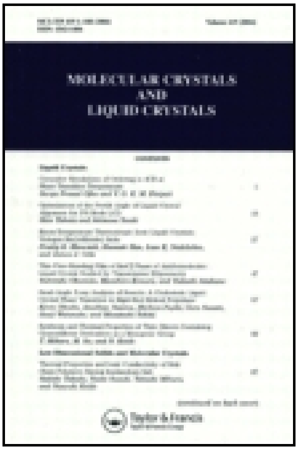

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Synthesis and Properties of A Fluorinated Analogue of Poly-(1,6-Heptadiyne)

Munir M. Ahmad [a] & W. James Feast [a]
[a] Durham University Chemistry Department, South Road, Durham, DH1 3LE, U.K.

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SYNTHESIS AND PROPERTIES OF A FLUORINATED ANALOGUE OF POLY-(1,6-HEPTADIYNE)

MUNIR M. AHMAD and W. JAMES FEAST
Durham University Chemistry Department, South Road, Durham
DH1 3LE, U.K.

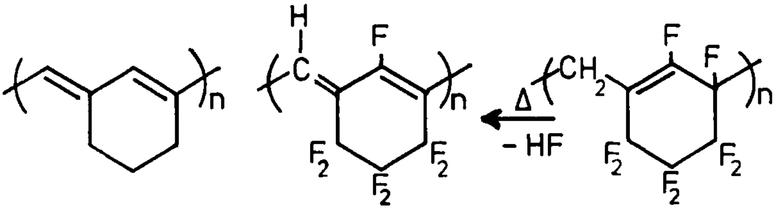
Abstract A highly fluorinated analogue of poly(1,6-heptadiyne) has been prepared and characterized. The two-stage synthesis involved the preparation of a precursor polymer via free radical initiated bulk polymerization of 3-methylene-octafluorocyclohexene; the soluble film and fibre forming precursor polymer was thermally dehydrofluorinated to give poly(1,7-7H-heptafluoromethylenecyclohexenylene). Characterization of the precursor polymer (gpc, ir, ^1H, ^{19}F and ^{13}C nmr spectroscopy) indicates that the monomer is incorporated exclusively via a 1,4-head-tail addition process. The product of the thermal dehydrofluorination is a fluorinated analogue of poly(1,6-heptadiyne) which shows a significantly higher intrinsic conductivity than the hydrocarbon and enhanced oxidative stability.

INTRODUCTION

The electronic structures of polyfluoroacetylene and polydifluoroacetylene have been the subject of a theoretical study based on LCAO-SCF-MO calculations at the CNDO/2 level of approximation.[1] The authors concluded that, with respect to the hydrocarbon, the fluorinated polyacetylenes would have increased electron affinities and smaller band gaps, leading them to predict higher intrinsic conductivities and greater capacities for becoming n-type conductors. The later prediction may be suspect since fluorinated carbanionic species are known to show a tendency to eliminate a fluoride ion even when no conventional simple elimination pathway is available,[2] never-the-less these are interesting predictions which merit experimental test. The preparation of well characterized samples of polyfluoroacetylene and polydifluoroacetylene presents considerable practical difficulty, however the synthesis of a fluorinated analogue of another thoroughly studied conjugated hydrocarbon polymer, poly(1,6-heptadiyne),[3] was described some twenty years ago.[4] We thought that a comparison of the hydrocarbon and fluorocarbon polymers, (1) and (2) respectively, would be of interest in relation to the predictions of Fukui and Shirakawa and have therefore reinvestigated the synthesis of polymer (2). In this paper we present evidence which establishes the validity of the synthetic route to poly(1,7-7H-heptafluoromethylenecyclohexenylene) described in outline by earlier workers[4] and report some preliminary data concerning the comparison of electrical and oxidative stability characteristics of the hydrocarbon and fluorocarbon polymers (1) and (2).

