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SHORT COMMUNICATION

Triple-Channel Solid-State NMR Investigation of Poly(vinylidene fluoride) Polymorphs

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Triple-channel solid-state NMR investigations of two different poly(vinylidene fluoride) (PVDF) materials are described. Carbon-13 cross-polarization magic angle spinning NMR spectra were recorded using simultaneous high-power decoupling on both the proton and fluorine channels. Both ^{1}H to ^{13}C and ^{19}F to ^{13}C cross-polarization experiments were applied, giving identical results apart from intensity variations due to the cross-polarization efficiency. An attempt was made to characterize the polymorphism of PVDF by means of solid-state triple-resonance spectroscopy. Two principal signals, for the CF$_2$ and the CH$_2$ groups, were observed, for both the non-polar α-phase and the polar β-phase. There was a small difference (*ca.* 4 ppm) in the chemical shift positions for these distinct crystalline modifications.

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INTRODUCTION

Poly(vinylidene fluoride) (PVDF) is one of the chemically simplest fluorinated polymers, having the monomer unit CH$_2$CF$_2$. It is heterogeneous and only partially crystallizes, depending on the physical conditions. The crystallinity ranges between 50 and 70%. PVDF is known to show extensive polymorphism. Five modifications have been discussed.[1] Transformations between the modifications occur when different processing procedures are applied.[2] Crystallization from the melt provides the non-polar α-modification whereas drawing at relatively low temperatures enhances the content of the polar β-modification. Interconversions between modifications can also be induced when strong electric fields are applied to PVDF films. The modifications are stable at ambient temperature.

In contrast to high-resolution solution-state NMR, with which fluorinated polymers have been extensively investigated,[3–5] only a few triple-channel solid-state experiments involving fluorine nuclei have been reported.[6] The simultaneous application of proton and fluorine decoupling drastically reduces line broadening caused by ^{1}H–^{13}C and ^{19}F–^{13}C dipolar interactions. Applications to semifluorinated polymers [e.g. PVDF–poly(methyl methacrylate) blends] in the solid state have been reported.[7–11] Cross-depolarization techniques provided especially valuable results about the mixing of the polymer components at the molecular level. Earlier investigations of the mixing problem, carried out without the capability of fluorine decoupling, produced poor-quality solid-state ^{13}C NMR spectra of PVDF, which were not valuable for the discussion of material effects.

EXPERIMENTAL

The experiments were performed on a Chemagnetics CMX 200 three-channel spectrometer operating at 200.13, 188.29 and 50.33 MHz for protons, fluorine and carbon, respectively. The spectrometer used a CE amplifier for protons, a Bruker CXP amplifier for fluorine and an AMT amplifier for carbon. A Chemagnetics HFX triple-channel APEX probe was used. This probe is designed for X-channel detection, allowing cross-polarization (CP) from both the H and the F channels, together with dual-channel decoupling. It contains a magic angle spinning (MAS) stator accepting 7.5 mm o.d. rotors, which allows spinning speeds of up to 7 kHz.

Cross-polarization was applied to increase the sensitivity. Apart from lack of suppression of the background signal (from fluoropolymer components) and different relative signal intensities, fluorine to carbon CP provided analogous results to those obtained from proton to carbon CP. The experimental parameters were proton and fluorine $\pi/2$ pulse durations 5 μs, CP

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contact time 3 ms, decoupling field strength on both the proton and the fluorine channels equivalent to 50 kHz, spectral width 20 kHz and 1024 transients for each spectrum. The spectra are referenced by replacement, using adamantane, to the signal for TMS. The reported chemical shifts are considered to be accurate to ±0.5 ppm.

We used two kinds of PVDF: a powdered sample (Kynar; Pennwalt Chemicals) that contained only the non-polar α-modification and drawn-film material (Solef X10N; Solvay, Belgium) that contained predominantly the polar β-modification. We estimated the α/β ratio of the latter by means of IR spectrometry to be 35:65. The absorption bands at 616 cm^{-1} were utilized.[12]

RESULTS AND DISCUSSION

The spectra shown in Fig. 1 demonstrate the effects of different CP and decoupling regimes. Only the doubly decoupled spectra show an exploitable resolution. Two intense resonance lines dominate the CP spectra if decoupling on both channels is applied.

