poly(vinyl chloride). The smaller value for poly(vinyl bromide) reflects the slower rate of polymerization compared to that of vinyl chloride in the presence of aldehyde (Table V) so that termination is able to compete more effectively with propagation.

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Observation of Stereoirregular Poly(fluoromethylene) by Fluorine-19 Nuclear Magnetic Resonance

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ABSTRACT: *cis*-1,2-Difluoroethylene and *trans*-1,2-difluoroethylene were polymerized by ^{60}Co γ radiation at 0 and 37 °C to give poly(fluoromethylene). The appearance of the 84.66-MHz ^{19}F NMR spectra of the polymers was remarkably sensitive to the solvent used for NMR, and stereosequence heptads could be resolved under certain conditions. Assignments were made at the pentad level. The polymers are highly stereoirregular, accounting for their lack of crystallinity. The polymerizations of cis and trans monomers at the same temperature gave polymers with identical tacticities. A reduction of the polymerization temperature enhanced the syndiotactic triad content. The stereosequence distribution at 0 °C is approximated reasonably well by a Bernoullian model with a P(m) value of 0.42.

^{19}F NMR has been a valuable probe of the microstructure of polymers containing fluorine.[1,2] The polymerization of 1,2-difluoroethylene to form poly(fluoromethylene) (PFM) was described in 1965 by Durrell et al.,[3] but since then there has been little interest in the polymer. The only reported NMR study was concerned with its relaxation behavior, and the microstructure was not examined.[4] However, PFM is of considerable interest from the latter point of view, since every backbone carbon is a pseudoasymmetric center and bears the same substituent. To the author's knowledge the only other polymer of this type which has been studied by NMR is poly(hydroxymethylene).[5] The purpose of this paper is to report the high-resolution ^{19}F spectra of PFM.

Experimental Section

cis-1,2-Difluoroethylene (bp −26 °C) and *trans*-1,2-difluoroethylene (bp −53 °C) were obtained from PCR Research Chemicals Inc. The monomers were degassed and fractionally distilled under high vacuum and then sealed in heavy-wall glass ampules (8.02 g, 125 mmol per ampule). Polymerizations were initiated by ^{60}Co γ radiation (effective dose rate = 0.37 Mrd/h) at temperatures of 37 and 0 °C (the rate of polymerization at −78 °C was negligible). The sealed ampules were exposed to γ radiation for 14–16 h, which was sufficient for 100% conversion to polymer at the higher temperature. Conversions at the lower temperature were less and averaged about 25%. An attempt to prepare PFM at 70 °C in heptane with a heterogeneous $TiCl_4$-$Al(C_2H_5)_3$ catalyst system was not successful.

NMR spectra were recorded with a ^{19}F frequency of 84.66 MHz in a variety of solvents on a Bruker WH-90 spectrometer. It was difficult to prepare uniform solutions containing more than about 10% by weight of polymer, owing to a gelation phenomenon in the solvents tested here. A typical spectrum was recorded from 30 000 scans with a 3.4-μs pulse (90° flip angle), 3.0-s repetition rate, 4.0-kHz sweep width, and 8K data points for the real spectrum. Chemical shifts were measured from internal hexafluorobenzene, which was assigned the value of 163 ppm.

Results and Discussion

^{1}H and ^{13}C NMR spectra of PFM did not exhibit any resolved fine structure, owing to the appreciable line broadening from heteronuclear spin coupling between the observed nucleus and ^{19}F, for which we did not have the facilities for broad-band decoupling. The proton resonance was a broad, asymmetric peak centered around 5.2–5.3 ppm. The proton-decoupled ^{13}C resonance was a doublet centered at 87.31 ppm, with a splitting of 163 Hz, corresponding to the $^{1}J_{^{13}C-^{19}F}$ value. The dispersion of ^{13}C chemical shift from stereochemical nonequivalence was less

