

Fluorine-19 NMR investigation of poly(trifluoroethylene)

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Abstract

An NMR investigation of poly(trifluoroethylene) is reported. Using known assignments of the fluorine solution-state spectrum, the defect level has been determined as well as a high degree of atacticity confirmed. The solid-state ¹⁹F NMR study concentrated on the detection of heterogeneities in the polymer. Transient oscillations in ¹H → ¹³C CP curves have been used in order to determine effective bond distances and, consequently, to detect motion of the polymer chain. The onset of motion has been confirmed by comparing the measured axially symmetric fluorine shielding tensor with the asymmetric tensor obtained from ab initio calculations carried out on the rigid molecule. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Poly(trifluoroethylene) (PTrFE) belongs to the family of fluoropolymers, which are electroactive. The special interest in these substances arises from their industrial applications (based on their electrical properties). Apart from poly(vinylidene fluoride) (PVDF), the most extensively studied system is the copolymer of trifluoroethylene and vinylidene fluoride, which has been the target of considerable research [1–5]. PTrFE itself exhibits pyro- and piezo-electricity, and also ferro-electricity, as shown by Oka and Kouzumi [6]. The assignment by Tonelli and Cais [7,8] of the peaks of the ¹⁹F solution-state spectra is the basis for determining the defect level of the polymer. Slichter [9] carried out motional studies on fluorine derivatives of polyethylene by measuring T_1 , T_2 and $T_{1\rho}$ relaxation times for proton and fluorine nuclei of static samples in the temperature range 70–350 K. McBrierty et al. [5] discussed the same relaxation parameters (for protons only) and observed three relaxation processes in PTrFE, mainly based on $T_{1\rho}$ data. Different relaxation parameters for the amorphous and mobile domains of PVDF have been used by Holstein and others

[10,11] in order to select signals from these regions separately.

PTrFE is a semi-crystalline polymer, with a crystallinity in the range 18–46% [6]. There seems to be disagreement about the crystal structure and chain conformation of PTrFE: Tashiro et al. [12] proposed a disordered all-*trans* conformation with an orthorhombic chain packing. Lovinger et al. [13], however, claim that PTrFE has a disordered conformation of TG, $\bar{T}\bar{G}$, and TT groups, with hexagonal packing. The proposed structure is said to be analogous to the paraelectric phase of P(VDF/TrFE) copolymers. Oka et al. [14] disagree with both proposals: they suggested, in compliance with density measurements and polar properties, a chain conformation consisting of T and G groups instead of being all-*trans*. Furthermore, they found two crystalline phases (denoted D and S), which were detected by X-ray and polarisation–current measurements.

Different glass transition temperatures have been reported for PTrFE. Gaur et al. [15] give a glass transition at 31°C. The glass transition temperature relevant for NMR experiments must lie in the range of $T_g(\text{PTrFE}) = 30\text{--}50^\circ\text{C}$.

2. Experimental

PTrFE was obtained from Elf Atochem as a white flaky powder. It has been dried and kept in a Teflon-sealed container before use.

Solution-state ¹⁹F NMR spectra were acquired using a Varian Inova 500 spectrometer operating at a fluorine

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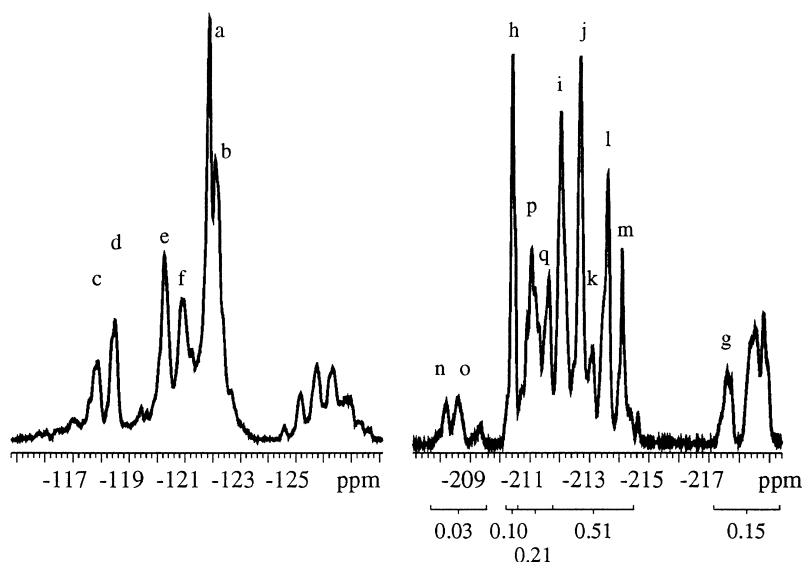


