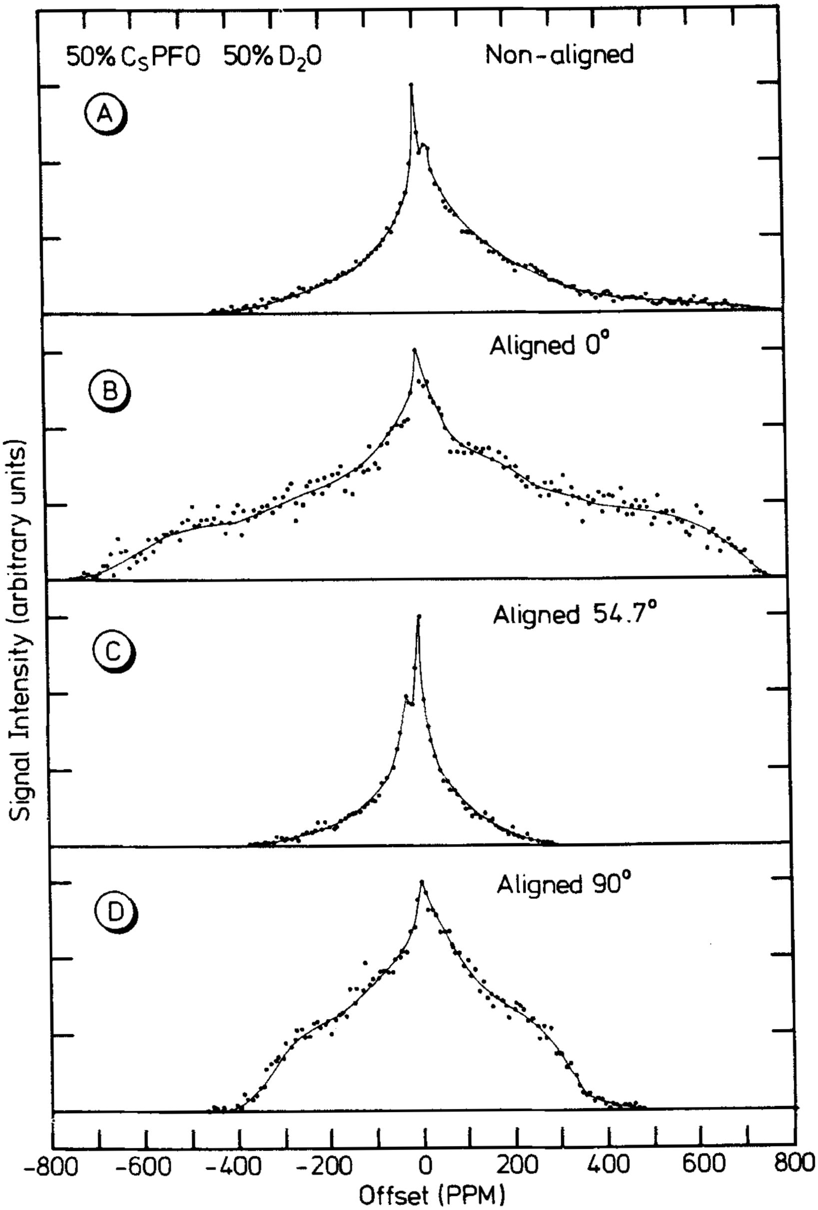

FIGURE 1 ^{19}F single pulse spectra of 50% CsPFO: 50% D_2O in the lamellar mesophase at room temperature of the non-aligned and aligned samples at different orientations with respect to B_0.

