

Solid state ^{19}F n.m.r. of deformed PTFE

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^{19}F n.m.r. chemical shift dispersions are used to study the anisotropy of crystallite orientation in uniaxially deformed samples of poly(tetrafluoroethylene) (PTFE).

Keywords Deformation; orientation; nuclear magnetic resonance; characterization; mesogenic group

INTRODUCTION

The deformation of polymers can produce partially ordered states, the characterization of which is of interest in understanding the properties of these deformed states and the way in which they are produced¹. Techniques to study the deformed states are, in general, sensitive to the orientation of local structures relative to some external perturbation². Nuclear magnetic resonance (n.m.r.) spectroscopy of solids and semi-solids is a technique which has not been greatly exploited for this purpose, but which has potential to yield information on crystallite orientation. In fact, studies of extruded poly-(tetrafluoroethylene) PTFE³ and unoriented PTFE⁴ have shown that molecular motion and the relationship of the n.m.r. chemical shift parameters to the molecular framework can be understood for this polymer. We report a study of the ^{19}F chemical shift spectra of partially oriented PTFE samples which have been subjected to a tensile stress. Order parameters calculated from these spectra compare favourably with theoretical predictions. The results of these experiments allow one to make conclusions about the deformed state and indicate that the n.m.r. method for studying deformed polymers may be useful in characterizing this state.

EXPERIMENTAL

^{19}F n.m.r. spectra were taken using a homebuilt n.m.r. spectrometer which operates at a frequency of 56.405 MHz ($B_0 = 1.408\text{ T}$) for the ^{19}F resonance, the design of which has been discussed previously⁵. To reduce the ^{19}F ^{19}F homonuclear dipolar interactions for observation of chemical shifts, the eight pulse sequence (MREV-8) was applied to the samples⁵ with stroboscopic detection. The resulting time responses were analysed by Fourier transformation with an on-line PDP-11 minicomputer. Typically the 90° pulse width was 1.3 μs and the MREV-8 cycle time was 48 μs . Scaling factors on a liquid hexafluorobenzene sample were measured to ensure the spectrometer was performing correctly. In every case, the measured scaling factors were the same as those calculated theoretically for the appropriate cycle time and pulse width⁶.

The PTFE samples were subjected to a tensile stress at room temperature on an Instron[®] testing apparatus, after

which they were allowed to relax to their equilibrium extensions. This deformation resulted in strains of 40, 75, 110, and 140% elongation. A small piece of each sample ($\sim 5 \times 5 \times 5\text{ mm}$) was mounted in an n.m.r. tube in such a way that the direction of linear extension, \vec{n} , could be rotated in a plane containing the magnetic field, \vec{B}_0 . The angle, β , between \vec{n} and \vec{B}_0 could be changed by a goniometer attached to the n.m.r. probe, with a precision of $\pm 0.5^\circ$. Spectra of each sample were taken for various orientations of \vec{B}_0 and \vec{n} . The accuracy of setting the initial orientation could have been in error, but this was less than 10° , as indicated by the data analysis. It is important to note that the samples were not actively under stress during the course of the n.m.r. experiments. The fact that spectra taken several months apart showed no detectable changes ensures that the sample did not undergo any long term relaxation. The temperature of the sample was 35–40°C to ensure that the samples were above the secondary phase transitions in PTFE⁴.

The original undeformed material was analysed to ensure that it was unoriented. In addition, strained samples were studied at an orientation orthogonal to the magnetic field and goniometer plane to ensure that no biaxial orientation exists.

THEORY

The position of a single ^{19}F resonance line subject to an axially symmetric chemical shift tensor is given by⁷:

$$\sigma(\eta) = \sigma_{\parallel} \cos^2 \eta + \sigma_{\perp} \sin^2 \eta \quad (1)$$

where σ_{\parallel} and σ_{\perp} are the chemical shift when the unique tensor axis is along the field or perpendicular to it, respectively. η is the angle between the unique axis and the magnetic field. For a (random or nonrandom) polycrystalline sample, many orientations, η , are simultaneously present and the n.m.r. spectrum is a band of overlapping lines. The exact shape of the band is determined by the distribution function, $D(\eta)$, which describes molecular orientation in the sample relative to the magnetic field:

$$D(\eta)d\eta = I(\sigma)d\sigma \quad (2)$$

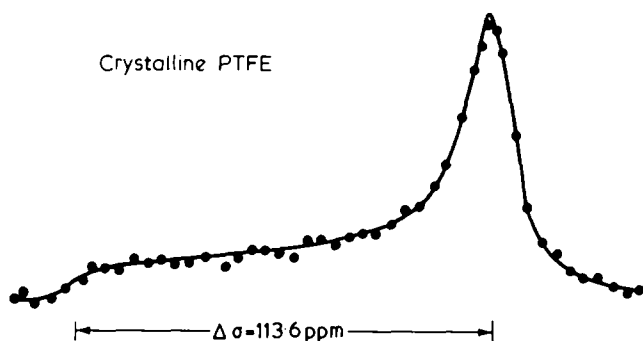


Figure 1 ¹⁹F n.m.r. spectrum of highly crystalline PTFE. Dots are experimental points. The solid line is a fit to the data by computer analysis

where $I(\sigma)$ is the intensity of the n.m.r. band at any σ . The bandshapes, $I_{\text{random}}(\sigma)$, for a random distribution were calculated by Bloembergen and Rowland⁸ and the bandshapes for several nonrandom models have been discussed in the literature^{9,7}. However, as emphasized by Spiess, *et al.*¹⁰, it is possible to obtain average information from a moment analysis of the n.m.r. band. We describe below the relevant parts for interpretation of our ¹⁹F data.

We shall assume that, if they were completely aligned, the unique axes of the PTFE chemical shift tensors would lie along the draw axis, \vec{n} . Thus one should refer the orientational distribution to this axis, rather than to the magnetic field. The relevant parameter to calculate is the first moment of the n.m.r. band relative to the isotropic position of a random distribution³:

$$\overline{\Delta\sigma_1} = \int (\sigma - \sigma_{\text{iso}}) I(\sigma) d\sigma / \int I(\sigma) d\sigma \quad (3)$$

For a polymer having crystalline and amorphous parts, one can divide the first moment into:

$$\overline{\Delta\sigma_1} = f_c \overline{\Delta\sigma_{1c}} + (1 - f_c) \overline{\Delta\sigma_{1a}} \quad (4)$$

where f_c is the crystalline fraction and $\overline{\Delta\sigma_{1i}}$ is the first moment of the i th component. The first moment depends critically on the distribution of chemical shift axes relative to the magnetic field. This distribution, in turn, depends on the orientation of the draw axis, \vec{n} , relative to the field and on the distribution of orientations of the chemical shift axes relative to \vec{n} , given by $P(\theta)$. We shall label as β the angle between the draw axis and the magnetic field. After some algebra, one obtains an expression for the first moment of the i th component as a function of the orientation, β , and of $P(\theta)$ ^{10,11}:

$$\overline{\Delta\sigma_{1i}} = \frac{2}{3} \Delta\sigma S_i - \Delta\sigma S_i \sin^2 \beta \quad (5)$$

where S_i is an order parameter measuring the effect that the macroscopic deformation has in orienting the chemical shift unique axes with respect to the draw axis. If all chemical shift axes in the sample are perfectly aligned along the draw axis, $S_i = 1$; if they are randomly distributed, $S_i = 0$. S_i depends on the distribution, $P(\theta)$, in the following way:

$$S_i = \int_0^\pi P_i(\theta) \frac{1}{2} (3\cos^2\theta - 1) \sin\theta d\theta \quad (6)$$

These results can be easily extended for the case in which the chemical shift tensor axes do not become oriented along the direction of extension, but rather along some axis related to it by a rotation.

RESULTS AND DISCUSSION

Figure 1 shows the ¹⁹F chemical shift spectrum of a highly crystalline PTFE powder. From a computer fit of this spectrum using a nonlinear least squares fitting routine, we estimate that the shielding anisotropy of the ¹⁹F resonance is 113.6 ± 5 ppm. Within the experimental error this value is the same as that found by Vega and English⁴, who report a shielding anisotropy of 118 ppm.