Fig. 1. 470 MHz ^{19}F spectrum of PTrFE with proton decoupling, referenced internally to CFCl_3 . The regions of interest are the CFH fluorine resonances (right) and CF_2 fluorine resonances (left). Their vertical scale is adjusted to the same maximum peak height.

frequency of 470.19 MHz. When H-decoupling was applied, the WALTZ-16 sequence was used. All experiments were done at ambient temperature, $T \cong 296$ K. Deuterated acetone was used as the solvent. The pulse angle was 29.9° , a recycle delay of 2.0 s was used, and 32 transients were acquired.

Solid-state NMR experiments have been carried out using a triple-channel Chemagnetics CMX 200 spectrometer, operating at 200.13 MHz for ^1H , 188.29 MHz for ^{19}F and 50.33 MHz for ^{13}C . Proton and fluorine spectra were recorded on a purpose-built Chemagnetics HF probe, accepting 4 mm o.d. zirconia rotors with drive tips made from Vespel. The sample had to be spatially confined in order to reduce the inhomogeneity in B_1 , especially for the measurements of B_1 -dependent relaxation parameters ($T_{1\rho}$, T_{HF} etc.). Carbon spectra were recorded on a triple-channel HFX probe in conjunction with 7.5 mm o.d. zirconia rotors. Fluorine spectra are referenced to CFCl_3 via C_6F_6 at -166.4 ppm with the decoupler off. The reported chemical shifts should therefore be corrected for the Bloch–Siegert effect, which amounts to ca. 1.4 ppm due to the proximity of fluorine and proton resonances. Carbon spectra are referenced to TMS using adamantane (with -38.4 ppm for the high-frequency peak). The temperatures quoted for variable-temperature experiments are calibrated using a chemical-shift thermometer of TTMSS [16].

Standard pulse sequences were used: Direct polarisation or cross-polarisation spectra were acquired with and without decoupling. The MREV-8 pulse sequence for fluorine observation with proton decoupling has been implemented by Scheler et al. [17]. The $T_{1\rho}$ -filter and the dipolar decoupling experiments have been described elsewhere [11]. The IRCP pulse sequence introduced by Melchior [18] is essentially a CP experiment with an inversion of one of the phases

of the CP pulses after a certain (inversion) time. Its parameters are described below.

The ab initio calculation of the ^{19}F shielding tensors were performed using the GAUSSIAN 94 program [19]. The ground-state geometries of the model compounds were optimised at the Hartree–Fock (HF) level of the theory using standard 3-21G basis sets from the GAUSSIAN 94 basis set library. The NMR shielding tensor calculations were carried out at the optimized geometries by means of the HF-GIAO (gauge-including atomic orbital) approach. The basis sets used in these calculations was 6-31G*.

3. Results and discussion

3.1. Solution-state NMR

Fig. 1 shows the ^1H -decoupled ^{19}F spectrum of our sample in acetone- d_6 . Tonelli et al. [7] and Cais et al. [8] have attempted to assign the solution-state ^{19}F spectrum of PTrFE synthesised in their laboratory. Their prediction of chemical shifts based on the rotational isomeric state (RIS) approximation showed good agreement with their experimental data. Two regions of peaks, ascribed to the CF_2 fluorines (-128 – -117 ppm) and the CFH fluorine (-219 – -208 ppm), should be noted. PTrFE, like other fluoropolymers, is atactic. The CF_2 resonance is sensitive to stereosequence dyads, so a singlet should be observed for the geminal fluorines in the racemic dyad. Two peaks can be observed in the relevant region (Fig. 1): -121.9 (a) and -122.1 ppm (b). The singlet is split because of sensitivity to tetrad stereosequences. On the other hand, the magnetically nonequivalent CF_2 fluorines of the meso dyad give rise to an AB quartet with $J_{\text{gem}} \approx 300$ Hz, the chemical shift difference presumably arising from conformational effects. The peak positions for

