(9) C. E. Wilkes, J. C. Westfahl, and R. H. Backderf, *J. Polym. Sci., Part A-1*, **7**, 23 (1969).
(10) H. J. Harwood and W. M. Ritchey, *J. Polym. Sci., Polym. Lett. Ed.*, **2**, 601 (1964).
(11) Reactivity ratios are defined to be $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$.
(12) M. Modena, C. Garbuglio, and M. Ragazzini, *J. Polym. Sci., Part B*, **10**, 153 (1972).
(13) D. T. Clark, W. J. Feast, I. Ritchie, and W. K. R. Musgrave, *J. Polym. Sci.*, **12**, 1049 (1974).
(14) D. W. McCall, D. C. Douglass, and D. R. Falcone, *J. Phys. Chem.*, **71**, 998 (1967), and references cited therein.
(15) A. D. English and A. J. Vega, *Macromolecules*, following paper in this issue.

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Multiple Pulse Nuclear Magnetic Resonance of Solid Polymers: Dynamics of Poly(tetrafluoroethylene)

Conventional NMR spectra of rare (^{13}C) or abundant (^{1}H, ^{19}F) spins in unoriented polymers are dominated by dipolar interactions. These dipolar spectra are less sensitive to details of the structure and motion than are chemical shift spectra. Chemical shift spectra of rare spins can be obtained by removing the large heteronuclear dipolar interactions by a high power dipolar decoupling field at the resonant frequency of the abundant spins. Chemical shift spectra of abundant spins can be obtained by removing the homonuclear dipolar interactions with a multiple pulse sequence.[1a] The rare spin case both with and without magic angle spinning has been used to study motion in solid glassy polymers at room temperature.[2] The results reported here are the first example of the use of abundant spin chemical shift spectra to examine the structure and motions of a solid polymer as a function of temperature.

Previous studies of poly(tetrafluoroethylene) (PTFE) by conventional[3] and multiple pulse[1] NMR have given some insight into the different types of polymer motion present in morphologically distinct regions. We report here ^{19}F multiple pulse studies of powdered poly(tetrafluoroethylene) that differentiate crystalline and amorphous fractions of the polymer and identify the types of macromolecular motion that take place in these fractions.

^{19}F NMR chemical shift spectra of PTFE, essentially free of dipolar broadening, have been obtained with a Bruker SXP-100 NMR spectrometer modified for high-temperature operation[4] using an eight-pulse cycle[5] with a cycle time of 43.2 μs ($\pi/2$ pulse = 2.2 μs). Spectra were recorded as a function of temperature (−150 to +350 °C) for samples which differed in crystallinity and molecular weight. Samples of varying crystalline content were prepared[6] by varying the rate at which the polymer melt was cooled;[7] the crystallinity was initially estimated from specific volume measurements[6] and found to vary from ~50 to ~80%. These spectra may be interepreted to yield values for the principal components of the chemical shift tensor, the crystalline content of the polymer, and details of the polymer macromolecular dynamics.

Slow exchange chemical shift spectra of PTFE are obtained at −128 °C and the principal values of the chemical shift tensor are found to be in good agreement with previous work,[1c] $\sigma_{11} = 41$, $\sigma_{22} = 141$, $\sigma_{33} = 178$ ppm with respect to CFCl$_3$. The chemical shift line shapes for all samples, regardless of crystallinity, are essentially the same in the absence of motional narrowing.

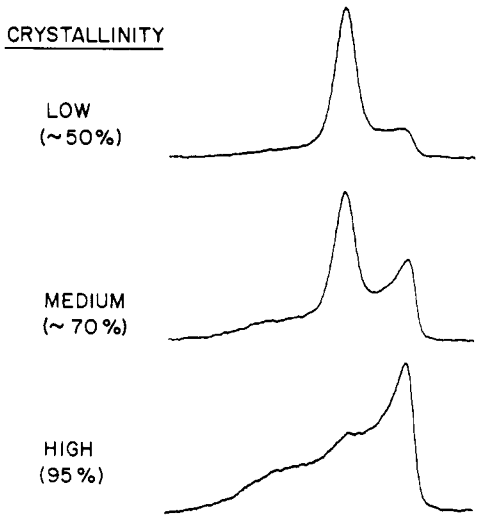

Figure 1. REV-8 chemical shift spectra of three samples of PTFE of differing crystallinity at 259 °C.

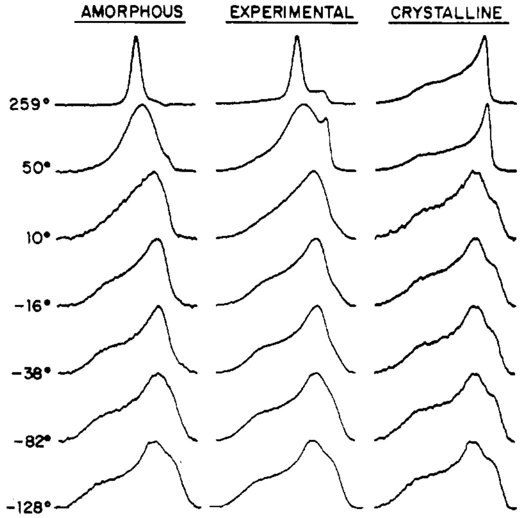

Figure 2. Experimental (~50% crystalline) and deconvoluted chemical shift line shapes for crystalline and amorphous PTFE as a function of temperature.