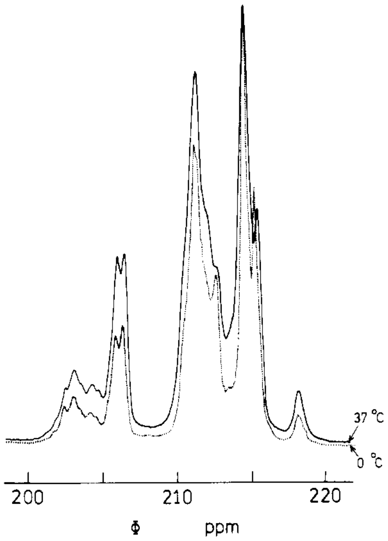


Figure 1. 84.66-MHz ^{19}F NMR spectra of PFM samples prepared at 0 °C (lower spectrum) and 37 °C (upper spectrum) from *trans*-1,2-difluoroethylene. The spectra were observed at 55 °C in acetone solution.

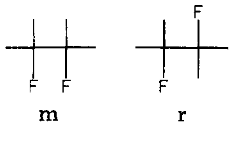
than 5 ppm. These spectra did not have resonances from any structure other than the regular repeat unit $-(CHF)-_n$.

The ^{19}F spectra of PFM show a complicated pattern at around 210 ppm, with a dispersion near 20 ppm due to stereoirregularity. Homonuclear $^{19}F-^{19}F$ spin coupling results in a 15-Hz broadening at most, which is insignificant compared to the large spread in chemical shift from tacticity, although it contributes to line widths of the order of 40 Hz. The $^2J_{^{19}F-^1H}$ coupling of about 47 Hz was eliminated by broad-band proton decoupling. A comparison of proton-coupled and -decoupled ^{19}F spectra gave a value for the nuclear Overhauser enhancement at 75 °C for a 5% by weight PFM solution in dioxane; the result was 1.30 ± 0.08, which agrees with the figure of 1.43 ± 0.05 reported by Yang.[4]

The spectra of PFM prepared from cis and trans monomers were *indistinguishable* when observed under identical conditions, indicating that inversion of the propagating radical was more rapid than addition of the next monomer unit. Relative peak intensities were affected by the polymerization temperature, however, as shown by the spectra in Figure 1.

Figure 2 shows that the appearance of the spectra was remarkably sensitive to solvent, but the observation temperature had only a minor effect over a 60 °C range by comparison. The solvents tested were, in order of their boiling points, acetone, dioxane, dimethylformamide, dimethyl sulfoxide, and 1,3-dioxolan-2-one. As many as 21 discrete peaks were resolved in dioxane, indicating a sensitivity at the level of configurational "heptads", for which there are 36 nonequivalent sequences.

It is quite evident that PFM as prepared here is stereoirregular or atactic. It was possible to obtain a reasonable simulation of the spectrum in acetone at the pentad level by assuming Bernoullian stereosequence propagation statistics with a P(m) value of 0.42, as shown in Figure 3. The parameters for this simulation are given in Table I, though it must be stressed that the pentad assignments are tentative. The Fischer projections for m and r stereosequence dyads are shown below:



