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High-Resolution Solid-State ^{13}C NMR of Fluoropolymers

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Despite the technological significance of perfluorinated polymers such as poly(tetrafluoroethylene), PTFE, commonly known by the trade name of Teflon, or the ionomer Nafion used in chloralkali electrolysis[1] and fuel cells,[2,3] no ^{13}C solid-state nuclear magnetic resonance (NMR) spectra of these temperature- and solvent-resistant materials can be found in the literature. The probable reason for this glaring omission is the large line broadening[4] that results from the combination of significant ^{13}C−^{19}F and ^{19}F−^{19}F dipolar couplings with large (>130 ppm) ^{19}F chemical shift anisotropies (CSAs).[5] The resulting large spread of ^{19}F frequencies makes it impossible to irradiate the ^{19}F decoupling power on or near resonance for all ^{19}F nuclei in an unoriented sample. This results in off-resonance line-broadening in the ^{13}C magic-angle-spinning (MAS) spectrum of fluoropolymers. In recent years, the off-resonance aspect of this problem has even been aggravated by the increase of the CSA-induced off-resonance shifts with the field strength of the NMR magnet. The ^{13}C cross-polarization/magic-angle spinning (CP/MAS) spectrum of PTFE at a Larmor frequency of 100 MHz and spinning speed of 5 kHz (Figure 1a) shows 30 ppm wide resonance features resulting from insufficient ^{19}F decoupling.

In this Communication, we show that these line-broadening problems can be overcome by using high-speed magic-angle spinning. At spinning rates of $\nu_r > 25$ kHz, the central lines of ^{19}F NMR spectra are narrowed to less than 1 ppm.[6−8] This indicates that MAS is sufficient to average ^{19}F−^{19}F dipolar couplings to nearly zero. As a result, ^{13}C−^{19}F dipolar couplings are also greatly reduced. This is confirmed by the reduced line width of the CP/MAS spectrum of PTFE at a spinning rate of $\nu_r = 28$ kHz (Figure 1b), acquired after ramped cross-polarization around the first sideband of the Hartmann−Hahn condition[9] but without ^{19}F irradiation during detection. Nevertheless, the spectrum is still undesirably broadened. In particular, it shows a splitting of ca. 500 Hz, which must be attributed to the two one-bond ^{19}F−^{13}C *J*-couplings that a ^{13}C nucleus in PTFE experiences. In addition, a broadening of each triplet peak is observed, which is at least partially due to the four two-bond ^{19}F−^{13}C *J*-couplings of each ^{13}C spin. Attempts to remove this splitting and broadening by standard continuous high-power ($\gamma B_1/(2\pi) = 116$ kHz) ^{19}F irradiation were unsuccessful (Figure 1c). The line width under these conditions is not significantly reduced because the time evolutions imposed by the decoupling field and by sample spinning interfere with each other.

However, we have found that the residual line broadening can be removed effectively by pulsed rotation-synchronized ^{19}F 180° pulses. As shown in Figure 2a, the decoupling pulse sequence consists of one 180° pulse at the end of each completed rotation period. The train of 180° pulses, e.g., with the *xy*-16 phase sequence,[10] keeps refocusing the ^{19}F−^{13}C *J*-couplings, while not recoupling the dipolar interactions. The approach of using one 180° pulse per cycle is reminiscent of pulsed heteronuclear decoupling during multiple-pulse homonuclear decoupling.[11] The pulsed decoupling at high-speed MAS works very well, yielding a CP/MAS ^{13}C