RESULTS AND DISCUSSION

The monomer for this work, 3-methyleneoctafluorocyclohexene, was prepared by the literature route,[4] and was obtained as pure compound (single component by gc-mass spec analysis) with physical and spectroscopic parameters in agreement with the literature data. The precursor polymer (3) was obtained by free radical polymerization of the neat monomer, it was a transparent colourless film and fibre forming high polymer ($\bar{M}_w > 10^6$; $\bar{M}_w/\bar{M}_n \sim 4$),[5] with correct elemental analysis (found C, 35.25; H, 0.63; F, 63.2% calculated for $(C_7H_2F_8)_n$ C, 35.29; H, 0.84; F, 63.86%). The main structural probe was nmr spectroscopy. The ^1H nmr spectrum, a doublet at δ = 3.6 ppm wrt int TMS (J_{HF} = 24 Hz), was not particularly informative but was consistent with the assigned



(1) (2) (3)

structure. The ^{13}C nmr spectrum recorded at 90.56 MHz in d_6-acetone is shown in Figure 1 and consists of a weak band at 125.90 (C_1), a doublet at 153.33 (C_2, J_{CF} = 275 Hz), a doublet of quartets at 89.45 (C_3, J_{CF} = 200 Hz, J_{CCF} ∿ 25 Hz), multiplets between 100 and 120 which can be assigned since one limb of a triplet of triplets at 108.51 (C_6, J_{CF} = 275 Hz, J_{CCF} = 25 Hz) is clearly resolved from the broad triplet at 110.88 (C_4 and C_5, J_{CF} = 275 Hz), the intense doublet at 23.90 (C_7, J_{CCF} = 25 Hz) completes the detectable signals. This spectrum is only consistent with a regular 1,4-head-tail enchainment of 3-methyleneoctafluorocyclohexene units in polymer (3); the simplicity of the spectrum argues for structural regularity and the CF coupling constant observed in the C_7 signal is consistent with a two bond coupling between the fluorine at C_3 and the C_7 carbon. The alternative head-head-tail-tail assembly would have resulted in a significantly smaller three bond CF coupling at C_7 and a greater complexity for the C_3 signal; a mixture of assembly modes would have generated a more complex spectrum since shifts are expected to be sensitive to such structural variations, we estimate that any head-head-tail-

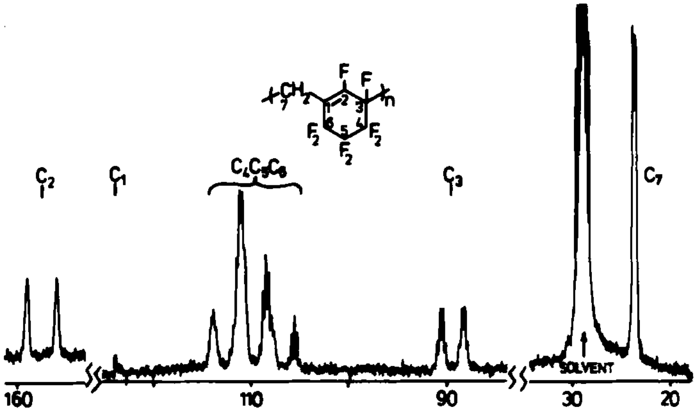


FIGURE 1 ^{13}C Nmr spectrum of polymer (3), scale ppm wrt int TMS tail or other structural defects cannot exceed a molar concentration of 3%. The ^{19}F nmr spectrum of polymer (3) recorded at 84.67 MHz was also consistent with the assigned structure, the shifts (downfield from int $CFCl_3$) and assignments being: broad bands at 104.82 (olefinic F @ C_2) and 159.83 (tertiary F @ C_3), and a set of three overlapping AB quartets derived from the CF_2 units at C_4, C_5 and C_6 which could be assigned as δ_A 104.9, δ_B 115.2 (J_{AB} = 288 Hz), δ'_A 122.3, δ'_B 132.5 ($J_{A'B'}$ = 281 Hz) and δ''_A 129.0, δ''_B 139.0 ($J_{A''B''}$ = 266 Hz).