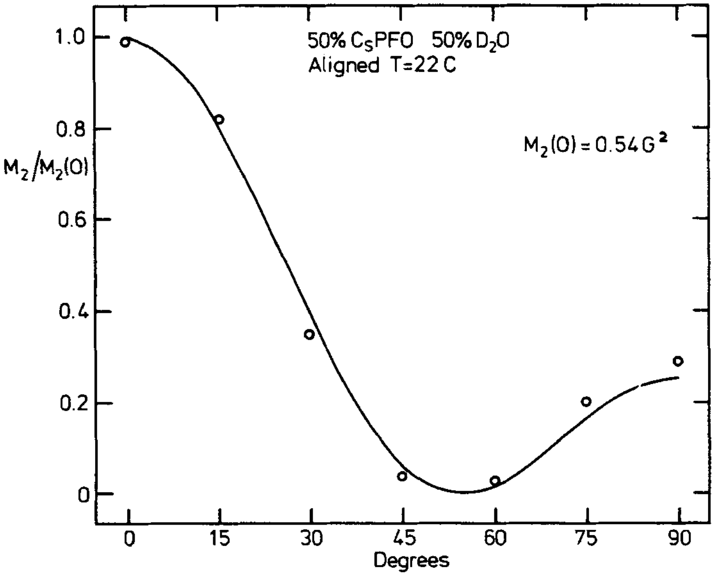

FIGURE 2 ^{19}F second moment angular dependence for an aligned sample of 50% CsPFO: 50% D_2O at room temperature.

the experimentally observed value of 0.22 ± 0.03 G^2 for the non-aligned sample.

The structure of the CsPFO molecule is not known, but assuming that distances and angles are similar to those in simple fluorocarbons,[26] the value of $[S^2M_2(0)] = 0.54\ G^2$ is an order of magnitude too small to be accounted for by reorientation around the long axis of the rigid molecule. This is probably attributable to the onset of intramolecular segmental rotations similar to those found by Boden *et al.*[20] for the hydrocarbon chain in the ternary sodium octanoate + octanol + water system.

Thus although it is possible in principle to determine the order parameter S, such a determination requires a knowledge of the second moment, $M_2(0)$, which in turn depends on the details of the motion. For dipolar interactions, this motion involves a correlated sum over the whole molecule, whereas for the chemical shift tensor, being more localized, such motional correlations are less important.

Multipulse spectra

a) 50% CsPFO: 50% D_2O.

Multipulse ^{19}F spectra of 50% CsPFO: 50% D_2O were recorded in the temperature range 20°C to 65°C in the lamellar mesophase up to the phase transition $T_c = 40 \pm 1$°C and above in the isotropic phase. Typical spectra at different temperatures are shown in Figure 3. The spectrum 3A at 22.3°C consists of two spectra of different intensities corresponding to the six CF_2 groups and single CF_3 group in the CsPFO molecule. The high resolution spectrum[27] of the CF_2 groups consists of three lines at -36.2 ppm (CF_2CF_3), -41.0 ppm ($(CF_2)_4$) and -46.3 ppm (CF_2CO_2) relative to CF_3COOH. Multipulse spectra show only one line corresponding to all these magnetically nonequivalent nuclei, because of the large chemical shift anisotropy and low multipulse sequence resolution. In the temperature range from 33°C to 40°C the sample begins to align in the magnetic field with accompanying changes in the spectrum. This is seen in Fig. 3B, where the new central peak appears from the aligned part of the sample. Randomly distributed crystallites orient in such a way that the magnetic field is parallel to the director of the lamellar plane and the average angle between long molecular axes of CsPFO molecules and B_0 is equal to zero. The large anisotropy of the bulk magnetic susceptibility is responsible for this orientation process. The degree of sample orientation depends on the time spent by the sample at any temperature. No systematic study of sample alignment was carried out however. Figure 3C shows the spectrum of an aligned sample after maintaining it for 30 mins at 39°C. Peak positions correspond to $\sigma_{s\parallel}$ for the CF_2 and CF_3 groups. Cooling down the sample to room temperature over about 10 min in the magnetic field preserves the alignment for many days.

Figure 3D shows the multipulse spectrum in the isotropic phase with peak positions corresponding to the isotropic averages of the chemical shift tensors.