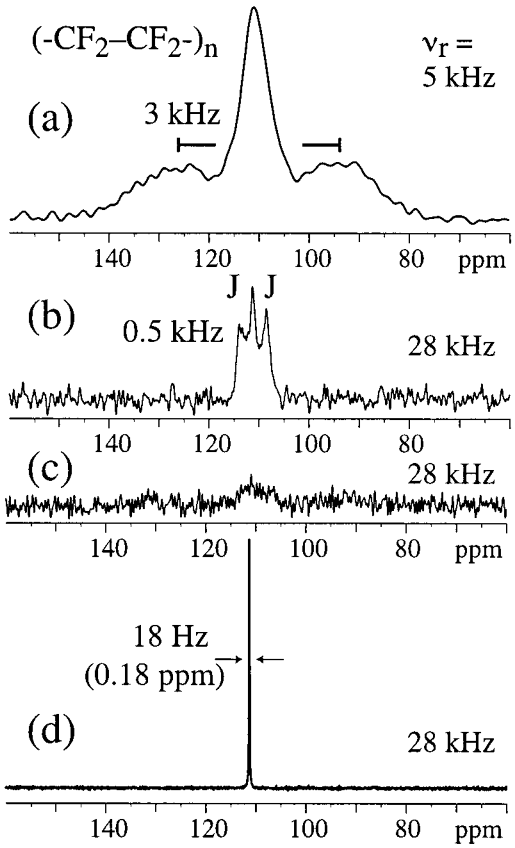

Figure 1. ^{13}C CP/MAS NMR spectra of PTFE, obtained as commercial thread seal tape, under various decoupling conditions. (a) Standard continuous-wave dipolar decoupling, irradiated near the ^{19}F isotropic chemical shift, at a spinning rate of $\nu_r = 5$ kHz. (b) Fast-MAS ($\nu_r = 28$ kHz) ^{13}C MAS spectrum after ramped cross-polarization (CP) from ^{19}F, without ^{19}F decoupling during detection. The ramped CP, with a 20% variation around the first sideband of the Hartmann−Hahn condition, was initially optimized on a ^{13}C-labeled protonated model compound, and then adjusted for the 6% smaller gyromagnetic ratio of ^{19}F relative to ^{1}H. (c) Same as (b), but with high-power (>90 kHz) continuous-wave ^{19}F decoupling (exactly on resonance). (d) Same as (c), but with pulsed ^{19}F decoupling, using a train of rotation-synchronized 180° pulses as indicated in Figure 2a. The small line width is characteristic of a highly uniform environment, showing that the signal arises from PTFE crystallites. The line narrowing may be facilitated by reductions of dipolar coupling due to fast uniaxial rotational diffusion of chains in the crystallites (ref 5). The spectra were obtained on a Bruker DSX-400 spectrometer at 100 MHz for ^{13}C, in a 2.5 mm rotor with Vespel endcaps (7 mm rotor with Kel-F cap for (a)), at ambient temperature (which includes frictional heating by 20−30 K at $\nu_r = 28$ kHz). The CP time was 1.5 ms, with a linear ramp on ^{19}F from 80% to 100%. The ^{19}F 90° pulse length was 2.5 μs and the acquisition time 80 ms. The recycle delay was 8 s; the measuring times for the spectra in (b), (c), and (d) were 0.5, 0.25, and 1 h.

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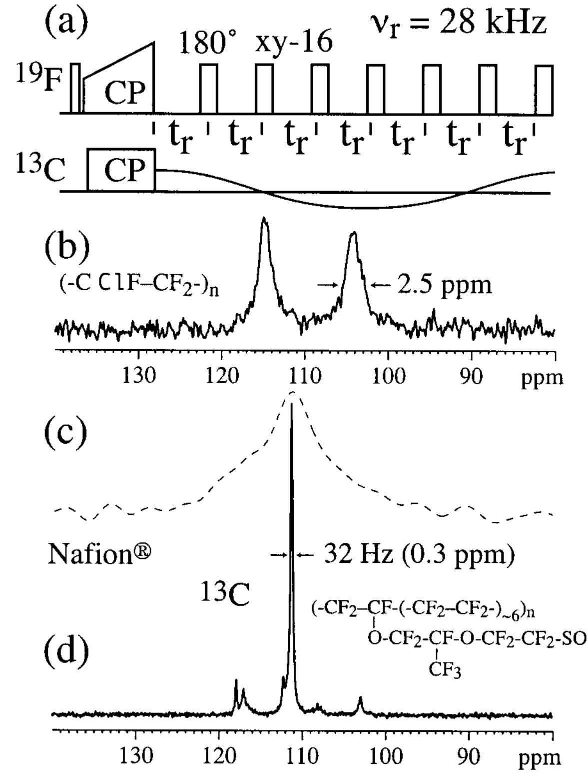

