obtained by the potentiometric titrations at ionic strengths of 0 and 0.1. From the α vs. pH curves obtained by the potentiometric titrations, it is found that the amino groups which were neutralized with HCl are 45–55% of the total amino groups in PEI. Thiele and Gronau[4] reported that the potentiometric titration curve of PEI with HCl reaches to the end point at about $\alpha = 0.67$, although the ionic strength of the titration system is very high. This behavior was interpreted by a possible strong interaction of charged neighbors on uncharged groups along the branched polymer chain,[5] i.e., "the nearest neighboring interaction" which was originally proposed by Katchalsky and coworkers.[9] In contrast to the α vs. pH curve obtained by the potentiometric titration, that obtained by the colloid titration shows three plateaus. Furthermore, the value of α at all pHs is larger than that obtained by the potentiometric titration. From these results, it is considered that "the nearest neighboring interaction" does not play an important role in the complex formation between PEI and KPVS.

The result of colloid titration was also investigated to obtain information about the stoichiometry for the salt-linkage formation of each amino group in PEI with $-OSO_2O^-$ groups in KPVS. The plateau regions mentioned above seem to be the pH regions where each amino group in PEI is dissociated completely: pH <5, primary; pH 7.5–8.5, secondary; and pH >10.5, tertiary. The difference in the α value between the plateau regions of pH <5 and of pH 7.5–8.5 is about 0.25, and the difference between the plateau regions of pH 7.5–8.5 and of pH >10.5 is about 0.5. Therefore, it is found the PEI contains 25% of the primary amino group and 50% of the secondary amino group. The contents of the primary and secondary amino groups agree with those estimated from the studies of polymerization mechanism[1] and NMR.[2] This indicates the stoichiometric salt-linkage formations of the primary and secondary amino groups with $-OSO_2O^-$ groups in KPVS. However, the content of the tertiary amino group is about 3%, as estimated by the curve of α vs. pH at the plateau region of pH >10.5. This could be understood by the explanation that the tertiary amino group is situated in the branching point of the PEI chain and does not form stoichiometrically the salt-linkage with the $-OSO_2O^-$ group in KPVS because of the steric hindrance of the polymer chain.

The study of the colloid titration reported above is not only interesting as an analysis of the mechanism of the complex formation between branched polyion and linear polyion, but it is also interesting as an assay of amino group contents in PEI.

References and Notes

(1) C. R. Dick and G. E. Ham, *J. Macromol. Sci., Part A*, 1301 (1970).
(2) G. M. Lukovkin, V. S. Pshezhetsky, and G. A. Murtazaeva, *Eur. Polym. J.*, **9**, 559 (1973).
(3) E. J. Shepherd and J. A. Kitchener, *J. Chem. Soc.*, 2448 (1956).
(4) H. Thiele and K. H. Gronau, *Makromol. Chem.*, **59**, 207 (1963).
(5) C. J. Bloys van Treslong and A. J. Staverman, *Recl. Trav. Chim. Pays-Bas*, **93**, 171 (1974).
(6) H. Terayama, *J. Polym. Sci.*, **8**, 243 (1952).
(7) J. W. A. van den Berg, C. J. Bloys van Treslong, and A. Polderman, *Recl. Trav. Chim. Pays-Bas*, **92**, 3 (1973).
(8) E. Kokufuta, S. Kokubo, M. Hirata, and S. Iwai, *Kobunshu Ronbunshu (Jpn. Ed.)*, **32**, 665 (1975); *Kobunshi Ronbunshu (Engl. Ed.)*, **4**, 880 (1975).
(9) A. Katchalsky, J. Mazur, and P. Spitnik, *J. Polym. Sci.*, **23**, 513 (1957).