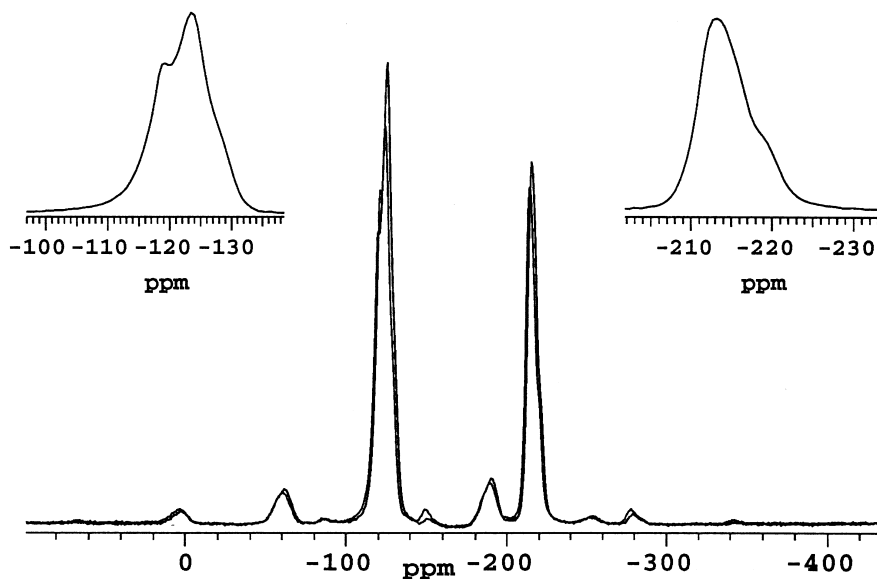


Fig. 2. Direct polarisation ^{19}F spectrum with (top) and without (bottom) ^1H decoupling under MAS at 12 kHz at ambient probe temperature (spectrometer frequency 188.29 MHz, $\gamma_{\text{F}}B_1/2\pi \cong 83$ kHz, dwell time 10 μs , 16 transients, recycle delay 2.5 s). The expansions shown are without decoupling.

this quartet are -117.9 (c), -118.5 (d), -120.2 (e) and -120.9 ppm (f). The true chemical shifts can be calculated to be -118.2 and -120.5 ppm.

Peaks at lower frequencies for both groups are due to monomer inversions of the head-to-head and/or tail-to-tail kind. More exactly, peaks at the lowest frequency (-218.4 – -218.8 ppm) arise from the racemic tail-to-tail fluorine of the CFH group. The meso fluorine causes resonances at higher frequency (≈ -217.6 ppm (g)) with lower intensities, so that we can infer a favoured racemic arrangement of the $-\text{CFH}-\text{CFH}-$ units. RIS calculations of Tonelli et al. [7] predict a splitting of the stereo-regular peaks due to stereochemical triads, with pentad fine structure on the heterotactic and isotactic peaks. Six peaks, viz. -210.4 ppm (rr) (h), -212.1 ppm (rm) (i), -212.7 ppm (rm) (j), -213.1 ppm (mm) (k), -213.6 ppm (mm) (l), and -214.1 ppm (mm) (m), can be assigned in that way. Comparison of the fluorine spectrum of highly regioregular PTrFE with that of our sample suggests that the peaks at -208.2 (n), -208.6 (o), -211.1 (p) and -211.6 ppm (q) arise from monomer inversions.

It is noteworthy that the influence of proton decoupling is small, only a few fluorine resonances in the CFH region showing this effect (for example at 210.4 ppm (h) ($J = 34$ Hz) and 214.1 ppm (m) ($J = 38$ Hz)).

Based upon the assignment of the peaks, an attempt has been made to estimate the defect level. The definition for the defect level given by Cais et al. [8] has been used. Three observationally distinct syndioregic CFH-centred regiosequence pentads can be found in PTrFE. The respective chemical shifts have been predicted by Tonelli et al. [7] as follows:

A: -207 – -210 ppm ($-\text{CF}_2-\text{CF}_2-\text{CFH}-\text{CF}_2-\text{CFH}-$),

B: -210 – -214 ppm ($-\text{CFH}-\text{CF}_2-\text{CFH}-\text{CFH}-\text{CF}_2-$),

C: -215 – -219 ppm ($-\text{CF}_2-\text{CF}_2-\text{CFH}-\text{CFH}-\text{CF}_2-$),

Peak integration yields the following approximate probabilities for regions A, B and C: A 1.5, B 11.5, C 7.5. The total contribution of the $-\text{CFH}-$ resonance area has to be normalised to 0.5. Following Cais' definition, the polymer has a defect level of $1/2(1.5 + 11.5) + 7.5 = 13.5\%$.

