Characterization of poly(carbon monofluoride) by ^{19}F and ^{19}F to ^{13}C cross polarization MAS NMR spectroscopy

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High speed ^{19}F MAS NMR and ^{13}C MAS NMR with ^{19}F to ^{13}C cross polarization allows spectroscopic identification of monofluorinated and geminally difluorinated carbon species in poly(carbon monofluoride).

Poly(carbon monofluoride), $(CF_x)_n$, is a stable, hydrophobic material prepared from graphite and elemental fluorine at high temperatures.[1] $(CF_x)_n$ materials, where x is greater than 0.60, are currently being produced on an industrial scale for use in Li/$(CF_x)_n$ batteries, and these are characterized by high energy density, wide operating temperatures and long storage life.[2] Poly(carbon monofluoride) is also used as a solid lubricant with wear performance better than that of graphite or MoS_2, especially in high temperature or oxidizing environments.[3,4] It is agreed that covalent incorporation of fluorine results in a puckering of the graphite structure into extended sheets of fused cyclohexane rings,[5–8] but other details of the structure of $(CF_x)_n$, including defect sites, are more poorly understood. Previous applications of NMR to this material have been wide-line ^{19}F investigations. One such study concluded that $(CF_x)_n$ is an array of *cis-trans*-linked boats, with all fluorine in axial positions. A more recent student used similar methods to support a *trans-trans*-linked chair structure, and that conclusion is supported by the available X-ray data.[6–9] The availability of technology for very rapid sample rotation has made possible high resolution NMR analysis of solids,[10,11] and several such ^{19}F magic angle spinning (MAS) NMR investigations have appeared in the literature.[12–15] Here we have used high speed MAS to obtain ^{19}F NMR spectra of $(CF_x)_n$ materials that are dominated by the isotropic chemical shifts of bulk and defect structures. Furthermore, we have confirmed our assignments by acquiring ^{13}C NMR spectra of the same materials using cross polarization from ^{19}F and fluorine decoupling.

Two samples of carbon monofluoride were obtained from Aldrich. Fast neutron activation determined the empirical formulae to be $(CF_{0.87})_n$ and $(CF_{1.12})_n$. Samples for NMR investigation were loaded and sealed under an inert nitrogen atmosphere in 4.0 and 5.0 mm zirconia MAS rotors using Delrin [poly(oxymethylene)] endcaps. High speed ^{19}F MAS NMR was performed on a home built spectrometer operating at a fluorine resonance of 188.8 MHz utilizing a 4.0 mm spinning module from Otsuka Electronics. The fluorine chemical shift was externally referenced to an ampoule of trichlorofluoromethane at 0 ppm. $\pi/2$ pulses of 3 µs or less were used. Reported spectra are the result of 1024 transients, utilizing a composite Bloch decay sequence[16] for probe background suppression and a 1 s recycle delay. ^{19}F to ^{13}C CP MAS NMR spectra were acquired on a Chemagnetics CMX-360 operating at 337.8 (^{19}F) and 90.5 MHz (^{13}C) using a probe from Otsuka Electronics spinning 5.0 mm rotors. The magic angle was optimized using the ^{79}Br resonance of KBr.[17] The ^{13}C chemical shift was referenced (17.4 ppm) and the ^{1}H–^{13}C Hartmann–Hahn matching condition was set using hexamethylbenzene. The ^{19}F–^{13}C match was then optimized on polytetrafluoroethylene (PTFE) by adjustment of the ^{19}F power level to coincide with the previously determined ^{13}C $\pi/2$ pulse width. The double-resonance NMR probe contained sufficient fluoropolymer that ^{13}C Bloch decay spectra obtained with ^{19}F decoupling were dominated by

background signals, even with background-suppression pulse sequences. Fortunately, probe background was greatly diminished with ^{19}F–^{13}C cross polarization, and background was negligible when the ^{13}C magnetization was generated using composite CP sequences. We optimized the CP contact time by measuring the important relaxation rates. For a sample of $(CF_{0.87})_n$ we measured a ^{19}F $T_{1\rho}$ of 33.4 ± 5.0 ms and 147 ± 18 µs for T_{FC}.[18] We selected a 1.5 ms contact time to provide excellent CP efficiency without unnecessary radio-frequency heating. The ^{13}C $\pi/2$ pulse width was 4.3 µs and high-power ^{19}F decoupling was used. Each ^{13}C NMR spectrum is the result of 2048 transients and a 3 s recycle delay.