An aligned sample with an internal C_6F_6 reference, enclosed in a capillary tube, was used to measure the chemical shift tensor elements for CF_2 and CF_3 groups at room temperature by taking the rotation plot of line positions, shown in Figure 4. Chemical shift tensor elements were obtained by least square fitting of the experimental data according to Eq. (11) assuming $S = 1$ (the best theoretical fits shown as continuous curves in Figure 4). These elements are: $\sigma_\parallel = -78.6$ ppm, $\sigma_\perp = -27.9$ ppm for the CF_2 group and $\sigma_\parallel = -97.8$ ppm, $\sigma_\perp = -80.7$ ppm for the CF_3 group. The chemical shift anisotropy was assumed to be the same for all CF_2 groups. However, different isotropic shifts were given to the magnetically inequivalent groups as resolved by high resolution NMR.[27] The computed spectrum of non-aligned 50% CsPFO: 50% D_2O was calculated according to Eqs. (13), (14) with a Gaussian broadening of 50 Hz. This is shown as a continuous curve in Figure 3A and is in good agreement with the experimental data.

Some information about the orientation of the CF_3 group in the CsPFO molecule can be obtained by comparing our data with measured values of the chemical shift anisotropy of a rotating fluoromethyl group. Mehring *et al.*[22]

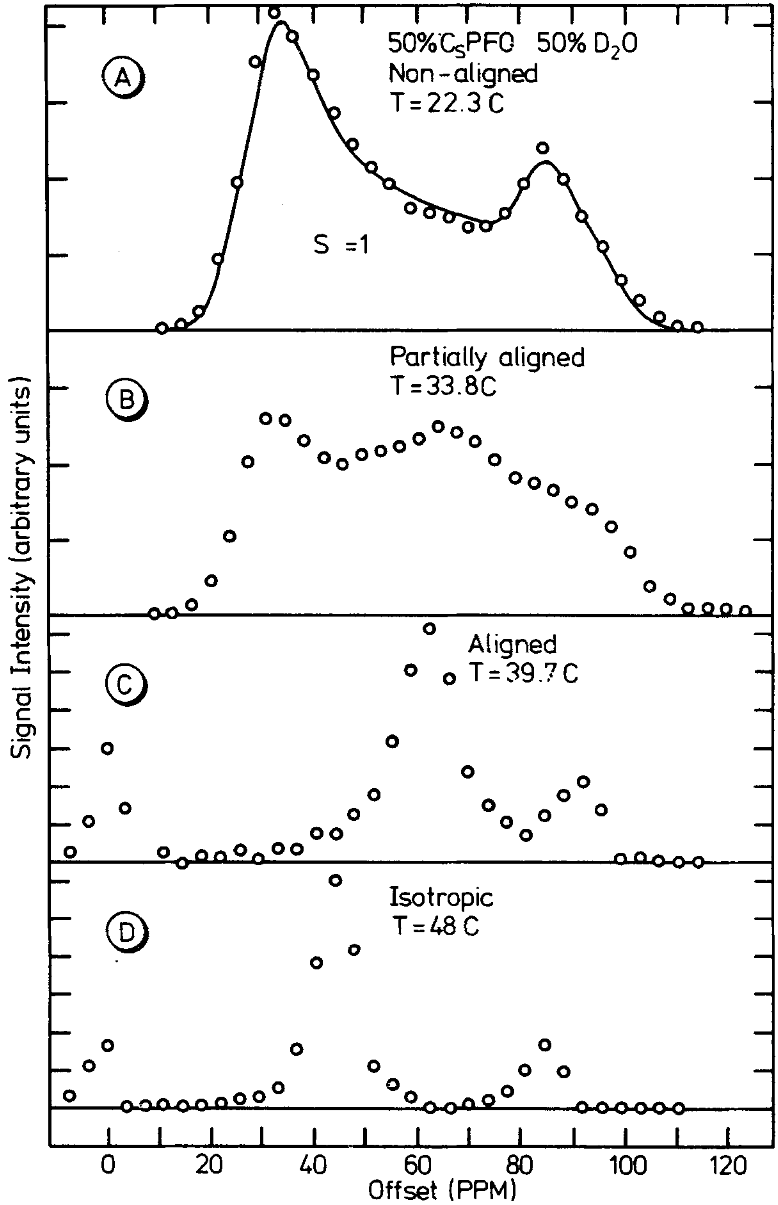

FIGURE 3 ^{19}F multipulse spectra of 50% CsPFO: 50% D_2O in the lamellar mesophase and isotropic phase. The curve on (1A) was calculated using the chemical shift tensor elements obtained from a rotation study of the aligned sample.

