

# High-Resolution Variable-Temperature $^{19}\text{F}$ MAS NMR Spectroscopy of Vinylidene Fluoride Based Fluoropolymers

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Received May 11, 1998; Revised Manuscript Received August 26, 1998

**ABSTRACT:** Variable-temperature (VT) solid-state  $^{19}\text{F}$  NMR spectroscopy with high-speed magic-angle spinning (MAS) has been used to study copolymers of vinylidene fluoride and hexafluoropropylene and of vinylidene fluoride and chlorotrifluoroethylene, and terpolymers of vinylidene fluoride, tetrafluoroethylene, and hexafluoropropylene. High-resolution spectra were obtained by simultaneously using MAS speeds up to 25 kHz and heating to 250 °C. Sufficient resolution was achieved to assign peaks by comparison to results obtained from solution-state NMR studies and to determine the monomer composition of the polymer.

## Introduction

A valuable tool for the analysis of the structure of fluorocarbon polymers is  $^{19}\text{F}$  NMR spectroscopy.<sup>1,2</sup> In  $^{19}\text{F}$  NMR, neighbors of a particular fluorine nucleus have a significant effect on its chemical shift. As a result, the type and quantity of monomer sequences can be determined in a fluorocarbon polymer on the basis of  $^{19}\text{F}$  chemical shifts.<sup>2–10</sup> The routine analysis of fluoropolymers and monomer ratio determination via  $^{19}\text{F}$  NMR spectroscopy have typically required the polymers to be in solution. Many fluoropolymers, however, are insoluble or intractable and therefore require analysis in the solid state.

Solid-state  $^{19}\text{F}$  NMR of fluorocarbon polymers is difficult due to the strong homonuclear  $^{19}\text{F}$ – $^{19}\text{F}$  dipolar coupling interactions and large chemical shift anisotropies (CSA), resulting in broad featureless spectra. Typically, the static line width for  $^{19}\text{F}$  in fluorinated polymeric materials is greater than 10 kHz.<sup>11–15</sup> Spectra can be further complicated by  $^{19}\text{F}$ – $^1\text{H}$  dipolar interactions.

Three approaches have typically been taken to obtain high-resolution  $^{19}\text{F}$  NMR spectra. One approach is to average the static line-broadening interaction in  $^{19}\text{F}$  NMR using combined rotation and multiple pulse spectroscopy (CRAMPS).<sup>16–19</sup> CRAMPS is not as useful for samples with large CSA such as  $^{19}\text{F}$  in fluoropolymers. The rotation rate is usually limited to <4 kHz, resulting in considerable overlap of the isotropic and rotational sidebands at moderate magnetic fields.<sup>16</sup> As a result most researchers studying fluoropolymers in the solid state have generally avoided this technique.<sup>15</sup> Another approach has been to spin the samples about an angle of 54°44' with respect to the applied magnetic field (magic-angle spinning or MAS), which will average both dipolar interactions and CSA.<sup>11,12</sup> The sample must be spun at a rate much faster than the static dipolar-broadened line width in order to obtain high-resolution  $^{19}\text{F}$  NMR spectra. Maciel and co-workers

**Table 1. Polymer Name and Monomer Composition**

polymer	monomer composition <sup>a</sup>
copolymer A	78.8% $\text{CH}_2\text{CF}_2$ + 21.2% $\text{CF}_2\text{CFCF}_3$
copolymer B	78.8% $\text{CH}_2\text{CF}_2$ + 21.2% $\text{CF}_2\text{CFCF}_3$
copolymer C	69.0% $\text{CH}_2\text{CF}_2$ + 31.0% $\text{CF}_2\text{CFCl}$
copolymer D	24.3% $\text{CH}_2\text{CF}_2$ + 75.7% $\text{CF}_2\text{CFCl}$
terpolymer A	50.5% $\text{CH}_2\text{CF}_2$ + 22.8% $\text{CF}_2\text{CF}_2$ + 26.7% $\text{CF}_2\text{CFCF}_3$
terpolymer B	61.1% $\text{CH}_2\text{CF}_2$ + 20.9% $\text{CF}_2\text{CF}_2$ + 18.0% $\text{CF}_2\text{CFCF}_3$