By variation of the decoupling power and the source of magnetization for CP it can be easily deduced which resonance arises from the carbons close to fluorines and which comes from carbon bonded to protons. The two kinds of CP regimes (^{1}H to ^{13}C and ^{19}F to ^{13}C) provide equivalent results except for differences in intensity caused by differing efficiencies of CP. The dynamics of the magnetization transfer show the differences of the proton- and fluorine-based CP experiments, as demonstrated in Fig. 2.

The chemical shifts in the powder material are 119.9 ppm for the CF_2 resonance and 43.2 ppm for the CH_2 resonance (Fig. 3). Comparable spectra of PVDF powder showing the same general features have been published.[7–11] However, the CH_2 resonance of the biaxially drawn material appears at 42.6 ppm and the CF_2 resonance shows a greater distribution of shifts, most intense at 123.0 ppm (although the contribution at 119.9 ppm is still present). The 123.0 ppm position is attributed to the β-modification. A deconvolution gives roughly the same order for the α/β ratio as determined by IR spectrometry and by solid-state ^{19}F NMR with fast MAS and proton high-power decoupling on the same material.

In addition to the main resonance lines of the CH_2 and the CF_2 carbons, further signals having low intensity are seen around 25 ppm. These shifts can be interpreted as arising from head-to-head or tail-to-tail sequences in the chain, as clearly revealed by solution-state resonance techniques.[4,5,13] Their appearance in the spectrum is not surprising, given the fact that the amount of deviation from the regular structure can be up to 6%.[14] However, an analytical discussion of differences between distinct PVDF materials is beyond the resolution of the solid-state spectra. The resonances should arise from both crystalline and amorphous domains, as shown by ^{19}F–{^{1}H} spectra.

As known from static proton and fast MAS fluorine solid-state NMR investigations,[15,16] differences in NMR relaxation properties can be exploited to suppress regions in the material with different molecular mobilities. Well separated spectra of the crystalline polymorphs and of the amorphous phase can be obtained.[16] An analogous approach for ^{13}C NMR using the different chain mobilities may be possible at ambient temperature (being well above the glass transition temperature of PVDF, −35 °C). However, no efforts in that direction have been made at the present stage of

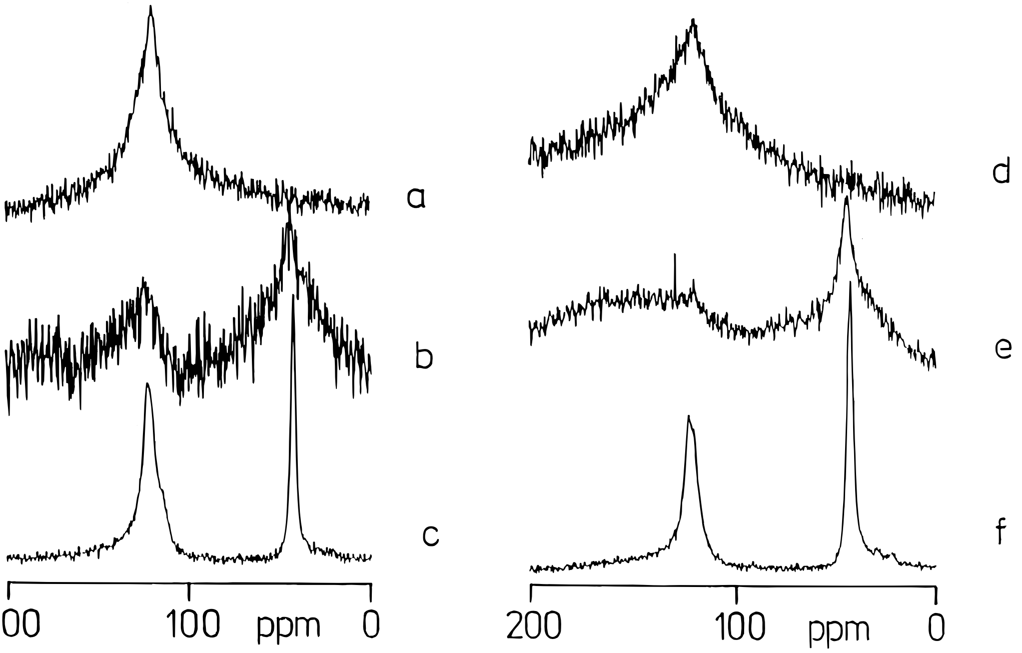

Figure 1. (a–c) Fluorine-to-carbon and (d–f) proton-to-carbon ^{13}C CP/MAS spectra of biaxially drawn PVDF. (a, d) Fluorine decoupled; (b, e) proton decoupled; (c, f) proton and fluorine decoupled.

