Solid-state NMR of Fluoropolymers

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Introduction

Fluoropolymers form an interesting class of materials, with properties of industrial importance. Those which also contain protons form a special class for NMR purposes because the existence of two abundant spin baths provides both difficulties and opportunities. High-resolution solid-state ^{19}F studies of such systems were not obtained until the mid-1990s because of difficulties associated with proton decoupling. However, modern specialised probes make such experiments reasonably straightforward [1,2]. Work has been carried out in our group (now dispersed to four locations!) on PVF, PVDF, PTrFE and various copolymers. Some of these studies, together with the work of other researchers, have been reviewed [3]. The polymers are mostly semi-crystalline, and emphasis has been placed on methods of preferentially selecting sub-spectra from the different domains. Of crucial importance is the presence of "reverse" units (and other imperfections) in PVDF and associated copolymers. Information on the development of such units (and on the assignment of weak signals) has been obtained by solution-state measurements of a telomer of PVDF. Relaxation times, measured as functions of temperature for a VDF-TrFE copolymer, provide evidence of mobility and, combined with chemical shift variations, reveal conformational changes at around the ferroelectric-paraelectric phase transition.

Cross-polarisation dynamics are complicated for fluoropolymers, but analysis of variable contact time experiments can be simplified and the process understood [4].

Choice of pulse sequence is vital for understanding the domain structure of semi-crystalline polymers, since selective spectra may be produced (see below).

Experimental

The materials have generally been obtained commercially. The PVDF telomer was kindly supplied by Dr. B. Ameduri (ENS, Montpellier).

Solid-state NMR spectra were obtained using either a Chemagnetics CMX-200 spectrometer, operating at 188.288 MHz for ^{19}F, or a Varian UNITYplus 300 instrument, operating at 282.21 MHz for^{19}F. A Bruker Avance 500 spectrometer (470.53 MHz for ^{19}F) was used for the solution-state spectra.

Selectivity

Separate spectra of different domains (typically crystalline and amorphous) in solid fluoropolymers may be obtained by a variety of techniques, mostly based on relaxation properties, which differ because of differing mobilities in the several domains. Thus, for ^{19}F observation under cross polarisation from ^{1}H, one may use T_1(H), T_1(F), $T_{1\rho}$(H), $T_{1\rho}$(F) or linewidth (for either ^{1}H or ^{19}F). Clearly, appropriate pulse sequences must be employed. A new selective pulse sequence involving H → F cross polarisation, 'Discrimination Induced by Variable Amplitude Minipulses' (DIVAM), shown in figure 1, has been introduced [5]. The sequence selects via the transverse relaxation times of the ^{1}H spin baths, and its operation has been analysed [6]. Figure 2 shows its application to a sample of P(VDF/TrFE). This concept has recently been extended to direct polarisation experiments on ^{19}F [7]. For this case, SIMPSON simulations have been carried out under a variety of conditions (off-resonance, shielding anisotropy and dipolar coupling). These reproduce the observed behaviour for PVDF.

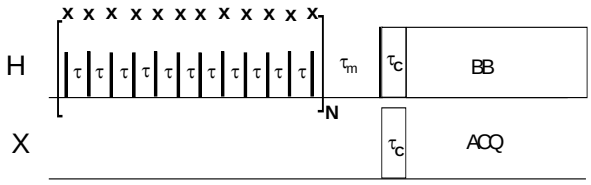

Figure 1: The DIVAM pulse sequence for cross-polarisation operation. The pulses are of fixed phase but variable nutation angle.

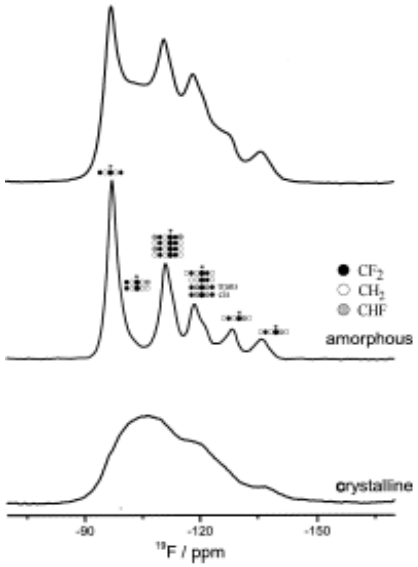

Figure 2: Fluorine-19 DIVAM spectra of P(VDF/TrFE).
Top: Full spectrum, minipulse angle θ = 0º. Middle: amorphous domain, θ = 30º. Bottom: Crystalline domain, θ = 7.3º.

