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The objective of this project was to develop the techniques associated with the preparation of samples of substituted perfluoropolyethers, including the preparation of a 10 to 20 gram sample of perfluoropolyether for lubricant testing by the USAF.

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Report on the synthesis of a lubricant sample (REF SPC 92-4022)

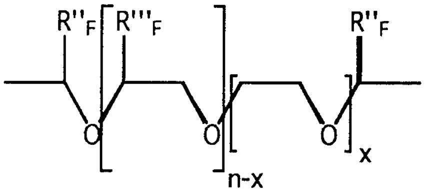
Prof. R.D. Chambers & Dr. M.P. Greenhall, University of Durham, UK.

(This report completes the first agreement)

15th February 1993

Introduction

The objective of this project was to develop the techniques associated with the preparation of samples of substituted perfluoropolyethers, including the preparation of a 10 to 20 gram sample of perfluoropolyether (1) for lubricant testing by the USAF.



on average $\{(n\text{-}x) > 9,\ x < 4.2\}$

$R''_F = CF_3CF_2CF_2$ (predom) or F
$R'''_F = CF_3CF_2CF_2$

[1]

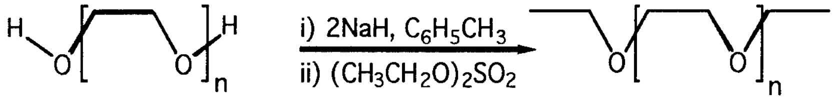
(Note: Chambers, US Patent 4,877,905)

Experimental

a) Starting materials

Samples of polyethylene glycol(600) $\{n = 13.2\}$, diethylsulphate, sodium hydride, and ditertiarybutylperoxide were used as supplied by Aldrich Chemical Company Limited. Hexafluoropropene was used as supplied by Fluorochem Limited. 50% Fluorine/Nitrogen mixture was used as supplied by Air Products.

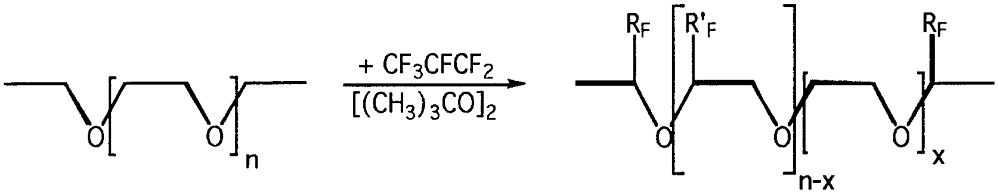
b) Endcapping of commercial polyethyleneglycol (600)



[2] [3]

Azeotropically dried polyethyleneglycol(600) (150.0g, 0.25moles) in toluene (350ml) was added slowly to sodium hydride (3 x toluene washed) (14.0g, 0.58moles) in a 3 necked 2 litre flask under a dry nitogen atmosphere. The reaction temperature was kept below 45°C during the addition and for 1 hour thereafter. The temperature was increased to 100°C over the course of 1 hour and maintained for 135 minutes. Diethlylsulphate (43.0g, 0.28moles) was then added to the mixture (25°C) over the course of 20 minutes. The mixture was stirred for 1 hour and then heated to 100°C for 2 hours. The mixture was cooled, filtered, and volatiles were removed under reduced pressure. The resulting oil was dissolved in dichloromethane (200ml) and passed through an alumina packed column, collecting the first portion of the product only. After solvent removal n.m.r. analysis indicated a pure sample of a pale yellow solid [3] (80.0g).

c) Reaction of [3] with hexafluoropropene



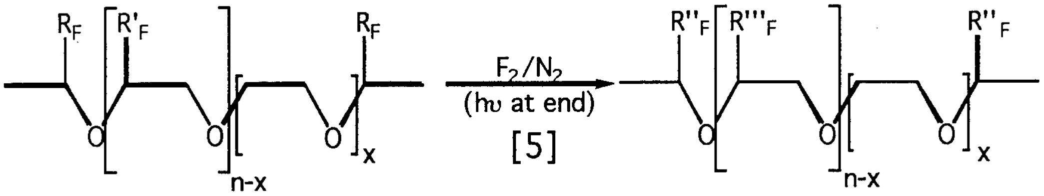
[3]