<sup>a</sup> The monomer composition of each polymer is derived from the mole percent of the monomer feed ratio.

obtained solid-state  $^{19}\text{F}$  NMR spectra of fluoropolymers using magic-angle spinning at rates of <22 kHz.<sup>11</sup> At these spinning rates the broadening from homonuclear dipolar coupling is still not completely averaged. The third technique is to heat the samples to very high temperatures (>300 °C) and acquire the static spectrum, without spinning.<sup>20</sup> The reported resolution for this technique appears to be greater than that reported by Maciel but is still not comparable to that obtained in typical solution spectra. Also, it may result in degradation of the sample.<sup>11</sup>

We have reported that it is possible to obtain dramatically improved resolution compared to those for any previous solid-state  $^{19}\text{F}$  NMR studies of fluoropolymers by combining very high-speed magic-angle spinning in conjunction with high temperature.<sup>21</sup> Our initial communication showed the improvements in resolution possible for a copolymer of vinylidene fluoride and chlorotrifluoroethylene.<sup>21</sup> Here we expand our high-speed variable temperature (VT) MAS  $^{19}\text{F}$  NMR studies to copolymers of vinylidene fluoride ( $\text{VF}_2 = \text{CH}_2\text{CF}_2$ ) and hexafluoropropylene (HFP =  $\text{CF}_2\text{CFCF}_3$ ), copolymers of  $\text{VF}_2$  and chlorotrifluoroethylene (CTFE =  $\text{CF}_2\text{CFCl}$ ), and terpolymers of  $\text{VF}_2$ , HFP, and tetrafluoroethylene (TFE =  $\text{CF}_2\text{CF}_2$ ), as outlined in Table 1. One of the primary applications of solution-state NMR spectroscopy of these types of fluoropolymers is the quantitative determination of relative monomer concentrations. We have compared the  $^{19}\text{F}$  solid-state and solution-state NMR analyses of the fluoropolymers reported here, since they can be well characterized by proven solution-state NMR techniques. We find excellent quantitative

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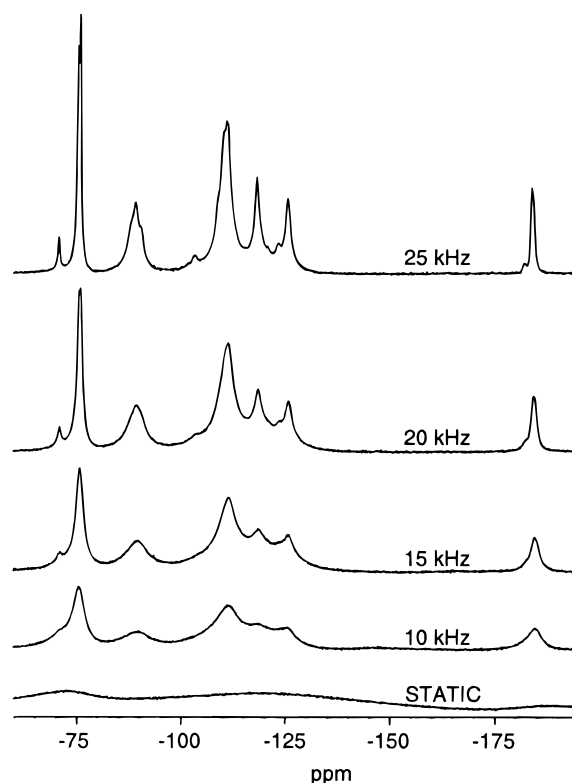
agreement between the solution-state and solid-state NMR results. This is critical to demonstrate the qualitative and quantitative integrity of solid-state  $^{19}\text{F}$  NMR for the analysis of *intractable* fluoropolymers.