Fig. 1 reports ^{19}F MAS NMR spectra of samples of $(CF_{0.87})_n$ and $(CF_{1.12})_n$ obtained with a spinning speed of 18 kHz. This spinning speed was necessary to average the ^{19}F–^{19}F homonuclear dipolar interaction as well as to place spinning sidebands away from spectral regions of interest. The most intense peak in both spectra, at −187 ppm, is assigned by comparison to the fluorines on C9 and C10 of either *trans-* or *cis*-perfluorodecalin, each at −186 ppm. Therefore, the −187 ppm resonance in Fig. 1 is confidently assigned to C–F groups.[19] A second isotropic peak, at −116 ppm, is present in both samples but is clearly larger for the sample with the higher fluorine content. This signal can also be assigned by comparison to perfluorodecalins, for which both the axial and equatorial fluorines in CF_2 groups in the 1, 4, 5, and 8 positions have shifts of −124 ppm.[19] The line widths of both ^{19}F resonances are likely due to chemical heterogeneity, as modest variations in sample temperature or spinning speed suggested no further line narrowing.

Further evidence for these assignments came from the ^{19}F to ^{13}C CP MAS spectra (Fig. 2). Both spectra have a majority resonance at 89 ppm and a shoulder that spectral deconvolution shows to be centered at 111 ppm. The latter feature is distinctly larger in the sample with the higher fluorine content. We assign the ^{13}C resonances by comparison to an earlier study of graphite hydrofluoride, $C_xF_{1-\delta}(HF)_\delta$, by Mallouk and co-workers.[20] $C_xF_{1-\delta}(HF)_\delta$ has a resonance at 88 ppm that was assigned to
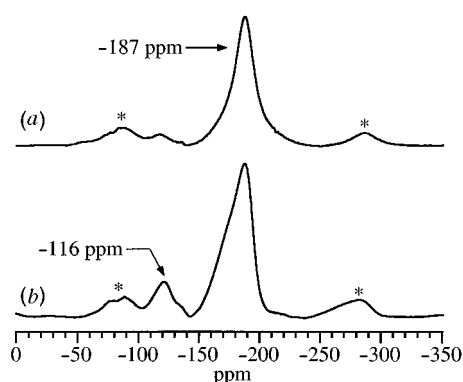

Fig. 1 188.8 MHz ^{19}F MAS NMR spectra of graphite monofluoride having empirical stoichiometries of (*a*) $(CF_{0.87})_n$ and (*b*) $(CF_{1.12})_n$. Spectra were acquired at 298 K using a spinning speed of 18 kHz. Asterisks denote spinning sidebands.
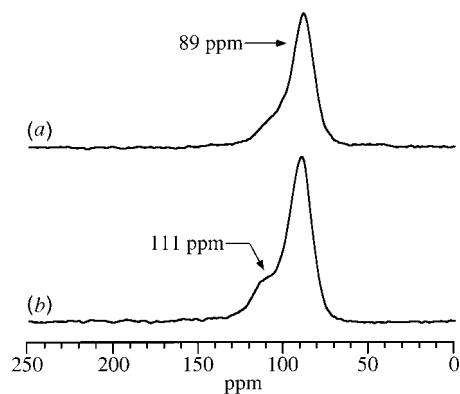
Fig. 2 90.5 MHz ^{13}C MAS NMR spectra of graphite monofluoride obtained with ^{19}F to ^{13}C cross polarization and high power ^{19}F decoupling. Spectra were acquired at 298 K with a spinning speed of 8 kHz. (*a*) $(CF_{0.87})_n$ and (*b*) $(CF_{1.12})_n$.

monofluorinated carbons, and this strongly supports a similar assignment for $(CF_x)_n$. $C_xF_{1-\delta}(HF)_\delta$ also showed a small ^{13}C signal at 112 ppm which Mallouk and co-workers assigned to CF_2 groups at the edge of grains. This supports assignment of the 111 ppm shoulder in Fig. 2 to the carbons in CF_2 groups. Our spectra clearly show that CF_2 groups are enhanced at higher fluorine incorporation, in agreement with Lagow's proposal for the fluorine siting in 'superstoichiometric' poly(carbon monofluoride).[21] However, we have also demonstrated the presence of smaller amounts of CF_2 in a sub-stoichiometric material. In this case, CF_2 groups are still reasonable as peripheral groups at sheet edges or in other defected structures. In principal, we should be able to establish a quantitative relationship between the levels of CF_2 in the ^{19}F and ^{13}C spectra, but the use of cross polarization in the latter case prevents such a comparison.

In conclusion, ^{19}F high speed MAS NMR analysis has permitted resolution of majority and defect sites in highly fluorinated graphite derivatives, and the interpretation of these experiments is supported by ^{13}C MAS NMR with ^{19}F to ^{13}C cross polarization and high power ^{19}F decoupling.

Notes and References

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