$R_F = CF_3CFHCF_2$ (predom) or H
$R'_F = CF_3CFHCF_2$

[4]

Into a 300ml stirred autoclave was introduced [3] (65.9g, 0.10 moles), and ditertiary butyl peroxide (5.2g, 0.0356 moles). Dissolved oxygen was removed by introducing high pressure nitrogen gas (15 Bar), stirring, and carefully venting (repeated twice). The autoclave system was then evacuated. Hexafluoropropene gas (*ca* 20g) was introduced and the autoclave was heated to 130°C with stirring. Hexafluoropropene was then allowed to pressurise the autoclave from a room temperature cylinder. The autoclave contents were heated to and then maintained at a temperature of 140°C for *ca* 2 hours until the uptake of hexafluoropropene gas had ceased. This procedure was twice repeated with fresh initiator. Finally a portion of product (*ca* 80g) with fresh initiator (7.5g) was reacted further with hexafluoropropene. The autoclave contents were heated to 140°C during which time the internal pressure rose to *ca* 20 Bar. After stirring for a period of 3 hours the autoclave was cooled and opened. N.M.R. analysis of the stripped product (an orange oil) indicated that there were *ca* 11.4 hexafluoropropyl groups per polyethylene glycol molecule. Given that the terminal ethyl groups have a high degree of substitution, this gives a minimum value of (n-x) as *ca* 9.4.

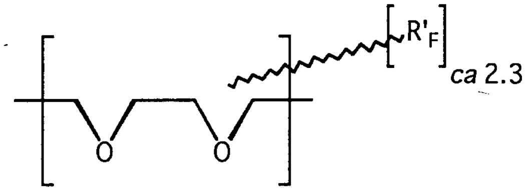
d) Reaction of [4] with fluorine/nitrogen mixtures



[4]

R_F = CF_3CFHCF_2 (predom) or H
R'_F = CF_3CFHCF_2
R''_F = $CF_3CF_2CF_2$ (predom) or F
R'''_F = $CF_3CF_2CF_2$

[1]



[5]

A solution of [4] (25.2g) in [5] (70.5g) was introduced into a stirred FEP reaction vessel. A F_2/N_2 mixture containing from 10% to 50% F_2 was passed into the vessel at room temperature. When the reactivity had decreased the mixture was transferred into an FEP tube through which 50% F_2/N_2 was bubbled and the temperature was raised to 65°C. At this time *ca* 60% of the hydrogen atoms had been replaced by fluorine. Perfluorination was effected by passing 50% F_2/N_2 through the mixture under ultra violet irradiation (100W then 1000W medium pressure discharge lamps). The volatile, now perfluorinated, solvent (53g) was removed under reduced pressure (200°C, <1mmHg) leaving a colourless viscous oil (20.1g). This oil was fractionated (200°C, <1mmHg) yielding [1] (14.1g) as a colourless residue. Many nmr samples were removed during fluorination to monitor the process, hence, the weight of the final product does not reflect the efficiency of the process. A sample of [1] (11.0g) was sealed in an evacuated ampule and dispatched to Euro. Off. Aerospace R+D (AFSC), 223/231 Old Marylebone Road, London NW1 5TH (Receipt was confirmed by A. Davison on 21.1.93)

Characterisation of Intermediates/Products

Estimation of degree of hexafluoropropene incorporation

To an nmr sample ($CDCl_3$ as solvent) was added 1 to 4 drops of α,α,α-trifluorotoluene. By determinining the ratio of high field ^1H & ^{19}F nmr integrals of the sample and trifluorotoluene it was possible to assess the extent of hexafluoropropene incorporation.

Estimation of degree of fluorination

To an n.m.r. sample ($CDCl_3$ as solvent in early stages of fluorination, neat in later stages) was added 1 to 4 drops of α,α,α-trifluorotoluene. By determining the ratio of high field ^1H & ^{19}F n.m.r. integrals of the sample and trifluorotoluene it was possible to assess the extent of fluorination knowing the extent of hexafluoropropene incorporation.

^{19}F N.M.R. of [1]

See Appendix 1 for 235MHz n.m.r. spectrum.