The ¹⁹F n.m.r. chemical shift spectra for the most highly oriented (140% elongation) PTFE sample are shown in Figure 2 as a function of orientation, β of \vec{n} relative to \vec{B}_0 . The shape of the ¹⁹F band changes dramatically as the orientation of \vec{n} relative to \vec{B}_0 is changed. These changes are a reflection of the anisotropy in the orientational distribution in this sample. According to equations (4) and (5), the first moment of this band relative to the isotropic position of a random sample will depend linearly on $\sin^2 \beta$. Figure 3 is a plot of the first moments of the spectra in Figure 2 versus $\sin^2 \beta$ showing that this relationship is obeyed for this PTFE sample. Because of the difficulty of setting the initial orientation of the sample in the magnetic field, we have found that it was probably in error by about

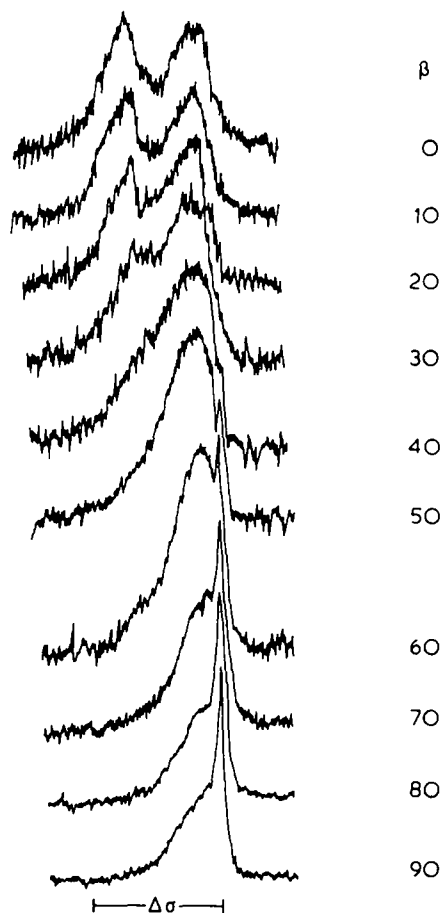


Figure 2 ¹⁹F n.m.r. chemical shift spectra of the deformed PTFE sample as a function of the orientation, β , of the stretch axis relative to the d.c. magnetic field. Scaling of each spectrum is not the same due to the sharp spike in spectra near 90°

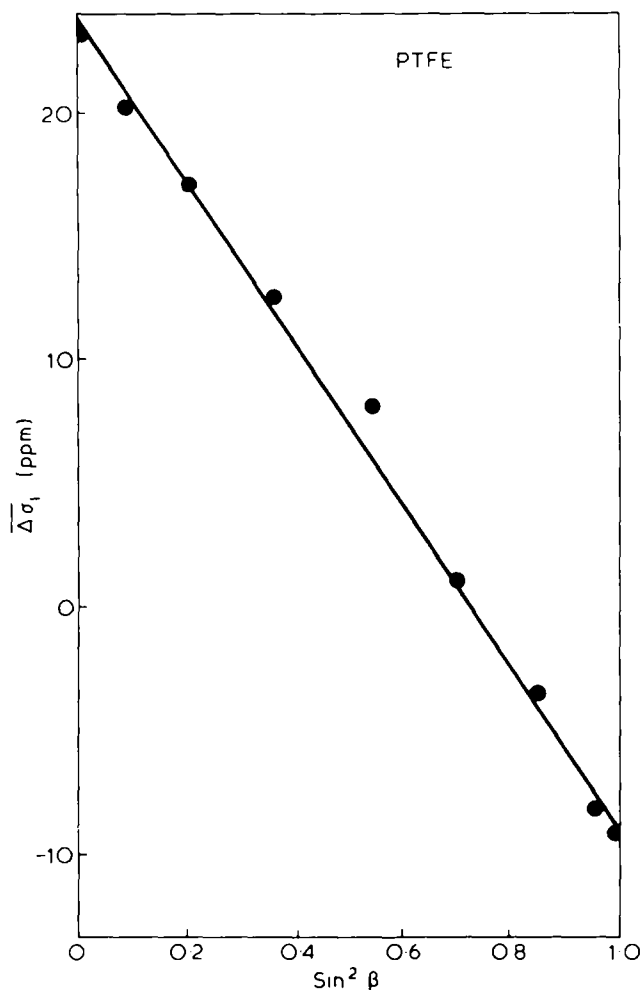


Figure 3 $\overline{\Delta\sigma_1}$ versus $\sin^2\beta$ for the deformed PTFE sample

3'. The results in Figure 3 have been corrected for this misalignment. Similar calculations for each of the PTFE samples give linear plots like Figure 3, from which similar information can be extracted.