Phase behaviour of a copolymer

Copolymers of vinylidene fluoride and trifluoroethylene undergo a ferroelectric-paraelectric phase transition on heating. Two samples have been studied [8], as-received (AR) and uniaxially-drawn single-crystalline film (SC). The latter is much more highly crystalline than the former. A combination of chemical shift changes and variations in relaxation behaviour with temperature throw some light

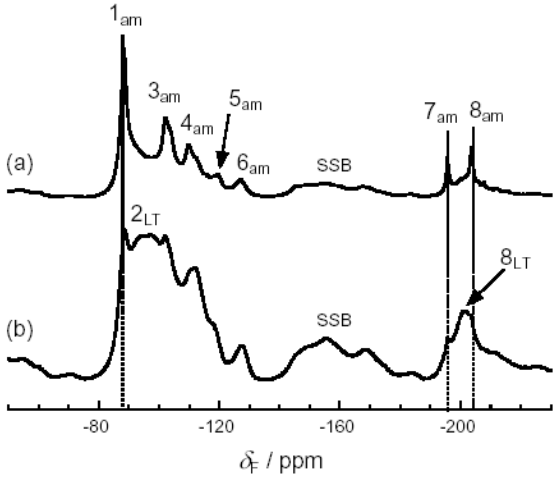

Figure 3: Direct polarisation MAS spectra of (a) AR and (b) SC P(VDF/TrFE) film. am indicates a peak for amorphous polymer.

on this process. In particular, whilst some signals show significant shift changes in the range 43 - 92ºC, others do not, revealing that VDF-TrFE head-to-tail sequences form the most stable part of the polymer chains with respect to *trans-gauche* conformational exchange motions below the transition temperature, T_c. However, the whole chain undergoes conformational exchange at about T_c, which occurs in the range 118 - 125ºC on heating. The ^{19}F bandshape changes significantly in the same temperature range. Also, $T_{1\rho}(F)$ for the crystalline material (Table 1) decreases to a common value of ca. 20 ms at 119ºC, indicating the onset of full chain rotation. All the measurements were subject to a pronounced hysteresis on cooling, the phase transition occurring between 85 and 77ºC.

Peak		1_{HT}	3	4	5	6	7_{HT}	8_{HT}
Temperature / ºC								
Heating	107	55	114	94	37	48	39	73
	119	21.6	22.0	20.0	20.2	19.2	21.9	21.3
Cooling	85	16.4	20.1	18.9	20.8	12.9	13.9	14.4
	77	28	36	42	54	53	43	33

Table 1. $T_{1\rho}(F)$ data for P(VDF/TrFE) SC film.
Note: This table is incorrectly formatted in ref. [8].

Imperfections in PVDF

Head-to-head ($-CF_2CF_2-$) and tail-to-tail ($-CH_2CH_2-$) units are commonly to be found in PVDF, and their concentration can profoundly affect the physical properties of the polymer. Weak RFDR cross-peaks [9] suggest that, although these reverse units occur primarily in amorphous domains, some are found in relatively rigid environments, probably at the interface of amorphous and crystalline domains. However, weak signals for other imperfections and/or impurities can also be observed in ^{19}F spectra. For instance, a highly mobile site gives rise to a resonance at $\delta_F = -115$ ppm. This has been attributed to $-CH_2CF_2H$ end groups. In order to understand better the occurrence of such signals, we have examined [10] solution-state ^1H and ^{19}F spectra of a telomer of PVDF of average molecular mass ca. 2000. Many weak signals can be observed. Part of the proton spectrum in the region of $\delta_H = 3.6$ ppm is shown in figure 4. The band consists of a triplet of doublets, which reduces to a simple doublet when fluorine-decoupled (and hence belongs to a $-CH_2C\boldsymbol{H}_2CF_2-$ group), plus two triplets which are unaffected by fluorine decoupling (and therefore are assigned to $-CH_2C\boldsymbol{H}_2X-$ protons, where X presumably has no protons or fluorines attached). Assignments of the entire ^1H and ^{19}F spectra may be made using the coupling patterns, together with COSY, TOCSY and HETCOR experiments. The results reveal the existence of both end groups and small molecules, present as a result of the synthesis procedure.

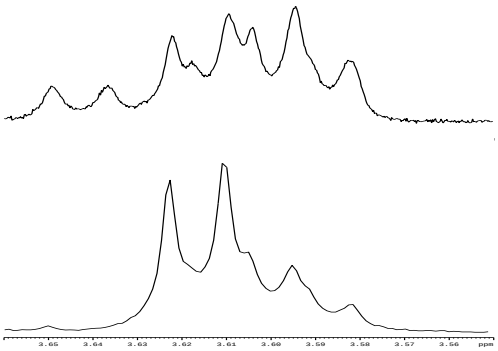

Figure 4. Parts of the proton spectra of a VDF telomer. Above: Fluorine-coupled. Below: Fluorine-decoupled.

Conclusions

NMR experiments, both for solid samples and solutions, reveal a wealth of detail about the chemical nature (including conformations), domain structure, imperfections and mobility of fluoropolymers.

Acknowledgements

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