3.2. Solid-state NMR

Fig. 2 shows an MAS direct-polarisation ^{19}F spectrum of PTrFE. The two peaks at ca. -120 and -220 ppm of the static ^{19}F -spectrum (not shown) are only marginally narrowed by proton decoupling. The remaining line broadening is due to homonuclear dipolar fluorine coupling and can be narrowed by MAS, as shown in Fig. 2, or with multi-pulse sequences such as MREV8 (see Fig. 3).

Further examination of the MAS fluorine spectrum reveals a small peak at -119 ppm (in the absence of decoupling). Also, a little shoulder (-127 ppm) shifted to low frequency of the peak at approximately -123 ppm can be seen. The CFH-peak at -213 ppm is neither purely Lorentzian nor purely Gaussian because of the existence of a small shoulder at -219 ppm. Experience from studies on poly(vinylidene fluoride) (PVDF) suggests that these additional peaks could be due to morphological heterogeneities of PTrFE, e.g. different crystalline and amorphous phases. Alternatively, they could stem from a heterogeneous chemical chain-structure, as is suggested by the approximate positions of peaks in the ^{19}F solution-state spectrum. Thus, we should tentatively assign peaks in the solid-state spectrum as follows:

- (CF₂ region) -119 ppm: high frequency doublet of the

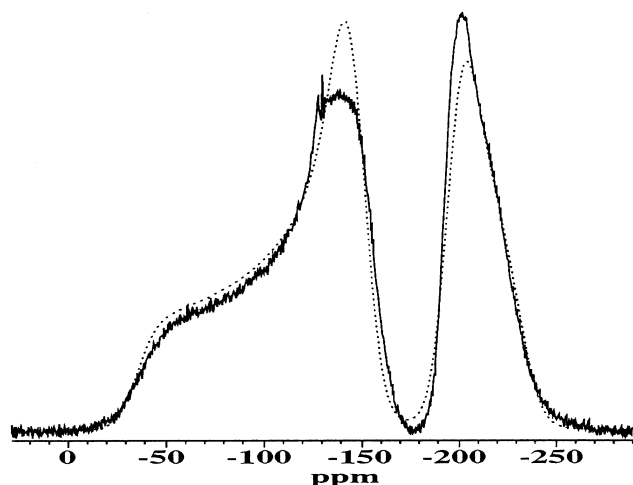


Fig. 3. ^{19}F MREV8 spectrum of a static sample of PTrFE. The dashed line is the theoretical fit to the experimental lineshape (for the parameters see text) with 2000 Hz Gaussian line broadening. 2048 points of FID were acquired. Experimental conditions were: pulse duration 1.4 μs , 64 transients, pulse delay 3 s, 512 points acquisition length, τ -delay 3 μs , proton decoupling with π -pulses on the proton channel (constant phase, pulse duration 2.47 μs , spacing 15.5 μs).

AB quartet, which arises from sensitivity to stereo-sequence dyads; -123 ppm: low-frequency doublet of the same AB quartet and singlet for fluorines in the racemic dyad; shoulder at ca. -127 ppm: head-to-head monomer inversions.

- (CFH region) -213 ppm: all peaks which arise from isoregular fluorines; shoulder at -219 ppm: head-to-head monomer inversions.

Fig. 3 shows a static spectrum of PTrFE recorded with an MREV-8 sequence. The FID under MREV-8 exhibits a single exponentially decaying baseline, which leads to a spike at the transmitter frequency. This effect could be partially removed by subtracting a fitted exponential prior to Fourier transformation. The pulse-sequence removes any homonuclear dipolar fluorine interactions and leaves the ^{19}F shielding anisotropy as the dominating line-broadening mechanism. We observe two well-defined axially symmetrical shielding anisotropy (SA) powder patterns. The relevant parameters are as follows:

CF₂-peak: $\delta_{\text{iso}} = -110$ ppm, $\sigma_{\perp} - \sigma_{\text{ref}} = 147.5$ ppm, $\sigma_{\parallel} - \sigma_{\text{ref}} = 35$ ppm

CFH-peak: $\delta_{\text{iso}} = -210$ ppm, $\sigma_{\perp} - \sigma_{\text{ref}} = 198.5$ ppm, $\sigma_{\parallel} - \sigma_{\text{ref}} = 233$ ppm

The comparison with ab initio calculation will be discussed below.

