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DETECTION OF THE PRESENCE AND LOCATION OF RESIDUAL HYDROGEN IN PERFLUORINATED POLYALKYLETHER FLUIDS USING POLARIZATION TRANSFER ^{13}C NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

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SUMMARY

A series of perfluorinated polyalkylether (PFPE) fluids was analyzed for residual hydrogen bonded to the polymeric backbone and the specific site of this bonded hydrogen in the molecular framework. Residual hydrogen bound to carbon within the predominantly perfluorinated molecular structure has been associated with thermooxidative instability [1] and is therefore of interest as a potential indicator of stability among samples. Application of an ^{1}H to ^{13}C polarization-transfer Nuclear Magnetic Resonance (NMR) technique provides spectra which contain peaks arising only for carbon atoms with directly bonded hydrogen. Such simplified spectra enable detection and unambiguous assignment of hydrogen atom binding site(s) using carbon-fluorine scalar couplings, and thereby provide a means of potentially assessing thermooxidative instability due to residual hydrogen. The relative concentration of carbon with attached hydrogen among samples was then estimated from the normalized peak intensities in the proton-decoupled ^{13}C spectra using the assignments from the polarization-transfer experiment.

INTRODUCTION

NMR spectroscopic analysis of organic compounds has proven to be one of the most useful techniques in determination of molecular structure. The chemical shift (δ) provides information on electron density about a given nucleus and is indicative of its chemical environment. Scalar (J) couplings indicate the number and type of magnetic nuclei in the vicinity of the nucleus of interest and often allow the exact location of the nucleus to be determined. Relative concentrations of specific nuclei among different samples can be estimated by comparison of peak intensities in the respective spectra, provided that the samples under comparison are of equal concentration and similar chemical structure. Of course, this information, in principle present in all spectra, is useful only if it is accessible. In many cases, the complex spectra resulting from strongly coupled and/or overlapping multiplet patterns render this information

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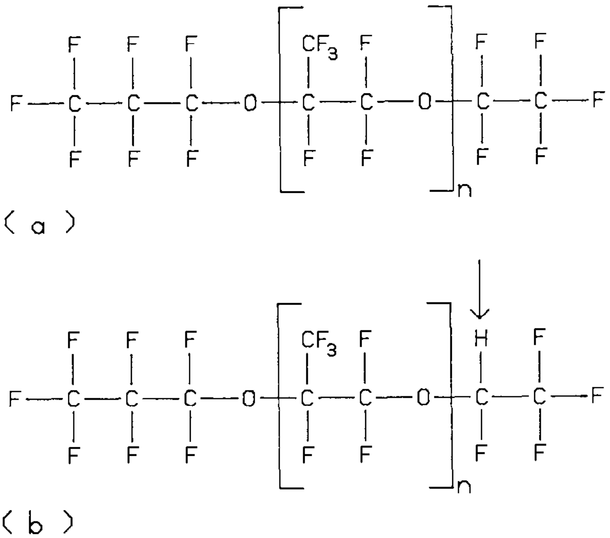

FIG. 1. General structure of perfluorinated polyalkylether fluids: (a) completely fluorinated and (b) hydrogen end-capped.

difficult or impossible to retrieve and interpret. Here we show a particularly striking example of how straightforward polarization transfer spectra provide unambiguous information.

This work focusses on using polarization transfer NMR in determining the relative concentration and location of hydrogen bound to carbon in a series of perfluorinated polyalkylether fluids, commonly designated as Krytox (trademark of Dupont*) [1], see fig. 1a. The fluids used in this investigation typically had a chain length in the range of n = 6 to 20. They have found widespread use as lubricants due to their excellent viscosity-temperature characteristics, oxidative and thermal stability, lubricity, low volatility, and flame resistance properties [2]. However, studies [1] indicate that these fluids are subject to partial thermal oxidative degradation at moderate temperatures (288°C) which may be attributable to the presence of unstable hydrogen terminated chains in the molecule, e.g. fig 1b. Confirmation of the presence, location, and concentration of bound hydrogen in these fluids may therefore provide a means of estimating relative stability among samples.

EXPERIMENTAL

All proton and ^{13}C NMR spectra were obtained on a Bruker MSL 300 spectrometer*. Samples were prepared by dissolving approximately 500 mg of each into a solvent system comprised of a 2:1 volumetric ratio of hexafluorobenzene, C_6F_6, and deuterated chloroform, $CDCl_3$. Proton decoupled ^{13}C NMR spectra were obtained at room temperature using a one-

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* Reference to a product or supplier is made for identification only, and does not represent an endorsement by the United States Government.

pulse excitation with multiple-pulse asynchronous decoupling (WALTZ). The ^{13}C polarization transfer [6] spectra were obtained using a 45° sorting pulse (13.5 μs) and a 1/2J delay of 3.8 ms, yielding positive absorptive peaks for all ^{13}C with directly bonded hydrogen. All carbon spectra were obtained with an acquisition time of 270 ms and 3 Hz Lorentzian apodization of the free induction decay.