Figure 2. (a) Pulse sequence with ramped CP and ^{19}F decoupling by one 180° pulse per rotation period. The phase sequence used is $x\ y\ y\ x\ x\ y\ y\ x\ -x\ -y\ -y\ -x\ -x\ -y\ -y\ -x$; the *xy*-16 phase sequence[10] will also work well. Detection is normal, i.e., not limited to the windows between the ^{19}F pulses. (b) Spectrum of PCTFE (also known as CTFE or Kel-F, distributed by McMaster-Carr). (c, d): ^{13}C CP/MAS NMR spectra of dry Nafion ionomer (Dupont Nafion-112, commercial fuel-cell-quality film of 2 mil = 50 μm thickness) acquired at (c) $\nu_r = 5$ kHz with regular continuous-wave ^{19}F-decoupling, and (d) $\nu_r = 28$ kHz under pulsed ^{19}F decoupling, using the pulse sequence of (a). The experimental parameters were similar as given in Figure 1, except for a reduced recycle delay of 2.5 s for Nafion, based on the ^{19}F relaxation as observed in the direct ^{19}F spectrum.

peak of PTFE at 111.3 ppm relative to tetramethylsilane, with an 18 Hz (0.18 ppm) line width (see Figure 1d). Compared to the standard CP/MAS spectrum of Figure 1a, the signal has been narrowed by more than a factor of 100. The decoupling sequence has a small duty cycle of $t_{180°}/t_r \sim 0.15$, with the 180° pulse length $t_{180°}$ and the rotation period t_r. As a result, the long observation time required for detecting the long time signal of this narrow resonance line does not represent a major power burden for the NMR probehead. At a spin rate of $\nu_r = 14$ kHz, the line width in the PTFE ^{13}C spectrum acquired under pulsed ^{19}F-decoupling is 30 Hz.

We have applied this new decoupling method to obtain high-resolution ^{13}C CP/MAS spectra also of other perfluorinated polymers. Figure 2b shows the spectrum of poly(chlorotrifluoroethylene), PCTFE, commonly known by its trade name of Kel-F. It exhibits two lines centered at 115 and 104 ppm, attributed to CF_2 and CFCl groups, respectively. The two bands are inhomogeneously broadened by ~2.5 ppm. A Hahn-echo experiment revealed a homogeneous line width of ~1 ppm.

Nafion is a copolymer of tetrafluoroethylene with ~15 mol % of a $CF_2{=}CFR$ monomer with a polar and ionic side group $R = -O-CF_2-CF(CF_3)-O-CF_2-CF_2-SO_3^-$. In structural studies of this material, most attention has been focused on the clusters formed by the ionic side groups.[12–14] The semicrystalline matrix, which provides the mechanical stability up to high temperatures while being sufficiently nanoporous for high water and cation permeability, has not been characterized in detail. In particular, the amount and arrangement of PTFE crystallites in Nafion are contentious.[8,15] ^{13}C NMR applied to (protonated) semicrystalline polymers and copolymers has been shown to provide such structural insights.[16,17]