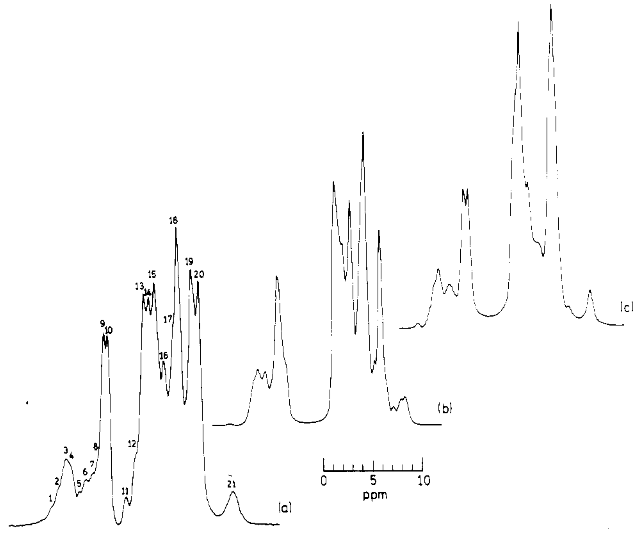


Figure 2. Effect of different solvents on the appearance of the ^{19}F spectra of PFM prepared at 37 °C. The solvents and observation temperatures are as follows: (a) dioxane, 75 °C; (b) dimethyl sulfoxide, 90 °C; (c) 1,3-dioxolan-2-one, 75 °C. The spectrum in dimethylformamide was very similar to b. Note the resolution of at least 21 lines in dioxane, which coalesce in 1,3-dioxolan-2-one to give a relatively simple spectrum, corresponding to a first approximation to isotactic, heterotactic, and syndiotactic triads in order of increasing chemical shift (left to right). The heterotactic sequences appear to be influenced most by solvent.

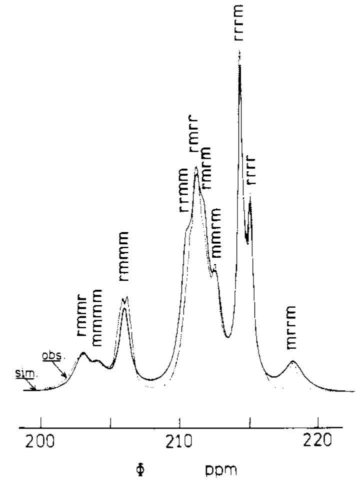


Figure 3. Computer simulation of the ^{19}F spectrum of PFM prepared at 0 °C and observed in acetone solution. The relevant parameters are given in Table I. The deviation of the simulated spectrum (full trace) from the observed spectrum (light trace) is greatest for the rmmm and mrrm peaks.

Table I
Parameters Used To Simulate the ^{19}F Spectrum in Acetone of PFM Prepared at 0 °C, Assuming Bernoullian Statistics with a P(m) Value of 0.42

pentad stereosequence	ϕ, ppm	line width, Hz
rmmr	203.06	120
mmmm	204.24	120
rmmm	206.10	75
rrmm	210.54	80
rrmr	211.26	80
mrmr	211.84	80
mrmm	212.74	80
rrrm	214.45	38
rrrr	215.15	50
mrrm	218.31	140

The same P(m) value and relative ordering of stereosequences, except with rmrm and rmrr interchanged, gave a close simulation of the spectrum in dimethylformamide as well, with appropriate detailed changes in absolute chemical shifts and line widths.

It was necessary to assign variable line widths to represent the differing degrees of line broadening from unresolved heptad stereosequences. The given stereosequence assignments are consistent with a bias toward racemic placement, which increased with decreasing temperature (Figure 1). However, m and r could just as easily be interchanged for an adequate simulation with a $P(\mathrm{m})$ value of 0.58. Definitive assignments cannot be obtained without a study of the appropriate model compounds.

The areas predicted by the present simulation deviate most noticeably for the rmmm and mrrm peaks. A better simulation is possible by assuming Markov 1 statistics with $P(\mathrm{m}|\mathrm{m}) = 0.526$ and $P(\mathrm{r}|\mathrm{m}) = 0.353$. The quantitative significance of the statistical treatment must remain in doubt, however, owing to the tentative nature of the assignments. An interleaved Bernoulli stereosequence propagation model[6] would perhaps be the most appropriate for the present system, where the probability of one dyad is related to the isomerization of the terminal radical and the probability of the next dyad is related to the addition of a monomer unit.

The absence of crystallinity in PFM[3] is hardly surprising given its degree of stereoirregularity. ^{19}F NMR is an excellent probe of the microstructure, though a detailed understanding of the ordering of the stereosequences according to chemical shift, and the dependence of the ordering and spacing on solvent, remains a challenging problem.