It has been shown^{3,4} that, for crystallites of PTFE, the unique axis of the ¹⁹F chemical shift tensor in this temperature range is coincident with the helix axis of the crystallites. Thus, the spectral changes can be explained by assuming that the deformation results in a partial ordering of the sample. The overlap of bands from the crystallite and amorphous regions make the analysis of the results difficult. According to equation (4), the first moment is a weighted average of the first moments of crystalline and amorphous regions. Thus, the first moment measures some average ordering in both phases. The position of the maximum for the amorphous resonance occurs in the region where it occurs for an unoriented sample. The crystalline resonance, on the other hand, does vary with β. For large values of β, there is significant intensity near the amorphous resonance maximum due to the resonance of the crystalline regions. In particular, at around 40–50°, intensity begins to build in the regions where the resonance of crystallites oriented perpendicular to the field occur, indicating that the crystallite orientational distribution is not narrow. The intensity in this region continues to grow as the orientation is changed until β=90°. The absolute intensity at the position of the maximum for the amorphous resonance never decreases below its value for

β=0 in these spectra. This implies that there are never fewer nuclei resonating with that frequency than at β=0, where the resonance from the crystallites is reasonably distinct from that of the amorphous regions.

Based on these observations, we make the assumption that the amorphous regions are unoriented and that the first moment, $\overline{\Delta\sigma_{1a}}$, is zero. Theoretical treatments¹² of the order parameter in uniaxially deformed amorphous polymers further support this assumption. When a molecule which is originally randomly coiled undergoes an affine deformation, the order parameter is given by:

$$S_a = \frac{1}{5N_i} \left(\lambda^2 - \frac{1}{\lambda} \right) \quad (7)$$

where N_i is the number of statistical links in the molecule and λ is the draw ratio. For all of our samples, $(\lambda^2 - \frac{1}{\lambda}) \leq 5.34$ and N_i is a large number, which leads to a very small value of S_a .

There is also the possibility that some biaxial order is produced upon deformation of the PTFE samples. In order to address this question experimentally, we examined n.m.r. spectra taken of a sample at various orientations with respect to the field, but we placed the draw axis perpendicular to the magnetic field in every case. The spectra are identical to that for β=90° of Figure 2 for every orientation examined. Thus, we conclude that tensile stress does not produce biaxial orientation in PTFE.

The crystalline fraction, f_c , is found by infra-red techniques¹³ to be 0.58 ± 0.05 . Thus, the value of S_c for the sample of Figure 2 may be calculated from equations (4) and (5) and the slope of the line in Figure 3 (–32.8 ppm) to be 0.50 ± 0.03 . Similar results for the other samples are summarized in Table 1.

One may model the distribution of crystallite orientations in the oriented samples in a number of ways. Perhaps the simplest model is to assume that the crystallite distribution about the axis of extension is Gaussian:

$$P(\theta) = e^{-\theta^2/2\Delta^2} \int_0^\pi e^{-\theta^2/2\Delta^2} \sin\theta d\theta \quad (7)$$

where Δ is the width of the Gaussian distribution and gives an indication of the deviation from perfect order. For each value of Δ one may evaluate equation (6) numerically to give a value of order parameter, S_c . The theoretical values of S_c calculated according to equation (6) for Δ in the range 0°–90° are shown in Figure 4 for such a Gaussian model. Thus, assuming a Gaussian model is correct for such a sample, one predicts the spread about \bar{n} for the sample whose spectra are shown in Figure 2 to

Table 1 Orientation parameters for PTFE ordering

% Elongation	S_c (Experimental) (± 0.03)	S_c (Theoretical)	Δ (Degrees) (± 3)
0	0.00	0.00	90
40	0.23	0.21	42
75	0.33	0.35	35
110	0.42	0.44	31
140	0.50	0.53	28