Selection methods have been exploited to a great extent in PVDF by Holstein and co-workers [11]. Their bases are differing relaxation efficiencies in different regions of the heterogeneous sample due to mobility differences:

- The immobile (crystalline) region can be selected by a long proton spin-lock prior to a short cross-polarisation

time, the so called $T_{1\rho}$ -filter. However, the cross-polarisation time has to be chosen so that spin diffusion between different domains is avoided whilst enabling sufficient polarisation to be transferred to spins at greater distances from protons (e.g. CF₂).

- The mobile (amorphous) region is emphasised by a dipolar dephasing experiment (in essence a delayed acquisition, in the absence of decoupling, after cross polarisation with a moderately long contact time, when the magnetisation of the crystalline region rapidly decays).

These experiments, with ^{19}F detection, have been applied to PTrFE with only limited effect. Fig. 4 shows the effect of a $T_{1\rho}$ -filter at elevated temperature. The difference between the single-pulse spectrum in Fig. 2 and the one presented in Fig. 4 has to be attributed to changes in the lineshape due to the raised temperature. However, the comparison between the top and bottom slices reveals that no influence of the spin-lock filter can be detected. The results of a different experiment at elevated temperature, which should reveal signals of mobile regions, are shown in Fig. 5. Comparison of bands between Figs. 4 and 5 shows that no real influence of selection can be detected.

3.3. Motion in the polymer

As is noticeable in Fig. 5, the CF₂ fluorine peak has a reduced intensity compared with the CFH fluorine resonance. This is readily explained by the reduced $^1\text{H} \rightarrow ^{19}\text{F}$ CP efficiency for the CF₂-group at elevated temperature, since fluorines in the CF₂-group are allowed to move relative to the proton. On the other hand we find, neglecting vibrational motion, that the triangular CFH-group is relatively rigid and retains its capability to cross polarise, provided the whole group does not undergo liquid-like rapid motion and thus average heteronuclear coupling completely. The onset of motion is monitored by the dependence of the ratio of the peak intensities upon temperature (see Fig. 6). For short contact times a steep decrease in the intensity of the CF₂ resonance for temperatures higher than 50°C can be noted. This temperature threshold coincides with the expected glass transition.

The experimental results of the multi-pulse experiment on the static sample (see Fig. 3) have been compared to results from ab initio calculations. The input structures were a syndiotactic and a regiotactic fluorinated alkane consisting of two monomer units, end-capped with CF₃ groups. The geometrical structure was optimised with the 3-21G basis set. NMR parameters, as listed in Table 1, were calculated with the larger polarised 6-31G* basis set, which is the recommended minimum basis set for calculating NMR shielding tensors [20]. The discrepancy between the fitted axial symmetry ($\eta_{\text{CFH}} = \eta_{\text{CF}_2} = 0$) and the asymmetry found from ab initio calculation ($\eta_{\text{CF}_2} = \text{ca } 0.5$ and $\eta_{\text{CFH}} = \text{ca } 0.5$) can be explained by a rapid averaging process, possibly partial rotation about the molecular