## Experimental Section

**Materials.** All samples were obtained from Dyneon LLC. The designation and corresponding monomer composition for each polymer used are summarized in Table 1. For solid-state NMR studies, each sample was ground in liquid nitrogen to a powder and analyzed without further sample preparation.

**NMR Spectroscopy.** All solid-state NMR spectra were acquired using a Chemagnetics CMX-300 MHz spectrometer operating at 282.2 MHz for  $^{19}\text{F}$ . A Chemagnetics double-resonance  $^1\text{H}/^{19}\text{F}$  probe with a Vespel spinning module housing, a 3.2 mm o.d. (62 mm<sup>3</sup> sample size) zirconia rotor, and Vespel end caps and drive tip was used. Single pulse excitation ( $\pi/2 = 2\mu\text{s}$ ) without  $^1\text{H}$  decoupling or background suppression techniques was used. Samples were spun at the magic angle at rates between 0 and 25 kHz and temperatures between 20 and 250 °C using air for the drive, bearing, and VT gases that had been dried to <10 ppm water. Temperature calibration was performed using  $\text{Pb}(\text{NO}_3)_2$  as a chemical shift thermometer. The  $^{207}\text{Pb}$  signal from  $\text{Pb}(\text{NO}_3)_2$  changes chemical shift as a function of temperature.<sup>27,28</sup> For spinning rates  $\sim 18$  kHz and 20 °C the temperature determined from  $\text{Pb}(\text{NO}_3)_2$  chemical shifts (actual temperature) was  $\sim 15$  °C higher than the variable temperature (indicated temperature). As the temperature was increased, the difference between the indicated and actual temperatures narrowed until about 160 °C, at which point the temperatures were the same. At 250 °C the indicated temperature was about 5 °C higher than the actual temperature. For slower spinning speeds (4–6 kHz), the indicated and actual temperatures were in agreement at low temperatures. At high temperatures the indicated temperature was  $\sim 20$  °C higher than the actual temperature. Over the entire temperature range 20–250 °C, the 18 kHz spinning speeds were consistently  $\sim 15$  °C higher than the 4–6 kHz speeds. The discrepancy in temperature between the high and low spinning speeds was believed to be caused by frictional heating. All calibration experiments were performed using fixed variable-temperature and bearing gas flow rates. Only the drive pressure was altered to change spinning rates. Depending on sample conditions, between 512 and 5120 data points were acquired with a spectral width of 150 kHz, corresponding to acquisition times between 3.4 and 34 ms, respectively. Sixty-four transients were acquired using a repetition delay of 4 s. Relaxation measurements showed that 4 s was sufficient to obtain quantitative spectra. Chemical shifts were referenced to polytetrafluoroethylene, which was assigned a chemical shift of  $-121$  ppm. Five-carbon sequences were assigned to particular resonances on the basis of solution-state studies of similar compounds.<sup>2–10,22</sup> Integrated areas of peaks in each spectrum were measured for each compound, and calculations of monomer ratios were based on these values. We estimate that each of the fixed integration values has an error of  $\pm 0.1\%$ . This value is based on the variations observed when the raw data were reprocessed for the same sample.

Information about monomer composition was supplied by Dyneon LLC on the basis of monomer feed ratios and solution-state NMR.<sup>23</sup> Solution NMR spectra were acquired using a Varian UNITY plus 400 FT-NMR spectrometer operating at 400 MHz for  $^1\text{H}$  NMR and 376 MHz for  $^{19}\text{F}$  NMR. Copolymer A was completely soluble in acetone- $d_6$  (99.9%) while copolymer B formed a homogeneous clear gel.  $^{19}\text{F}$  NMR spectra were then obtained using trichlorofluoromethane ( $\text{CFCl}_3$ ) as an internal standard. For copolymers A and B the procedure used to determine the monomer composition for both solution and solid-state NMR analysis was the same. This procedure is described in the Results and Discussion sections. Copolymers C and D were accurately weighed with a known amount of the cross integration standard 1,4-bis(trifluoromethyl)benzene and completely dissolved in acetone- $d_6$  (99.9%). The dissolved