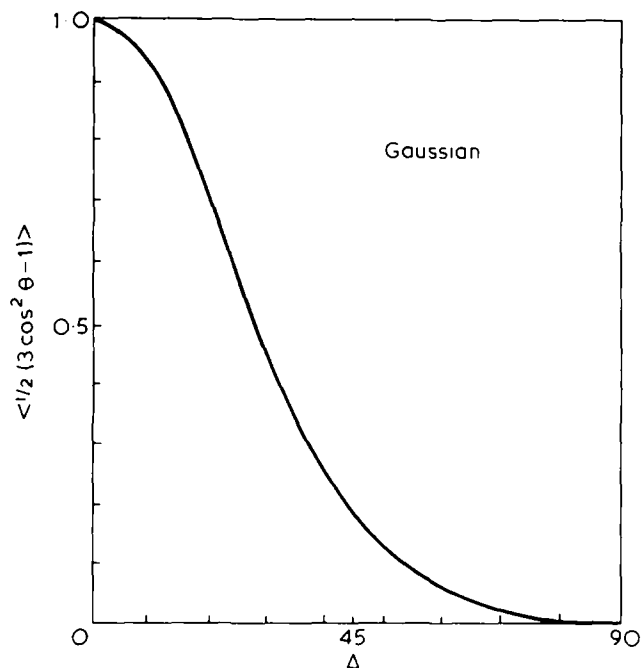


Figure 4 $\langle \frac{1}{2}(3 \cos^2 \theta - 1) \rangle$ for a Gaussian probability distribution as a function of the width, Δ , of the normalized Gaussian. $S = \langle \frac{1}{2}(3 \cos^2 \theta - 1) \rangle$

have a width, Δ , of $30 \pm 3^\circ$. Similarly, one may describe each of the other samples by the values, Δ , listed in Table 1. Note that one would predict a significant build-up of intensity at the values around σ , for values of β in the range 40° – 50° ($90 - \Delta$) as observed.

Several calculations of the effect of macroscopic deformation on the orientation of crystallites have been published. Wilchinsky¹⁴ used a model of rigid crystallites in a viscous fluid to predict the dependence of average crystallite orientation on the draw ratio ($\lambda = L/L_0$).

$$\langle \cos^2 \theta \rangle = \frac{\lambda^3}{\lambda^3 - 1} \left\{ 1 - \frac{\tan^{-1}(\lambda^3 - 1)^{1/2}}{(\lambda^3 - 1)^{1/2}} \right\} \quad (8)$$

It is assumed that the imposed stress is borne by the viscous matrix with the resulting flow causing the crystallite orientation. The results of our study are plotted in Figure 5, together with the theoretical predictions of Wilchinsky. Within the experimental error, the present results agree with the predictions of the theory.

CONCLUSIONS

N.m.r chemical shift dispersions can provide information on orientational distributions in polymers. If the relationship of the principal axes of the chemical shift tensor to the polymer framework is known, conclusions can be drawn about the orientational order of the polymer framework. We have demonstrated a first moment analysis for the ¹⁹F n.m.r. spectrum of PTFE. Order parameters deduced from this analysis agree very closely

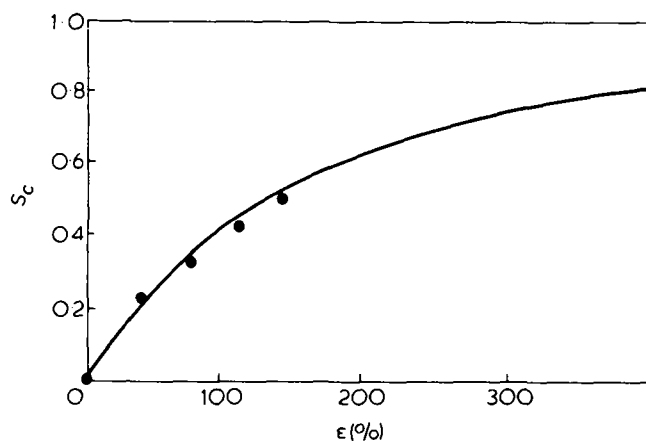


Figure 5 Plot of S_c , the order parameter, as a function of elongation. The solid line is the theoretical prediction of Wilchinsky¹⁴. $\epsilon [= 100(L - L_0)/L_0]$ is the percent elongation

with the theoretical predictions of Wilchinsky¹⁴. The exact values depend on the assumption that the amorphous material is not oriented.

The case of PTFE represents a simple system for these analyses, because in the temperature region in which this work was performed the crystallite and chemical shift axes are coincident. In more complicated polymers, a similar technique could be used, but a more complete analysis will be required to relate the first moment to the orientation of the structures. The technique is not restricted to ¹⁹F n.m.r. but may be used in cases where one may observe an unobscured n.m.r. resonance in a polymer.

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