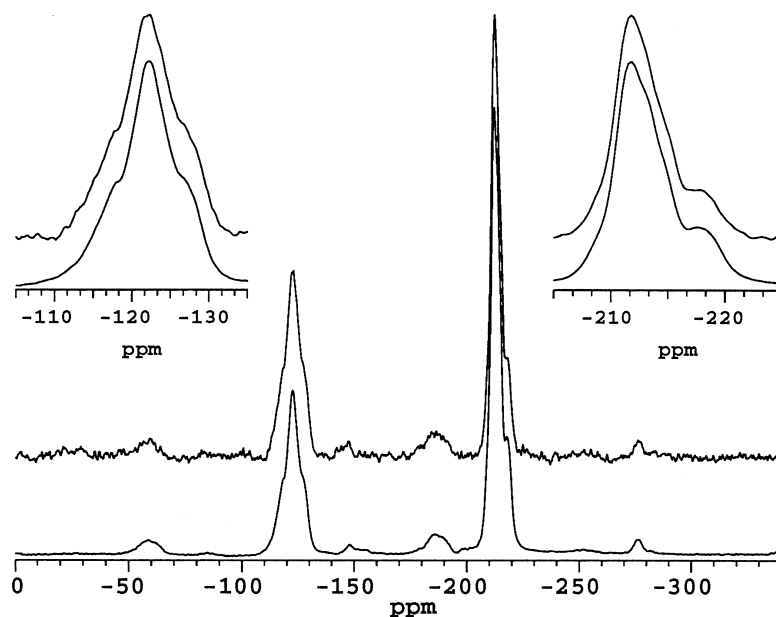


Fig. 4. Fluorine-19 spectra obtained using the $T_{1\rho}$ -filter prior to CP for PTRfE at $T = 100^\circ\text{C}$, with MAS at 12 kHz, ^1H -decoupled. Top: spin lock of 20 ms, bottom: no spin lock for comparison, contact time $t_c = 0.2$ ms. The two spectra are normalised to the same height for the tallest peak.

chain axis. This process must occur below the glass transition. The low efficiency of proton decoupling is a further indication of a mode of motion at ambient temperatures.

The determination of dipolar coupling constants can help to scrutinise motional processes in greater detail. A full understanding of cross-polarisation dynamics between two abundant spin systems is difficult to attain [22–24]. However, in cases with strongly coupled spin pairs oscillations in magnetisation of the receiving nucleus occur because the CP transfer is initially coherent. These oscillations

depend on the effective strength of dipolar coupling between the two nuclei. In order to measure dipolar coupling constants more precisely by these means the inversion-recovery cross-polarisation pulse sequence (IRCP), originally introduced by Melchior [18], was used. This pulse-sequence is particularly useful to monitor coherent (short-time) magnetisation transfer between different nuclei. To measure dipolar coupling constants and hence distances, in principle, any combination of proton, fluorine and carbon resonances can be used for cross polarisation (CP).

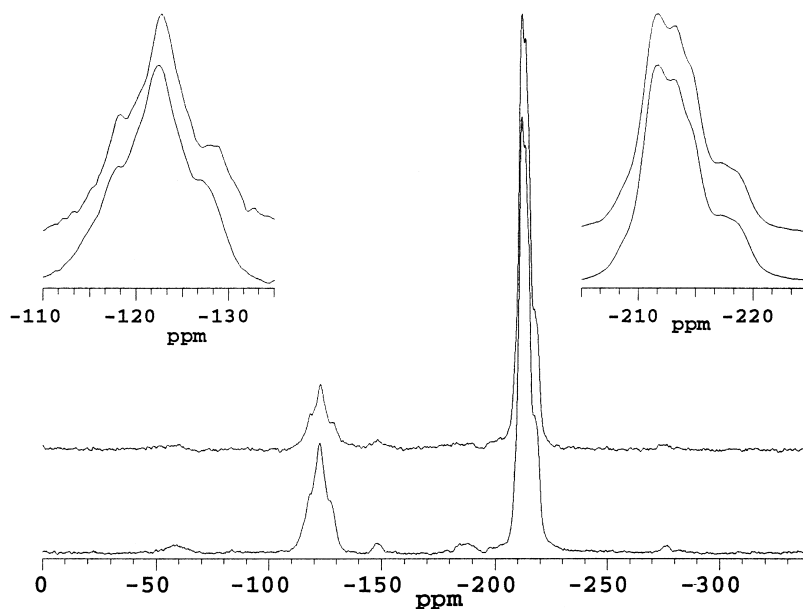


Fig. 5. Fluorine-19 spectra obtained using the dipolar dephasing experiment on PTRfE at $T = 100^\circ\text{C}$, with MAS at 12 kHz, ^1H -decoupled, contact time $t_c = 0.5$ ms. Top: dipolar dephasing for 500 μs , bottom: no dephasing for comparison. The two spectra are normalised to the same height for the tallest peak.