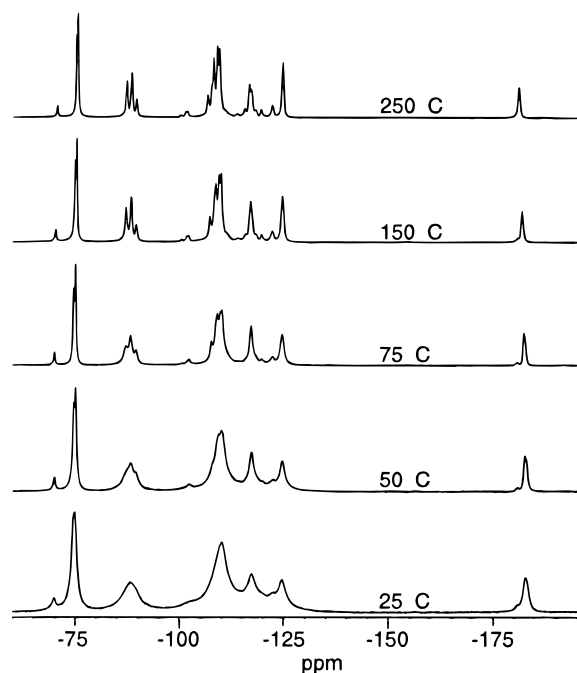


**Figure 1.** Variable-speed MAS  $^{19}\text{F}$  NMR spectra of terpolymer B, composed of 61.1%  $\text{VF}_2$ , 18.0% HFP, and 20.9% TFE (mole percent). Each spectrum was acquired at room temperature (25 °C) with 64 transients and 3072 data points.

polymer solution was then spiked with small amounts of acetic acid- $d_4$  (99.5%) to shift any interfering water signals in the  $^1\text{H}$  NMR downfield from spectral regions of interest. As a result the cross integration standard has a resonance separate from that of the polymer in  $^1\text{H}$  NMR. In the copolymers, the only source of  $^1\text{H}$  signals is from the vinylidene fluoride ( $\text{VF}_2$ ) monomer units. The integrated areas of the methylene hydrogens in  $\text{VF}_2$  and aromatic hydrogens from the integration standard were obtained to calculate the absolute weight percent composition of  $\text{VF}_2$ . The weight percent chlorotrifluoroethylene (CTFE) was determined by difference. Terpolymer A formed a homogeneous clear gel in acetone- $d_6$  whereas terpolymer B completely dissolved in the solvent. The mixtures were then spiked with about 8  $\mu\text{L}$  of 1,4-bis(trifluoromethyl)benzene and 1 drop of  $\text{CFCl}_3$ . The 1,4-bis(trifluoromethyl)benzene was used as a  $^1\text{H}/^{19}\text{F}$  NMR cross integration standard, and  $\text{CFCl}_3$  was the  $^{19}\text{F}$  NMR internal standard. The integrated intensities of the methylene hydrogens in  $\text{VF}_2$  and the aromatic hydrogens from the integration were measured in the  $^1\text{H}$  NMR. These  $^1\text{H}$  NMR integration values were then compared with the  $^{19}\text{F}$  NMR integrated intensities of the trifluoromethyl fluorines from the integration standard, the trifluoromethyl fluorines from the hexafluoropropylene (HFP), and the methylene fluorines. A  $^1\text{H}/^{19}\text{F}$  NMR cross integration calculation technique was then used to determine the relative weight percent of  $\text{VF}_2$ , HFP, and tetrafluoroethylene (TFE).