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Photooxidation of Di-*n*-butyl Sulfide Using Sensitizers Immobilized in Polymer Films

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ABSTRACT: The photooxidation of di-*n*-butyl sulfide ($\mathrm{Bu_2S}$) to di-*n*-butyl sulfoxide ($\mathrm{Bu_2SO}$) was investigated in methanol solution by using various dyes as singlet-oxygen sensitizers. The rates of $\mathrm{Bu_2SO}$ formation are zero order in [$\mathrm{Bu_2S}$] and in the concentration of dissolved oxygen and thus serve as a measure of sensitizer efficiency. The quantum yields for $\mathrm{Bu_2SO}$ formation, using sensitizers dissolved in methanol, were 1.17, 1.31, 0.201, 0.024, 0.0081, 0.0064, and <0.0031 for rose bengal (RB), tris(2,2′-bipyridyl)ruthenium(II) [$\mathrm{Ru(bpy)_3}$], saffranine O (SO), rhodamine B, victoria blue B, 1-amino-4-hydroxyanthraquinone, and malachite green, respectively. RB, SO, and $\mathrm{Ru(bpy)_3}$ were immobilized in poly(vinyl chloride) [PVC] films and RB was immobilized in cellulose acetate (CA) films. $\mathrm{Bu_2S}$ photooxidation quantum yields for the films were 1.2–1.8, 0.019–0.024, 0.026–0.044, and 0.018–0.020 for RB/CA, RB/PVC, $\mathrm{Ru(bpy)_3}$/PVC, and SO/PVC, respectively. Photodegradation of immobilized sensitizers to colorless products was also monitored. RB/CA, RB/PVC, SO/PVC, and $\mathrm{Ru(bpy)_3}$/PVC films were 50% photodegraded after irradiation for 0.15, 5, 7, and 320 h, respectively. The results indicate that polymer films retard transport of solvent, dissolved oxygen, and/or substrate to sites occupied by the photosensitizer and that there is an attendant decrease in the photooxidation quantum yield relative to that of photosensitizers in solution. Substrate photooxidation and sensitizer photodegradation are parallel processes, probably involving energy transfer from sensitizer to $^3\mathrm{O}_2$ in the former case and electron transfer to form sensitizer radical cation and superoxide in the latter.

Molecular oxygen in its first (singlet) electronic excited state ($^1\mathrm{O}_2$) undergoes a variety of reactions, including 1,4-cycloaddition to dienes, the "ene" reaction with alkyl-substituted olefins to produce hydroperoxides, 1,2-addition to electron-rich olefins, oxidation of phenols, and oxidation of dialkyl sulfides to dialkyl sulfoxides.[1] These reactions are of interest both because they have useful synthetic applications and because $^1\mathrm{O}_2$ has been implicated as the reactive species in photooxidations of biological systems[2] and of synthetic high polymers.[3]

Recently, attention has focused on photosensitized $^1\mathrm{O}_2$ reactions employing sensitizers immobilized on various solid supports.[4–15] Immobilized sensitizers offer an advantage over dissolved photosensitizers because they can be employed in solvent systems in which the sensitizer is normally insoluble. Also, immobilization of a sensitizer limits side reactions between sensitizer and oxidizable substrate and facilitates the separation of the photosensitizer from reaction products.

In general, three approaches have been taken in the design of immobilized photosensitizers. In one,[4–6,12] the sensitizer is covalently bound to cross-linked polystyrene beads, via reaction of the sensitizer with chloromethylated polystyrene. A primary advantage of this approach is that the sensitizer is highly resistant to separation from the support material, thus permitting use of the photosensitizer in a wide variety of solvent systems. Although the scope of this approach is unlimited in principle, relatively few photosensitizers can be linked to polymer supports simply and conveniently. Also, absorption and scattering of incident radiation by the polymer beads complicates the use of covalently bound photosensitizers in studies (such as determination of photooxidation quantum yields) in which the intensity of the absorbed radiation must be well-known.

A second approach is immobilization of a photosensitizer by absorption onto a solid support such as silica gel.[8,9,16] This method is convenient, but the sensitizer can be de-

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