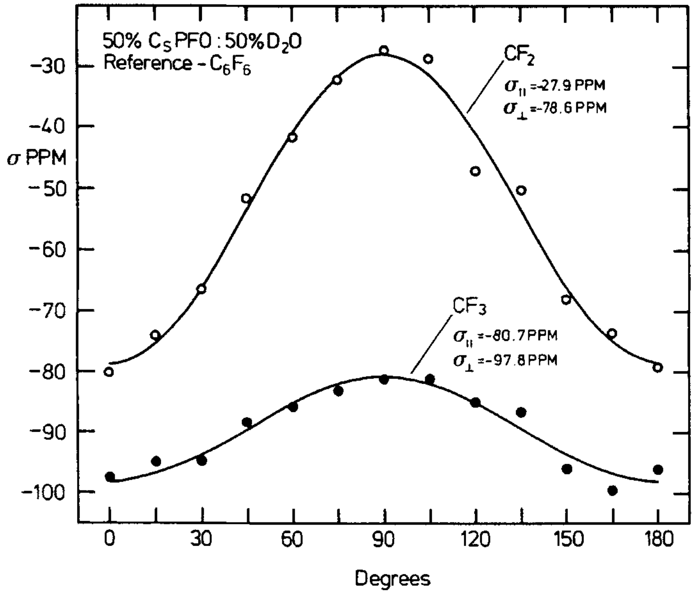

FIGURE 4 Angular dependence of CF_2 and CF_3 group line positions for an aligned sample of 50% CsPFO: 50% D_2O in the lamellar mespohase at 22°C. Least square fitted curves correspond to the values of the chemical shift tensor elements indicated.

obtained for this group rotating about its C_{v3} axis in solid CF_3COOAg at room temperature $\sigma_{\parallel} - \sigma_{\perp} = -74.0$ ppm. Emsley and Lindon[28] quote a table of values, obtained by liquid crystal solvent techniques, which cluster around −70 ppm, confirming Mehring's result.

In our case the fluoromethyl shift tensor undergoes averaging due to three types of motion:

a) rapid reorientation about the C_{v3} axis,

b) rotation of the C—CF_3 bond about the long molecular axis, with which it makes an angle α;

c) vibration of the CsPFO molecule as a whole or wagging of the chain. If one assumes that the latter motion is simply a vibration of the molecule as a rigid whole (i.e. the order parameter, as we define it, is constant right down the chain), then using the transformation properties of $T_{20}(\sigma P)$ a value of $\alpha = 36°$ is estimated.

It seems entirely plausible that the structure of the CsPFO alkyl chain is similar to the PTFE structure. From the structural information as quoted by Garroway *et al.*,[29] we have, therefore estimated that the C—C bond in PTFE is inclined at about 33° to the chain axis. This result agrees rather well