Spectra obtained at 259 °C for samples of PTFE varying in crystallinity are shown in Figure 1. The chemical shift line shapes for any of the melt recrystallized samples may be simulated by a linear combination of two line shapes. The two line shapes are generated from a linear combination of the spectra of any two samples. These line shapes are identified with crystalline and amorphous portions of the polymer. Variable temperature spectra are deconvoluted into amorphous and crystalline line shapes by the same method as the 259 °C spectra and examples of these line shapes are shown in Figure 2. The crystallinity of each melt recrystallized sample is determined from a linear combination of amorphous and crystalline line shapes. The crystallinity determined by this method is independent of temperature (0 to 300 °C) and correlates well with percent crystallinity determined from density measurements.

The temperature dependence of chemical shift spectra of amorphous and crystalline polymer, obtained by deconvoluting experimental spectra, indicate that polymer chain motions in the crystalline and amorphous regions are fundamentally different and may be described in terms of two distinct macromolecular motions: an anisotropic motion (undoubtedly reorientation about the chain axis) and an effectively isotropic motion. Motion in the crystalline region is anisotropic to the melting point, whereas motion in the amorphous region at low temperatures is dominated by reorientation about a local "chain axis" and at higher temperatures by motions orthogonal to the chain axis which eventually lead to nearly isotropic motion near the melting point.

The chemical shift spectra of polycrystalline samples presented here conclusively demonstrate the grossly different types of motion that occur in the crystalline and amorphous fractions. Previous conventional NMR studies[8,9] of PTFE required highly oriented fiber samples to establish reorientation about the chain axis as the dominant motion in the crystalline region.

A line shape analysis of the processes responsible for the observed motional narrowing will be presented in the near future; this analysis requires the use of the proper theory.[10,11]

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References and Notes

(1) (a) D. Ellett, U. Haeberlen, and J. S. Waugh, *J. Polym. Sci., Polym. Lett. Ed.*, **7**, 71 (1969); (b) A. N. Garroway, D. C. Stalker, and P. Mansfield, *Polymer*, **16**, 171 (1975); (c) M. Mehring, R. G. Griffin, and J. S. Waugh, *J. Chem. Phys.*, **55**, 746 (1971).

(2) (a) J. Schaefer, E. O. Stejskal, and R. Buchdahl, *Macromolecules*, 8, 291 (1975); (b) *ibid.*, **10**, 384 (1977).

(3) D. W. McCall, D. C. Douglass, and D. R. Falcone, *J. Phys. Chem.*, **71**, 988 (1967), and references cited therein.

(4) A. D. English and O. T. Garza, *Macromolecules*, preceding paper in this issue.

(5) W.-K. Rhim, D. D. Elleman, and R. W. Vaughan, *J. Chem. Phys.*, **59**, 3740 (1973).

(6) These samples were prepared by Dr. C. A. Sperati of Plastic Products and Resins Department, E. I. du Pont de Nemours and Co., Parkersburg, W.Va.

(7) C. A. Sperati and H. W. Starkweather, *Fortschr. Hochpolym.-Forsch., Suppl.*, 465 (1961).

(8) D. Hyndman and G. F. Origlio, *J. Appl. Phys.*, **31**, 1849 (1960).

(9) V. J. McBrierty, D. W. McCall, D. C. Douglass, and D. R. Falcone, *Macromolecules*, **4**, 584 (1971).

(10) A. J. Vega and R. W. Vaughan, *J. Chem. Phys.*, **68**, 1958 (1978).

(11) A. J. Vega and A. D. English, submitted for publication.

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CORRECTIONS

Sung Gun Chu and Petr Munk: Thermodynamic Properties of Polystyrene in Mixed Solvents Studied by Sedimentation Equilibrium. Volume 11, Number 5, September–October 1978, page 879.

Due to typographical errors, eq 2 and 44 are stated incorrectly. The correct equations read

$$c_i = n_i M_i / \bar{V}_m \tag{2}$$

$$\frac{\omega^2 r c_3}{RT\,(\mathrm{d}c_3/\mathrm{d}r)} = \frac{1}{M_3(1 - \bar{v}_3{}^*\rho)} + \frac{2A_2 c_3}{1 - \bar{v}_3{}^*\rho} + \ldots \tag{44}$$

The correct equations have been used in subsequent analysis.

Douglas S. Saunders and Mitchell A. Winnik: Cyclization of Hydrocarbon Chains Attached to a Planar Chromophore. Volume 11, Number 1, January–February 1978, page 25.

In Tables IV and V, the titles should read ". . . Conformation of the C(1)–C(2) Bond)". On pages 31 and 32 all references to the rotational state of the C(2)–C(3) bond should be changed to refer to the C(1)–C(2) bond, and the last sentence of the body of the paper should read ". . . chains which hit at low carbon number require the bond between carbons 1 and 2 to be in the gauche conformation".