Etsuo Kokufuta

Institute of Applied Biochemistry, The University of Tsukuba, Sakura-mura, Niihari-gun, Ibaraki 300-31, Japan

Received October 16, 1978

Composition and Microstructure of Fluoropolymers. High-Temperature High-Resolution FT NMR

Nuclear magnetic resonance has been a powerful tool for the study of polymer composition and structure for nearly 30 years. High-resolution NMR has been much more useful than broad-line NMR due to the correlation between specific resonances and specific nuclear sites within the polymer. However, high-resolution NMR has until recently[1] only been applicable to those polymers that are either soluble or have a low melt viscosity at a sufficiently low temperature such that an NMR spectrum may be obtained. Fluoropolymers do not fall into either of these two classes. Initial studies of fluoropolymers by medium resolution NMR[2] indicated that sufficient resolution could be obtained for melt samples of tetrafluoroethylene–hexafluoropropylene copolymer at 310 °C to allow a compositional analysis. These studies and later solution studies of general polymer microstructure have indicated that better resolution and sensitivity would be necessary to allow the extraction of accurate compositions and microstructural detail. We report here the development and application of high-temperature high-resolution FT NMR to compositional and microstructural studies of fluoropolymers: poly(tetrafluoroethylene) and poly(tetrafluoroethylene) copolymers with hexafluoropropene and ethylene.

We have obtained high-resolution ^1H (90 MHz) and ^{19}F (84.68 MHz) FT NMR spectra at temperatures up to 400 °C. These spectra have been obtained with a Bruker SXP-100 NMR spectrometer using a specially designed probe. The use of such high temperatures either to permit dissolution of the polymer or reduce the polymer melt viscosity to a sufficiently low value requires that the probe be fabricated from materials stable at high temperature. These requirements are satisfied by using solid support pieces stable at high temperature and a polyimide adhesive[3] to support the NMR coil. High-resolution spectra that are free from nearly all background signals can be obtained with this probe when a gas cooled external field frequency lock is used.

^{19}F NMR spectra of a copolymer of tetrafluoroethylene and hexafluoropropene obtained at 360 °C show an improvement in resolution by a factor of 5 and an increase in sensitivity by a factor of 100 compared to earlier work.[2] These spectra are accumulated with sufficient delay between radiofrequency pulses so that the integrated intensities observed for each ^{19}F resonance are directly proportional to the population of that site in the polymer.[4] The spectrum is shown in Figure 1a and the copolymer composition is 8.5 ± 0.5 mol % HFP. The spectral resolution obtained for bulk melts of this copolymer does not reveal any microstructural details; spectra of solutions of low molecular weight copolymer exhibit better resolution but still do not contain microstructural information.

^{19}F and ^1H NMR spectra of copolymers of ethylene and tetrafluoroethylene (E/TFE) have been obtained in the melt and in solution at 350 and 290 °C, respectively. Microstructural information is present in spectra of both solution and melt samples. Previous efforts to identify a solvent for this copolymer[5] and other fluoropolymers have not been successful. Solvents for fluoropolymers do exist[6] but they must meet several criteria: the boiling point of the solvent should be at least 20 °C higher than the melting point of the polymer, the solvent usually must be heavily fluorinated, and the cohesive energy density of the solvent and polymer melt should be similar.[7] High temperature polymer solution spectra do afford fairly high resolution

0024-9297/79/2212-0351$01.00/0

Table I
^{19}F NMR Microstructural Data for E/TFE Copolymers

sample	[TFE]	N_{TTE}[a]	N_{TTT}[a]	N_{ETE}[a]	$\bar{n}_T$[b]	R[c]	r_1r_2[d]
1	0.456	0.049	0	0.951	1.03	88.5	0.008
2	0.479	0.069	0	0.931	1.04	92.1	0.005
3	0.507	0.089	0.006	0.905	1.05	96.6	0.001
4	0.519	0.115	0.03	0.855	1.10	94.4	0.002

structure	chemical shift,[e] ppm
ECF_2CF_2E	113
$E\overset{*}{C}F_2\overset{+}{C}F_2(\overset{x}{C}F_2)_nCF_2CF_2E$ (n = 0, 2, 4)	* 111.9 + 121.7 x 119.6

[a] N_{XXX} = triad concentrations. [b] $\bar{n}_T$ = number average sequence length of TFE. [c] R = run number. [d] r_1, r_2 = reactivity ratios. [e] With respect to external CFCl$_3$.