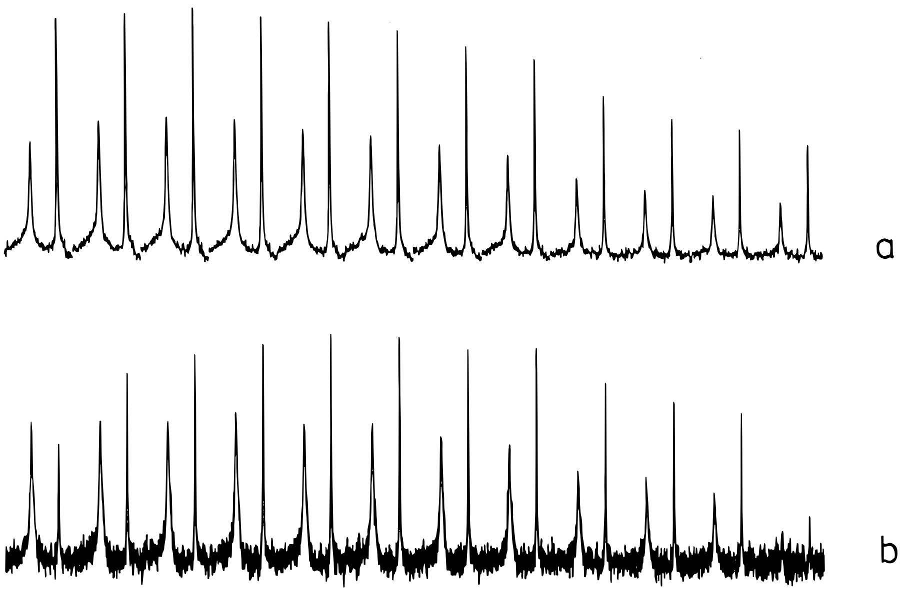

Figure 2. Cross-polarization dynamics for PVDF film using MAS at 2.5 kHz: (a) ^{1}H to ^{13}C; (b) ^{19}F to ^{13}C. Contact times: 0.4, 0.8, 1.2, 1.6, 2.0, 2.4, 3.2, 4.0, 7.2, 10, 12 and 15 ms.

the study. The superposition of the magnetizations for crystallites and for the amorphous regions can be discussed in a similar manner to the case for polyethylene.[17] The latter give rise to a broadening around the base of the prominent resonance lines arising from the former. The effect is more pronounced for the CF_2 resonance because of the larger influence of fluorine on the ^{13}C chemical shift.

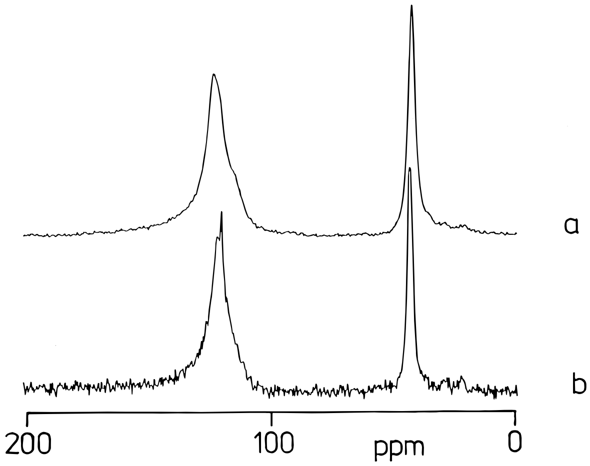

Figure 3. Comparison of the ^{13}C CP/MAS spectra of PVDF (^{19}F to ^{13}C cross-polarization): (a) biaxially stretched film; (b) powder. MAS: 7 kHz, contact time 3 ms.

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