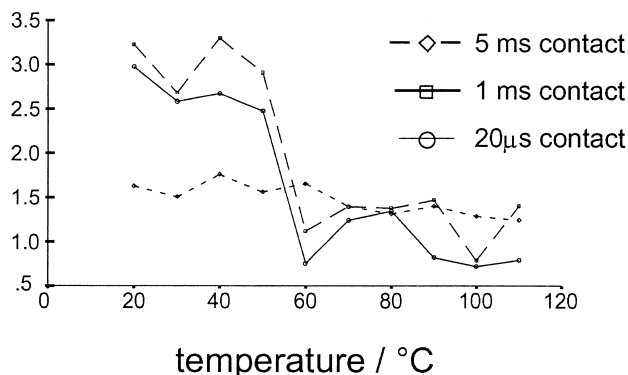


Fig. 6. Ratio, $r = I_{CF_2}/I_{CFH}$, of integrals over peaks for the CFH and CF₂ resonances in a CP experiment vs. temperature. The three different curves represent ratios of intensities at different contact times.

However, dipolar oscillations are best observed in dilute spin pairs such as are present in the case of $^1\text{H} \rightarrow ^{13}\text{C}$ CP for PTrFE. Of course, fluorine decoupling (as well as proton) has to be applied during acquisition in order to avoid linebroadening.

The analysis of the transient oscillations consists of the Fourier transformation of the integral intensity of the carbon peaks measured at equidistant intervals of contact time. Offsets, exponential rise, and decay of the magnetisation curves have been subtracted from the curves by using suitable exponentials. As pointed out by Hirschinger et al. [25,26], the IRCP experiment has the advantage of showing more pronounced oscillations than simple CP while still being describable by the same theoretical model. That is why data from IRCP experiments were taken in order to determine dipolar coupling constants.

The Fourier transformations of the dipolar oscillations at ambient temperature are shown in Fig. 7. The peak

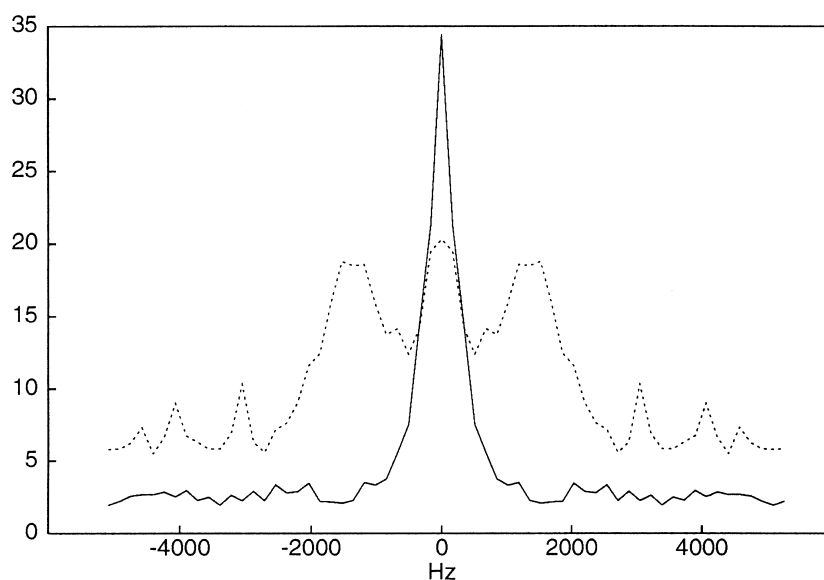


Fig. 7. Fourier transformation of the dipolar oscillations in an IRCP experiment on PTrFE at ambient probe temperature. The CFH carbon(dashed) exhibits a doublet with a peak separation of 3 kHz whereas the CF₂ carbon only has one peak.

Table 1

Calculated shielding tensors for regiotactic and syndiotactic PTrFE, together with observed values as obtained from MREV-8 fluorine spectrum (see Fig. 3) Definitions are as follows: isotropic shielding $\sigma_{\text{iso}} = 1/3(\sigma_{XX} + \sigma_{YY} + \sigma_{ZZ}) - \sigma_{\text{ref}}$, where σ_{ref} has been determined for CFCl₃ by Hindermann et al. [21], asymmetry $\eta = (\sigma_{YY} - \sigma_{XX})/(\sigma_{ZZ} - \sigma_{\text{iso}})$ and anisotropy $\Delta\sigma = \sigma_{ZZ} - 1/2(\sigma_{XX} + \sigma_{YY})$