## Results

The  $^{19}\text{F}$  MAS NMR spectra of a terpolymer of  $\text{VF}_2$ , HFP, and TFE (designated terpolymer B) are shown in Figure 1. All of the spectra in Figure 1 were acquired with 64 transients at 25 °C and acquired using 3072 points. The static spectrum is typically very broad for fluoropolymers, and in Figure 1 there are three broad peaks corresponding to  $\text{CF}_3$  ( $\sim -75$  ppm),  $\text{CF}_2$  ( $\sim -115$  ppm), and  $\text{CF}$  ( $\sim -180$  ppm). The primary line-

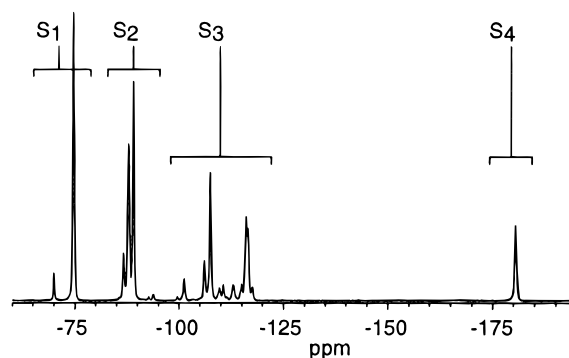


**Figure 2.** VT MAS  $^{19}\text{F}$  NMR spectra of terpolymer B, composed of 61.1%  $\text{VF}_2$ , 18.0% HFP, and 20.9% TFE (mole percent). Each spectrum was acquired with 64 transients and 3072 data points at spinning speeds of 23 kHz for 25, 50, and 75 °C and 22 kHz for temperatures above 150 °C.

broadening mechanisms are homonuclear  $^{19}\text{F}$ – $^{19}\text{F}$  dipolar interactions and shielding anisotropies. Another possible contribution to the broadening is  $^{19}\text{F}$ – $^1\text{H}$  dipolar interactions. Spinning rates of 10 kHz were required to observe regions which could be described by three-carbon sequences. Spinning rates of 20 kHz gave a resolution similar to the best one reported by Maciel and co-workers for similar fluoropolymers.<sup>11</sup> At spinning rates of 25 kHz the resolution is significantly better than that observed at 20 kHz.

The dramatic improvement in resolution that occurs when fluoropolymer terpolymer B is heated in the NMR probe while spinning at rates greater than 22 kHz is shown in Figure 2. Each spectrum was acquired with 64 transients at spinning speeds of 23 kHz for temperatures  $\leq 150$  °C and 22 kHz for temperatures  $> 150$  °C and acquired using 3072 data points. The resolution in these spectra is typical for the fluoropolymers reported in this publication. The increase in resolution at high temperature is the result of increased molecular motion of the polymer, which helps to partially average dipolar interactions. The combination of high-speed MAS and increased molecular motion provides a resolution comparable to that for *solution-state* spectra of these and similar fluoropolymers. The chemical shifts of the peaks observed in the solid-state NMR spectra typically correspond to within 1 ppm of the reported *solution-state* chemical shifts. We have investigated fluoropolymer samples that were originally studied by Maciel and co-workers using only high-speed MAS.<sup>11</sup> The additional resolution possible using both high-speed MAS and high temperatures allows us to accurately quantitate the monomer ratios for each fluoropolymer.

**Copolymer A.** Figure 3 shows the  $^{19}\text{F}$  MAS spectrum of copolymer A, a copolymer of vinylidene fluoride ( $\text{VF}_2$ ) and hexafluoropropylene (HFP) prepared using typical monomer feed ratios given in Table 1. The



**Figure 3.** VT MAS  $^{19}\text{F}$  NMR spectrum of fluoropolymer copolymer A, composed of 78.8%  $\text{VF}_2$  and 21.2% HFP (mole percent). The spectrum was acquired with 64 transients, 22 kHz MAS, 250 °C, and 4096 data points. Assignment of the resonances is given in Table 2.