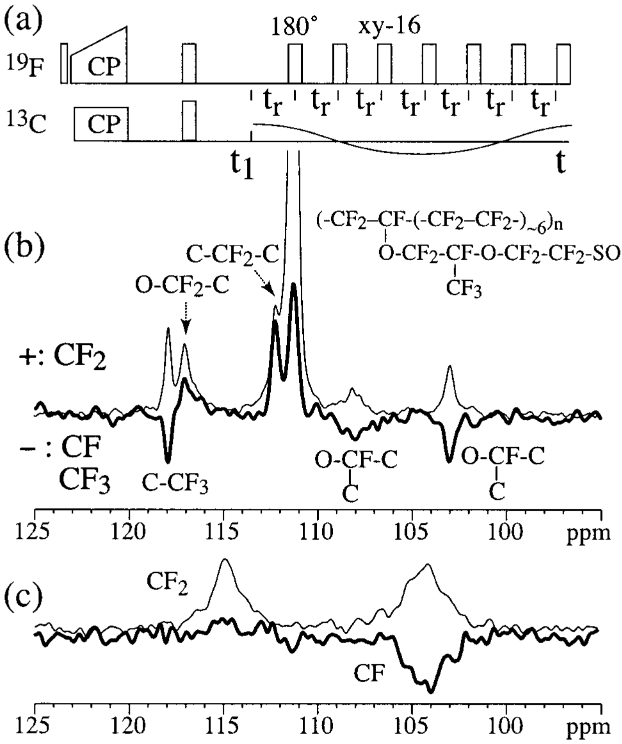

Figure 3. (a) Pulse sequence for obtaining a *J*-modulated ^{13}C CP/MAS spectrum. (b) Dark line: *J*-modulated ^{13}C CP/MAS spectrum of Nafion, obtained with the pulse sequence shown in (a), at $t_1 = 3.57$ ms, which is 100 times the rotation period. CF_2 signals are positive, CF and CF_3 signals negative. Measurement time: 5 h. Light line: unmodulated CP/MAS spectrum of Nafion (obtained using the pulse sequence of Figure 2a) shown for reference, processed with the same line broadening as the *J*-modulated spectrum. (c) Dark line: *J*-modulated ^{13}C CP/MAS spectrum of PCTFE, at $t_1 = 3.57$ ms. Measurement time: 2 h. Light line: unmodulated CP/MAS spectrum of PCTFE. The stronger reduction of the CF_2 signal magnitude in the *J*-modulated spectrum is probably due to the stronger dipolar couplings in the CF_2 unit.

The ^{13}C spectrum of Nafion (Figure 2d) obtained with the pulse sequence of Figure 2a is dominated by a sharp line at 111.3 ppm. The position and its small width of 32 Hz indicate a chain conformation and degree of order similar to that of crystalline PTFE. Five smaller bands are also observed, at 117.9, 117.0, 112.2, 108.1, and 102.9 ppm, with integrated intensities of 1.1, 1.9, 2.0, 1.0, and 1.1, respectively. On the same relative scale, the intensity of the 111.3 ppm peak is 12.8.

The peak assignment is facilitated by an experiment in which the signal intensities are modulated by the $^{19}F-^{13}C$ *J*-couplings, analogous to the “attached proton test” widely used in solution NMR of protonated molecules.[18] The simple extension of the pulse sequence to achieve this modulation is shown in Figure 3a. The modulation function $\cos^k(\pi J t_1)$ for a CF_k group is equal to $(-1)^k$ at $t_1 = 1/J = 3.6$ ms. Thus, CF and CF_3 signals are negative, while those of CF_2 groups and of quaternary carbons are positive in the modulated Nafion ^{13}C NMR spectrum of Figure 3b (dark line). Combining this information with the well-known downfield shifts induced by F and O substituents, the assignments shown in Figure 3b are obtained. They are also consistent with the integral peak areas and the molecular structure. The only unassigned signal is that of the $CF_2SO_3^-$ segment. The peak integrals virtually exclude that it contributes to the OCF_2 peak. It either coincides with the main CF_2 signal or is broadened beyond detectability.

It is also interesting to note that the dominant signal of the PTFE-like $(-CF_2-)_n$ regions is much more strongly reduced in the *J*-modulated spectrum than are the side group signals. This indicates stronger dipolar dephasing during the *J*-modulation period t_1. Note that this dephasing is more pronounced here than during signal acquisition, since the *J*-modulation period is devoid of any pulses for heteronuclear decoupling. Whether the differential dephasing during the *J*-modulation period is purely due to the reduction of the fluorine density by the oxygen atoms in the side branches, or whether mobility plays a significant role, will be further investigated.

Figure 3c shows the *J*-modulated spectrum of PCTFE and an unmodulated reference spectrum. The assignment of CF_2 and CF groups to the two peaks is thus straightforward.

The high ^{13}C resolution and suppression of the $^{19}F-^{19}F$ dipolar couplings achieved here enable many experiments for characterizing the segmental mobility and internuclear distances in Nafion and other fluorinated polymers, which will shed more light on the local and supramolecular structure of these important materials.

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