RESULTS AND DISCUSSION

Initial attempts at resolving the extent and location of bound hydrogen were conducted using proton magnetic resonance on a series of five samples. Four showed a significant presence of hydrogen in the form of an apparent doublet at $\delta \approx 6.0$ ppm, J=53 Hz, while the remaining sample showed none, within experimental error. One possible explanation is that this doublet arises from scalar coupling to fluorine. The magnitude of the splitting (J=53 Hz) suggests that the observed hydrogen nucleus is removed by two chemical bonds from the fluorine to which it is coupled, dictating the presence of a structural residue such as $-CH_2F-$ or $-CHF-$. However, at least seven chemically different carbon sites on the molecule (see fig. 1a) could give rise to this spectrum, and there was also the possibility that the residual hydrogen signal was associated with an impurity rather than the bulk PFPE fluid.

To confirm and more precisely define the location of bound hydrogen on the molecule, ^{13}C NMR spectra were obtained with and without proton decoupling on each of the five samples. A typical proton decoupled ^{13}C spectrum is shown in fig 2a, demonstrating the variety of complex multiplets arising from the numerous carbon-fluorine scalar couplings. Although complete assignment of all peaks was not possible, the salient features of this spectrum, including the triplet of triplets (δ = 116.5 ppm, $^1J_{CF}$ = 290 Hz, $^2J_{CF}$ = 33 Hz), the doublet of quartets (δ = 103.5 ppm, $^1J_{CF}$ = 267 Hz, $^2J_{CF}$ = 36 Hz) and an apparent quartet partially buried in the triplet are consistent with the structure of fig. 1a. Although this spectrum in general supports the structure of fig. 1a, the complexity arising from overlapping multiplet patterns precludes definitive evaluation of the extent of residual bound hydrogen. The proton-coupled ^{13}C spectrum of this sample, acquired without proton irradiation during relaxation, is shown in fig 2b. In the region between 94.5 and 100.0 ppm the peak intensities are reduced relative to the proton decoupled spectra, suggesting the presence of scalar and/or dipolar coupling of these carbons to hydrogen. The loss in intensity in this region may be attributable to the absence of nuclear Overhauser enhancement (noe) in the proton-coupled spectrum: in proton-decoupled ^{13}C spin systems where molecular correlation times are small relative to the inverse Larmor frequency, and dipolar coupling to hydrogen is a dominant relaxation mechanism, non-Boltzmann spin state distributions are established, resulting in higher signal intensity for the affected transitions [4,5]. The maximum theoretical noe in the case of ^{13}C observation with proton decoupling results in a twofold signal enhancement [5]. The loss in intensity in this region therefore is in part due to the spatial proximity of hydrogen to the carbon in this chemical shift region (94.5-100.0 ppm), whether bonded to these carbon atoms or not. An additional factor contributing to the observed reduction in peak intensity in this region is the likely presence of scalar coupling of hydrogen to carbon, resulting in additional splittings of