Polymer (3) is thermally dehydrofluorinated by heating in a stream of nitrogen or under vacuum to give poly(1,7-7H-heptafluoromethylenecyclohexenylene) (2) with correct elemental analysis; samples of this polymer have an intrinsic conductivity of ca 10^{-4} to 10^{-5} $(\Omega\ cm)^{-1}$.[5]

The conversion process could be followed by infrared spectroscopy as recorded in Figure 2 for the region between 800 and 2000 cm.^{1} It can be seen that the absorptions progressively broaden and resolution is lost during the conversion process (which corresponds to a visible change from transparent and colourless to opaque and black), in particular the band assigned to the carbon-carbon double bond stretching mode in the pristine precursor polymer (3) occurs at 1695 cm^{-1} and progressively shifts to 1675 cm^{-1} during the conversion to conjugated polymer (2), at the same time the peak broadens from a width at half height of 30 cm^{-1} in the starting polymer to a value of 60 cm^{-1} in highly converted film (d).

The conductivity of a sample of polymer (2) was unchanged by exposure to air for 72 hours, or iodine vapour for 36 hours. The infrared spectrum of a sample of polymer (2) showed no evidence of oxidation (no -OH or $\gt C=O$ stretching absorptions) after several weeks exposure to the air.

CONCLUSIONS

A highly fluorinated analogue of poly(1,6-heptadiyne) has been

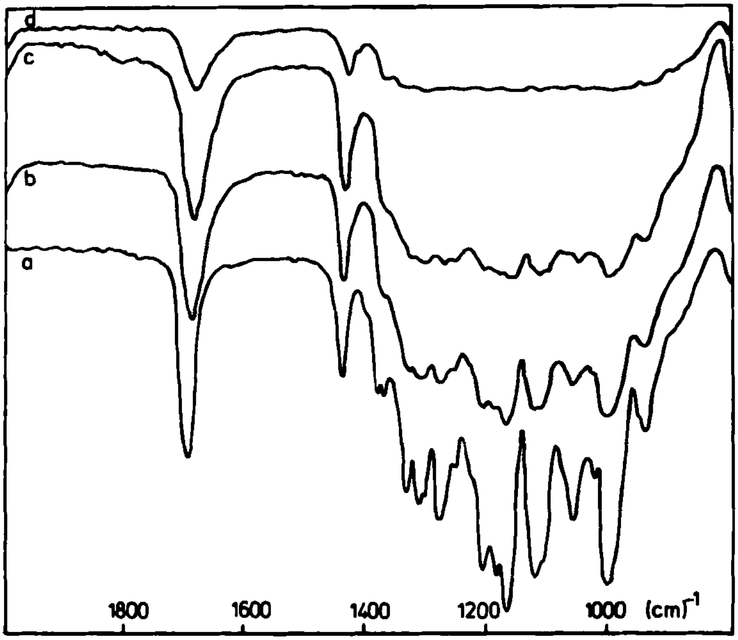


FIGURE 2 Transmission infrared spectra for (a) pristine polymer 3; (b) after heating at 200°C; (c) 240°C and (d) highly converted to structure (2).

synthesised via dehydrofluorination of a precursor polymer. The overall structural features of the precursor polymer (3) have been unambiguously established and confirm the assignments of earlier workers.[4] Fine details of structure of both precursor (3) and conjugated polymer (2) remain to be established; for example, the repeat until of (3) is chiral but no information on tacticity can be deduced from the presently available data; also the geometry at the exocyclic methylene in the repeat unit of (2) is yet to be established, although on the basis of consideration of models it seems likely to be trans. More sophisticated spectroscopic studies of these structural matters and of the process of conversion of (3) to (2), are in hand.

Preliminary studies of the electrical properties of (2) indicated an intrinsic conductivity 10^7 times greater than the hydrocarbon analogue.[5,3] Polymer (2) does not appear to be oxidized by iodine or oxygen. These observations offer some support for the predictions of Shirakawa et al.[1] concerning the effects of fluorine substituents on the electronic properties and oxidative stability of polyenes.

Study of the conjugated polymer (2) appears to offer opportunities for obtaining insights into structure/property relationships in the conducting polymer field. For example, the all trans structure would be capable of supporting two types of soliton,[6] in the first the charge or spin bearing carbons carry only perfluoroalkyl substituents and in the second alternately hydrogen and fluorine atoms. Further work is in progress.

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