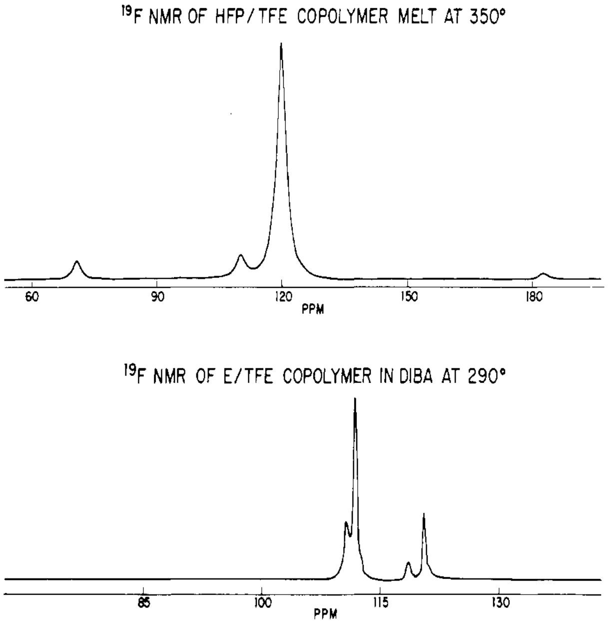

Figure 1. 84.68-MHz ^{19}F-NMR spectrum of TFE/HFP copolymer at 350 °C. The composition is determined to be 8.5 mol % HFP. 84.68-MHz ^{19}F-NMR spectrum of E/TFE copolymer in diisobutyladipate (8 wt %) at 290 °C. Chemical shifts are referred to external CFCl$_3$.

(~5–10 Hz) spectra and polymer melts approach this resolution (20–30 Hz at a melt viscosity of ~10^2 P). It is often more difficult to extract microstructural information from melt spectra than from solution spectra because the attainable resolution in a melt spectrum is proportional to the viscosity (molecular weight); however, this feature can be used to qualitatively correlate polymer microviscosity with microstructure. A typical solution ^{19}F NMR spectrum of E/TFE copolymer at 290 °C is shown in Figure 1b. Melt spectra of the same polymer obtained at 350 °C show nearly as much detail; however, polymer decomposition is rapid at this temperature.

Samples of E/TFE were prepared by batch radical copolymerization at 65 °C in a medium of CCl$_2$FCF$_2$Cl using perfluoropropionyl peroxide as the initiator. Ethylene content was subsequently determined by elemental analysis.[8] ^{1}H NMR spectra could be interpreted to determine the relative concentrations of E alternating with TFE and E dyads. The resolution obtained in the ^{1}H NMR spectra is comparable to that obtained for the ^{19}F spectra; however, the ^{1}H NMR spectra barely resolve the different dyad resonances due to the inherently small chemical shifts for protons as compared to fluorine. The ^{19}F NMR spectra of E/TFE copolymers dissolved in diisobutyl adipate at 290 °C may be interpreted in terms of triad sequences (TFE alternating with E, TFE dyads, and TFE triads) to determine the microstructure. NMR spectral parameters for the observed triad sequences are given in Table I. The ^{19}F sequencing information may be presented either in terms of number average sequence length[9] or run number;[10] this information also allows the calculation of the product of reactivity ratios (r_1r_2).[11] As is evident from either the number average sequence lengths or the run numbers for E/TFE copolymers of various compositions that are given in Table I, E/TFE copolymers are highly alternating. (The equimolar copolymer alternates approximately 94% of the time.) This conclusion is in good agreement with previous studies of these copolymers by infrared[12] and ESCA.[13] The average product of reactivity ratios found for all four samples is 0.004 ± 0.003 and is in reasonable agreement with previous results of 0.006 ± 0.003.[12]