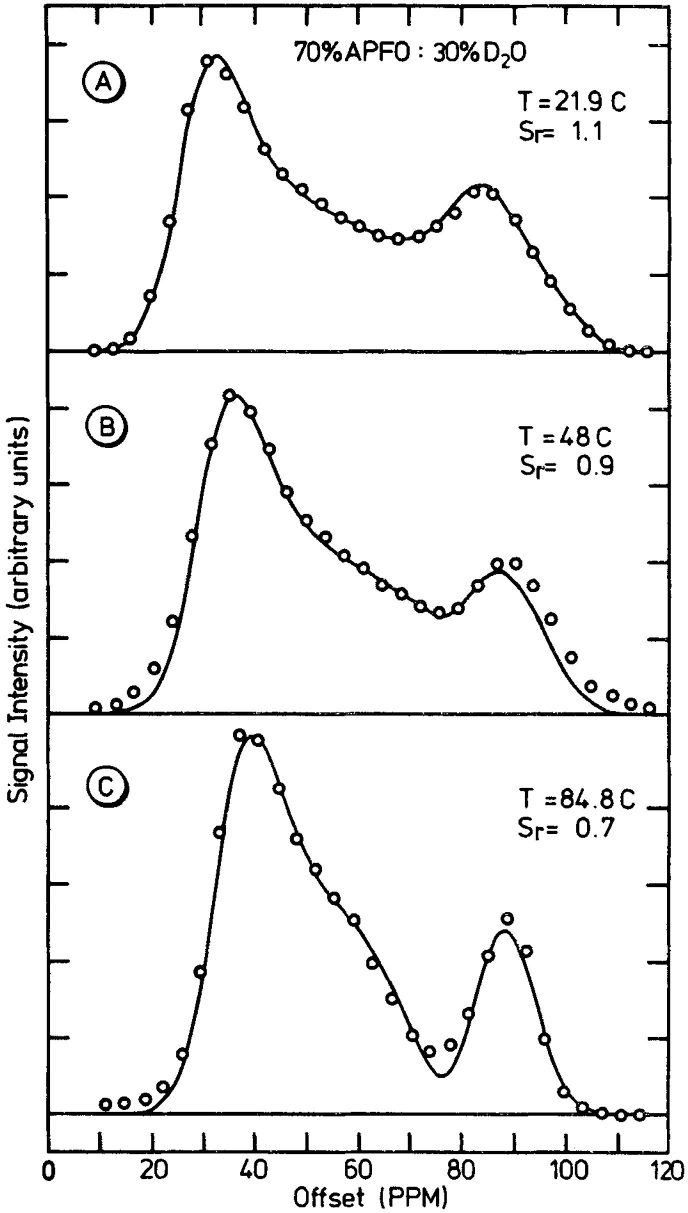

FIGURE 5 ^{19}F multipulse spectra of 70% APFO: 30% D_2O in the lamellar mesophase at different temperatures. Fitted curves correspond to the values of the relative order parameter S_r indicated and the broadening of 50 Hz.

with our measured value of α and would seem to confirm our assumption that the two structures are similar.

b) 72.2% CsPFO: 27.8% D_2O, 70% APFO: 30% D_2O.

Multipulse[11] spectra of 72.2% CsPFO: 27.8% D_2O and 70% APFO: 30% D_2O were recorded in the temperature range from 20°C to 86°C. The spectra of 70% APFO: 30% D_2O obtained at different temperatures are shown in Figure 5. The distance between peaks decreases and the spectra narrow with increasing temperature almost separating at the highest temperatures. The 72.2% CsPFO: 27.8% D_2O spectra show the same general pattern.

The temperature dependence can be understood in terms of changes of the order parameter S, which decreases with increasing temperature. This is directly related to the amplitude of the wagging motion of the long molecular axes with respect to the lamellar director. Starting with the chemical shift tensor elements determined for 50% CsPFO: 50% D_2O at room temperature where $S = 1$ was assumed, spectra for 70% APFO: 30% D_2O were fitted according to Eqs. (12a), (12b), (13) and (14) to give values of the relative order parameter S_r. A Gaussian broadening of 50 Hz was used for most of the spectra, reflecting the much lower efficiency of the multipulse sequence in removing dipolar interactions between unlike spins, i.e. between ^{19}F and ^{1}H of the NH_4 group. Typical examples of fitted spectra are shown in Figure 5. It was possible to fit all the spectra with almost the same accuracy. The same was done for 72.2% CsPFO: 27.8% D_2O, but here a broadening of 35 Hz was used in most cases indicating the high efficiency of the multipulse sequence in removing dipolar interactions between ^{19}F spins.

Values of the relative order parameter S_r in the lamellar mesophase obtained in this way are shown in Figure 6 as a function of $(T_c - T)$. Values of transition temperature T_c from the lamellar mesophase to the isotropic phase were estimated by optical observation. Our values are: $T_c = 92 \pm 3$°C for 70% APFO: 30% D_2O and $T_c = 105 \pm 3$°C for 72.2% CsPFO% 27.8 D_2O. In determining the relative order parameter S_r with respect to 50% CsPFO: 50% D_2O at 22°C, $S = 1$ was assumed in order to obtain the chemical shift tensor elements $\sigma_\parallel^p$ and $\sigma_\perp^p$. These elements are, however, already scaled by the molecular motion existing in this sample at 22°C. Unscaled values of the order parameter S may be found if values of the chemical shift tensor elements for the rigid molecule are known. It was not possible to determine them because of the overlapping of the CF_2 and CF_3 group spectra at the frequency of 9 MHz used here. However, using the known values of the chemical shift tensor elements for CF_2 groups in teflon at liquid nitrogen temperature[29] the value of $S = 0.49$ was estimated for 50% CsPFO: 50% D_2O at 22°C. This is also shown in Figure 6.