^{13}C N.M.R of [1]

At 62.9MHz multiple overlapping resonances between 102 and 127ppm

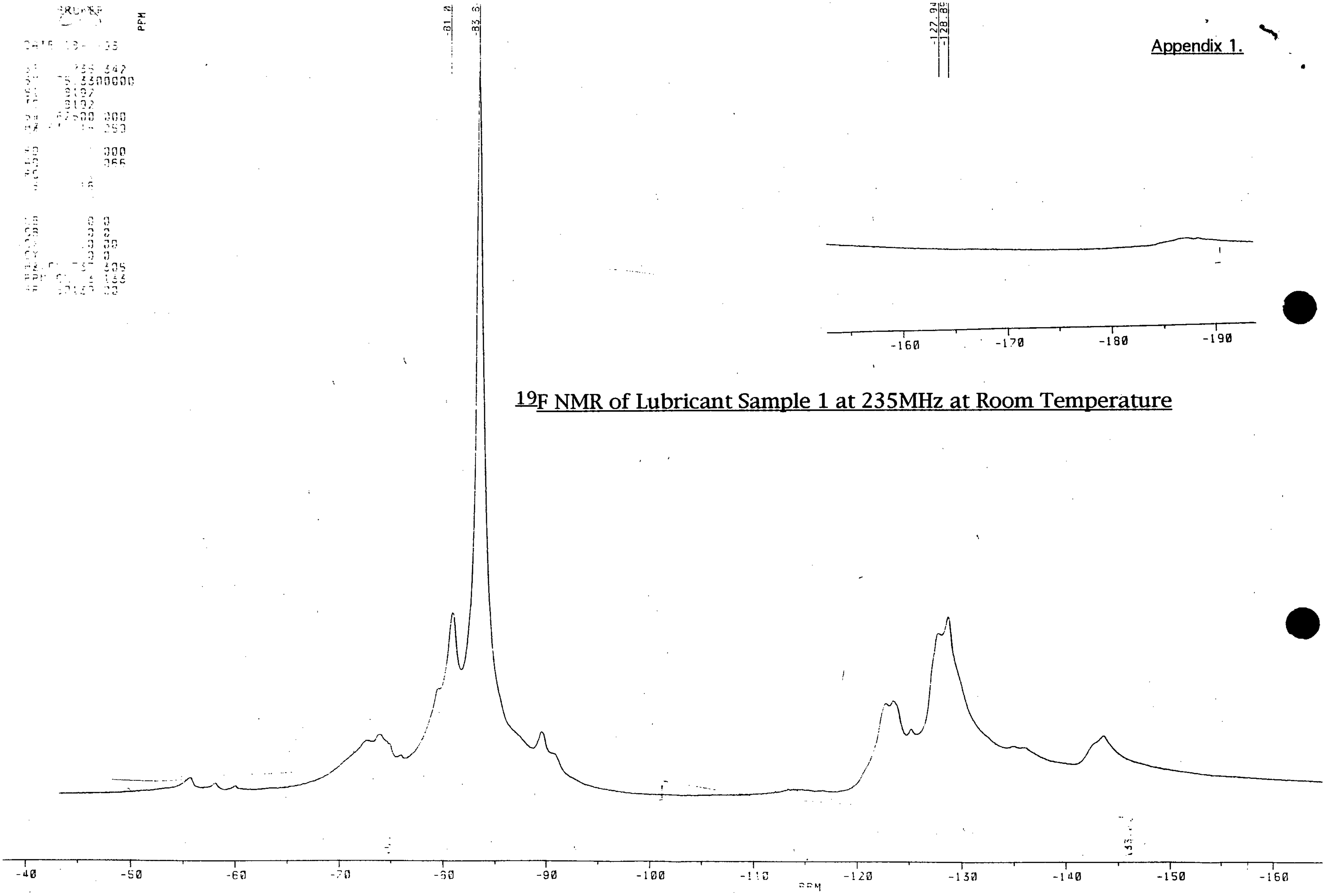
Elemental Analysis of [1]

Elemental analysis indicated 0.0% Hydrogen and 22.6% Carbon.

Summary

A perfluorinated polyether of novel structure has been produced. Aspects of the larger scale synthesis of such materials have been developed. We look forward to further development of syntheses of new materials of novel structure, for testing as lubricants in arrangement with Wright Patterson AFB, Ohio, USA.

Appendix 1.



19F NMR of Lubricant Sample 1 at 235MHz at Room Temperature