^{19}F NMR spectra of poly(tetrafluoroethylene) (PTFE) obtained at temperatures up to 400 °C show no evidence for any structure other than that of homopolymer. The presence of branching at a level above 0.01% is excluded. Spectra obtained at lower temperatures show evidence of contributions from amorphous and crystalline polymer as previously reported.[14] High-temperature spectra show only a single resonance of width ~300 Hz, indicating that both the amorphous and crystalline fractions are averaging their respective environments sufficiently fast on the NMR time scale so that no distinction remains. Direct evidence of the crystalline/amorphous content and the polymer dynamics in each region can be obtained from multiple pulse NMR experiments.[15]

Acknowledgment. We gratefully acknowledge the advice and/or assistance of J. P. Jesson, P. Z. Meakin, M. L. Sheer, D. P. Carlson, and D. W. Ovenall. We also acknowledge the skilled technical assistance of D. J. Jones and R. O. Balback.

References and Notes

(1) M. Mehring, "NMR Basic Principles and Progress", Vol. 11, Springer-Verlag, New York, 1976.
(2) C. W. Wilson, *J. Polym. Sci.*, **56**, 516 (1962).
(3) Solid support pieces may be easily fabricated from either Vespel (Du Pont) or Macor (Corning Glass Works). The polyimide adhesive used was NR-150 manufactured by Plastic Products and Resins Department, E. I. du Pont de Nemours and Co., Wilmington, Del. 19898.
(4) The spin–lattice relaxation times are CF$_3$, 2.2 s; CF, 2.0 s; and CF$_2$, 1.9 s.
(5) R. L. Johnson, *Encycl. Polym. Sci. Technol., Suppl. 1*, 268 (1976).
(6) Fluoropolymer solvents include diisobutyladipate, Fluorolube MO-10, perfluoronaphthalene, and perfluorobenzophenone.
(7) H. Burrell, "Polymer Handbook", Wiley, New York, 1978, p IV-337.
(8) Elemental analysis for hydrocarbon content was carried out using a Coleman C and H analyzer.

(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.

A. D. English* and O. T. Garza

E. I. du Pont de Nemours and Company, Inc., Central Research and Development and Plastic Products and Resins Departments, Wilmington, Delaware 19898

Received November 6, 1978

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.

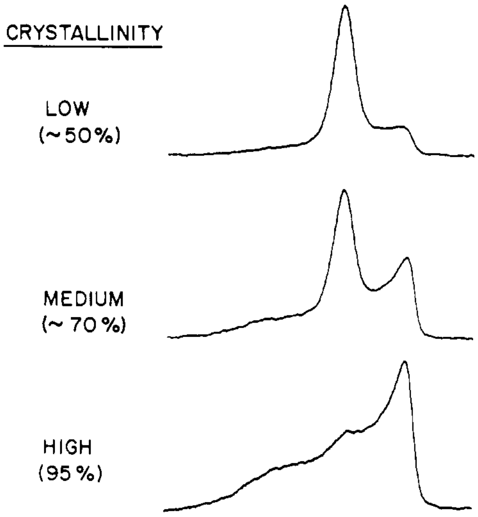

Figure 1. REV-8 chemical shift spectra of three samples of PTFE of differing crystallinity at 259 °C.

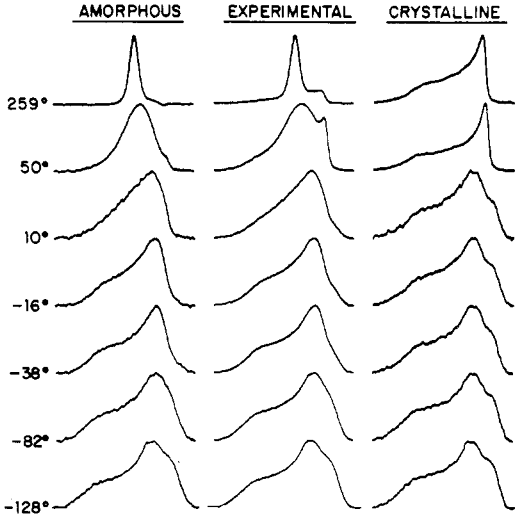

Figure 2. Experimental (~50% crystalline) and deconvoluted chemical shift line shapes for crystalline and amorphous PTFE as a function of temperature.

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

0024-9297/79/2212-0353$01.00/0