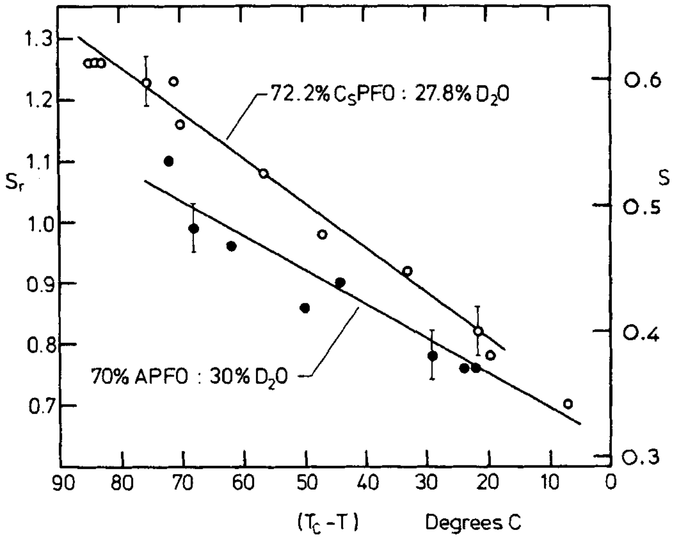

FIGURE 6 Temperature dependence of the relative order parameter S_r and the order parameter S for 72.2% CsPFO: 27.8% D_2O = open circles, and 70% APFO: 30% D_2O = filled circles.

The most striking feature of the data presented in Figure 6 is the apparent linear dependence of the order parameter on $(T_c - T)$. This behaviour is unlike that observed in nematic liquid crystals.[6,18] Our estimated values of S at the lowest temperature in Figure 6 are however similar to those usually observed in these materials.[18]

It is worth emphasising that all the spectra recorded were fitted with shift tensors, scaled by a single parameter S_r. This is strong evidence for the constancy of the order parameter along the chain, and thus of the rigidity of the molecule. Unfortunately the small shift anisotropy of the fluoromethyl group means that it is relatively insensitive to variation of S_r. We would therefore not claim too much in this regard. However the agreement between the angle α estimated from the known structure of PTFE and that calculated from the shift data on the assumption of a rigid molecule provides additional confirmation that the order parameter does not change significantly along the chain.

This result contrasts with quadrupolar work of analogous deuterated systems,[5,30] where, even allowing for the effects of the rotational averaging of the D_3 group on a somewhat differently defined order parameter, there is still a fall-off in its value away from the polar head. Perhaps simple steric considerations give rise to the apparent rigidity of the fluorocarbon system.

5 CONCLUSIONS

Although the theory of multiple pulse NMR experiments has been developed mainly for rigid lattice solids we have shown that the technique can be applied to advantage in liquid crystal systems. In the particular compounds studied molecular motions do not appear to have much restrictive effect in determining the degree to which the residual homonuclear dipolar interactions are removed.

Unlike dipolar second moment measurements obtained from single pulse experiments, measurement of the chemical shift anisotropy, using multipulse techniques, gives, in general, an unambiguous determination of the order parameter without reference to structural models of the molecule provided the full shift tensor components are known.

We have shown that CsPFO and APFO molecules, in the systems studied, appear to behave as rapidly rotating rigid rods and can consequently be described by a single order parameter S, which we have measured as a function of temperature.

Our measurements have been performed at 9 MHz. Higher frequency work offers the possibility of testing the accuracy of our conclusions regarding the constancy of the order parameter of the various chemically inequivalent groups along the molecular chain.

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