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$^{1,2}$, and the advent of fast MAS probes (> 25 kHz) gives an alternative approach. Work has been carried out in our group on PVF, PVDF, PTrFE and various copolymers. Some of these studies, together with the work of other researchers, have been reviewed$^{3}$. Choice of pulse sequence is vital for understanding the domain structure of semi-crystalline polymers, since selective spectra may be produced (see below). Relaxation times, measured as functions of temperature, provide evidence of mobility and, combined with chemical shift variations, reveal conformational changes. Cross-polarisation dynamics are complicated for fluoropolymers, but analysis of variable contact time experiments can be simplified and the process understood$^{4}$.

Selectivity: Solid fluoropolymers are mostly semi-crystalline, so we place emphasis on methods of preferentially selecting sub-spectra from the different domains. Separate spectra of such domains (typically crystalline and amorphous) may be obtained by suitable choices of discriminating pulse sequences, 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). A new selective pulse sequence involving H $\rightarrow$ 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$^7$.

Applications: Head-to-head (-CF$_2$CF$_2$-) and tail-to-tail (-CH$_2$CH$_2$-) units are commonly to be found in PVDF and associated copolymers. Their concentration can profoundly affect the physical properties of the polymer. Evidence from discriminating NMR experiments shows that these are largely in amorphous domains, as expected. However, RFDR two-dimensional spectra suggest$^8$ that some are in rigid regions of the sample, and we speculate that the interface between domains is involved. Delayed acquisition spectra show that the spectral region assigned to reverse units also contains a signal from a very mobile grouping. We believe this to arise from CHF$_2$ end groups, even though the polymer has a molecular mass of ca. 10$^6$ Daltons. Information on the development of such units (and on the assignment of weak signals) has been obtained by solution-state $^1$H and $^{19}$F NMR measurements$^9$ of a telomer of PVDF of molecular mass ca. 2000 Daltons.

Copolymers of vinylidene fluoride and trifluoroethylene undergo a ferroelectric-paraelectric phase transition on heating. Two samples have been studied$^{10}$, 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 on the transition process. In particular, whilst some signals show significant shift changes in the range 43

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 PVDF.

- 92ºC (i.e. well below the transition), 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. However, the whole chain undergoes conformational exchange at about T_c, which occurs in the range 118 - 125ºC on heating. The 19F bandshape changes significantly in the same temperature range. Also, T_1(F) for the crystalline material 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.

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.

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References
Solid-state $^{19}$F NMR of Fluoropolymers: Developments & Applications

Robin K. Harris$^1$ & Shinji Ando$^2$

$^1$ Department of Chemistry, University of Durham, South Road, Durham DH1 3LE, U.K.
Phone +44-191-334-2021; FAX +44-191-384-4737; email r.k.harris@durham.ac.uk

$^2$ Department of Polymer Chemistry, Tokyo Institute of Technology.
email sando@polymer.titech.ac.jp

Fluoropolymers/ Solid-state $^{19}$F NMR/ Selective pulse sequences/ Domain structure/ Relaxation

Fluorine-19 is an excellent nuclide for studying the structure and dynamics of solid fluoropolymers by NMR. The characteristics of $^{19}$F magic-angle spinning NMR for systems containing both fluorine and hydrogen will be discussed. A number of pulse sequences for selectively recording spectra of crystalline and amorphous domains will be introduced and their effects illustrated. Applications of $^{19}$F spectra to several fluoropolymers and copolymers will be shown, including PVDF and P(VDF/TrFE), with emphasis on detecting reverse units and end groups. Variable-temperature spectra give evidence of chain conformation changes and phase transitions. They indicate that head-to-tail linkages in P(VDF/TrFE) are relatively rigid conformationally.

Relaxation times are also used to study molecular-level mobility.