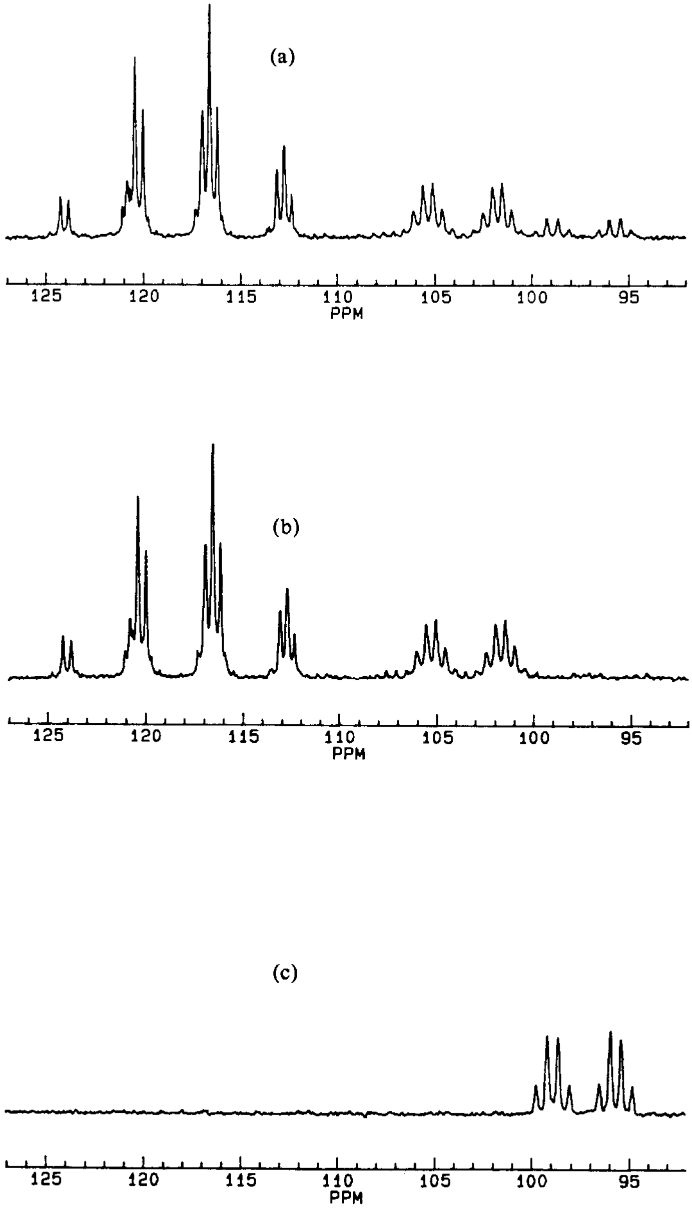

FIG. 2. ^{13}C NMR spectra of a typical perfluorinated polyalkylether fluid: (a) proton decouple (b) proton coupled, (c) DEPT spectrum (proton decoupled).

the peaks and corresponding lower intensity. Unfortunately, any such scalar couplings which may be present are unresolvable due to the very weak signal in this region. However, these results are significant in that they provide strong evidence for the presence of hydrogen in close spatial proximity to carbon and thus the possibility of direct bonding of hydrogen to carbon. We therefore sought an analysis technique which would not only determine the presence of directly bonded (scalar coupled) hydrogen to carbon but would also provide unambiguous assignment of the location of bound hydrogen in the molecular framework.

Advances in NMR hardware and software in recent years have allowed for much greater flexibility in the manipulation of nuclear spin states by radiofrequency (RF) pulses. The ^{13}C DEPT (Distortionless Enhancement by Polarization Transfer) pulse sequence [6] takes advantage of these improvements by allowing spin state information of one type of nucleus (proton) to be shifted to another type (carbon) by the process of polarization transfer. In this sequence, a heteronuclear multiple-quantum coherence is created between, say, carbons and protons, and later transformed back to observable carbon single-quantum coherence by appropriate RF pulses [5]. This sequence is particularly useful in our circumstance because we are interested in identifying sites in the perfluorinated molecular framework containing residual hydrogen directly bonded to carbon. The ^{13}C DEPT pulse sequence therefore results in an enormously simplified NMR spectrum consisting only of peaks from carbon atoms with directly bonded hydrogen while preserving the carbon-fluorine scalar couplings. These couplings are then used to identify the specific site of bound hydrogen.

Figure 2c contains the ^{13}C DEPT NMR spectrum of the sample studied above. In contrast to the spectra of fig. 2a and 2b, the DEPT spectrum contains only a doublet (J=244 Hz) of quartets (J=42 Hz) with chemical shift of δ = 97.3 ppm. This identifies the chemical shift of the carbon containing directly bonded hydrogen (97.3ppm) and allows assignment of the specific site of this carbon within the molecule: the scalar coupling of 244 Hz for the doublet indicates a single fluorine atom directly bonded to the carbon containing hydrogen. The splitting of each of these peaks into a quartet with a scalar coupling of J=42 Hz corresponds to two-bond removal of three symmetry-identical fluorine atoms from the carbon with directly bonded hydrogen. No other peaks are present in this spectrum, indicating that only one carbon in the molecule contains hydrogen. The corresponding molecular structure is shown in fig. 1b. The ^{13}C DEPT sequence has thus provided a means by which extremely complex ^{13}C NMR spectra of perfluorinated molecules can be simplified and analyzed for residual hydrogen in a straightforward manner.

The remaining four PFPE fluids were studied as above and found to contain the same terminal -CHF-CF_3 moiety as the first sample, with varying concentrations. No other sites of hydrogenation were detected. Estimates of the relative hydrogen concentrations were made based on the peak intensities in the normalized, proton decoupled, ^{13}C NMR spectra. This is reasonable since the bulk sample concentrations and the chemical nature of the samples were the same, resulting in approximately equal NOE contributions. As shown in Ref. [7], these relative concentrations were found to correlate well with absolute concentrations determined by time-of-flight secondary ion mass spectrometry (TOF-SIMS) and Fourier transform infrared spectroscopy (FTIR).

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