	CF ₂			CFH		
	σ_{iso}	$\Delta\sigma$	η	σ_{iso}	$\Delta\sigma$	η
Regiotactic	166	106	0.590	246	52	0.419
Syndiotactic	163	90	0.444	244	45	0.565
Observed	110	112.5	0	210	34.5	0

separation for the CFH signal is 3 kHz, which corresponds to a proton-carbon distance of 1.5 Å (from use of the following equation [23,27]):

$$\omega_{\text{osc}} = \frac{\mu_0 \gamma_{\text{H}} \gamma_{\text{C}} \hbar}{8\pi r^3 \sqrt{2}} \quad (1)$$

where ω_{osc} represents the angular oscillation frequency, γ_{H} and γ_{C} are the gyromagnetic ratios, and r is the interatomic distance between proton and carbon. The calculated distance is clearly longer than the expected 1.1 Å for average C–H bond distances. Nonetheless, an oscillation frequency corresponding to 1.5 Å is possible if one allows for molecular motion (for instance chain rotation) which leads to a scaling factor which depends on the type of motion (e.g. factor 2 for axially symmetric motion).

The same experiment has been repeated at lower temperature (ca. -30°C). The result is presented in Fig. 8. The measured dipolar oscillation frequency of 5.5 kHz corresponds to 1.2 Å between carbon and proton. Although this is still slightly larger than the expected value, the

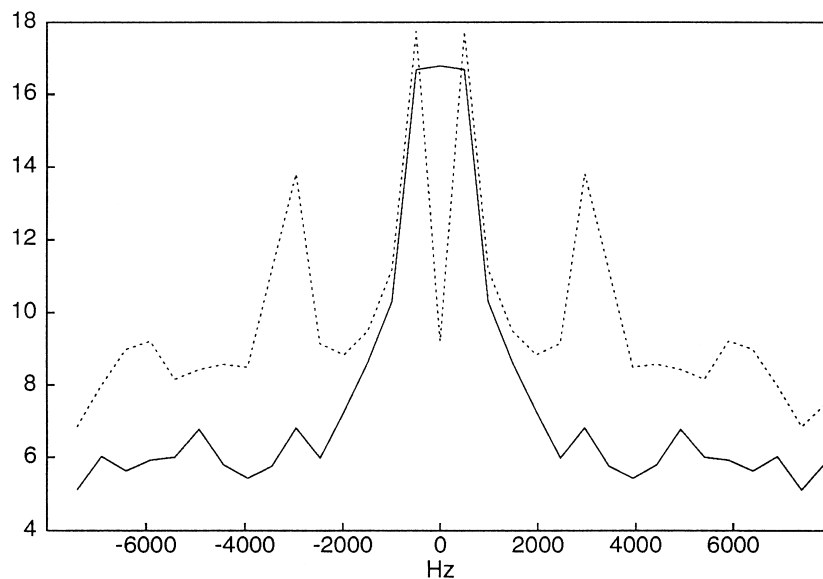


Fig. 8. Fourier transformation of the dipolar oscillations in an experiment on PTrFE at $T = -30^{\circ}\text{C}$. The CFH carbon (dashed) exhibits a doublet with a peak separation of 5.5 kHz and a central 'doublet' arising from incomplete correction of the baseline. The CF_2 carbon shows only one peak.

implication is that molecular level motion has been significantly slowed at -30°C .

4. Conclusions

As has been shown, the present polymer contains a considerable amount of head-to-head monomer inversion. The defect level was determined on the basis of solution-state NMR. Selection schemes based on differences in relaxation parameters at various temperatures show only marginal influence, if at all. Since we expect partial crystallinity [6,12,13], this can only mean that relaxation parameters differ by less than an order of magnitude, which renders $T_{1\rho}$ -filter and dipolar dephasing experiments ineffective. Two modes of motion could be shown by a number of NMR experiments. The onset of mobility (α -relaxation) at about 50°C was proved by a steep decrease of the $^1\text{H} \rightarrow ^{19}\text{F}$ CP efficiency for the CF_2 fluorines, which are at a considerable distance from the protons. Low proton-decoupling efficiency is also an indication for motion still being present at ambient temperatures (below the glass transition). It was possible to prove that this motion is considerably hindered at -30°C by measurement of dipolar oscillation frequencies, utilising the IRCP experiment. β -relaxation, occurring below T_g , is normally ascribed to local motion of side-chains. However, in the present case there are no such side-chains, so localised motion of the main chain must be invoked.

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