**Table 2. Chemical Shifts of Copolymer A**

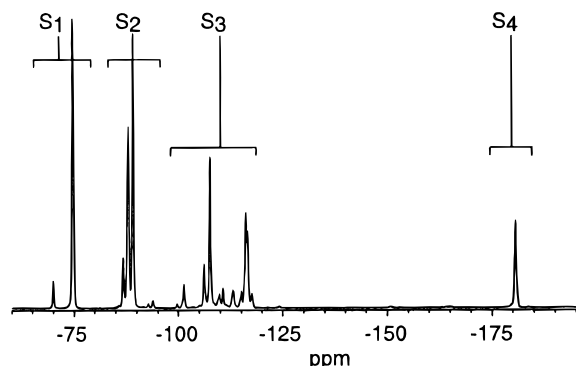
spectral range corresponding to area $S_n^a$	chemical shift (ppm)	fragment <sup>b</sup>	integrated area
$S_1$	-70.4	02420	2287.7
	-75.1	22402	
	-75.3		
$S_2$	-86.0		3519.9
	-87.1	20202	
	-88.4		
	-89.5		
	-93.1	20200	
$S_3$	-94.2		3481.9
	-100.0	04202	
	-101.6		
	-103.8	20242	
	-106.4	40224	
	-107.8	20224	
	-110.1		
	-111.0	20220	
	-112.0		
	-113.4	02200	
$S_4$	-115.1		727.3
	-115.4		
	-116.9	02240	
	-118.0		
	-180.0	242	
	-180.8	042	

<sup>a</sup> Figure 3. <sup>b</sup> 0 =  $\text{CH}_2$ ; 2 =  $\text{CF}_2$ ; 4 =  $\text{CFCF}_3$ .

spectrum was obtained with 64 transients at 22 kHz MAS and 250 °C and acquired using 4096 data points. Chemical shift assignments for each peak according to probable five-carbon sequences and the integrated areas for different regions used for monomer ratio calculations are presented in Table 2. The peak assignments in terms of five-carbon sequences were made by comparing our results to those of *solution-state*  $^{19}\text{F}$  NMR studies of similar polymers.<sup>3–6,22</sup> We obtained comparable resolution to those of the *solution-state* NMR studies previously published.

The high resolution in the solid-state NMR spectrum allows the quantitative determination of the integrated intensity of each peak or regions of peaks. The HFP monomer unit is the only source of  $\text{CF}_3$  and  $\text{CF}$  groups in the polymer. The  $^{19}\text{F}$  atoms in these groups resonate at -70, -75, and -180 ppm, respectively. The number of HFP monomer units ( $N_{\text{HFP}}$ ) can be determined on the





**Figure 4.** VT MAS  $^{19}\text{F}$  NMR spectrum of fluoropolymer B, composed of 78.8%  $\text{VF}_2$  and 21.2% HFP (mole percent). The spectrum was acquired with 64 transients, 21 kHz MAS, 250  $^\circ\text{C}$ , and 4096 data points. Assignment of the resonances is given in Table 3. Note: Copolymer B has both additional curesite monomer and TFE impurity, as shown by peaks at  $-108.8$ ,  $-109.8$ , and  $-119$  to  $-125$  ppm.

basis of the integrated areas of peaks according to the following equations.

$$N_{\text{HFP}} = S_4 \quad (1a)$$

$$N_{\text{HFP}} = \frac{1}{3}(S_1) \quad (1b)$$

$S_N$  is the relative integrated intensity due to either the CF,  $\text{CF}_2$ , or  $\text{CF}_3$  regions of the spectrum as shown in Figure 3 and Table 2. The two values of  $N_{\text{HFP}}$  obtained from eqs 1a and 1b were averaged to reduce any experimental error from the measurement of the integrated intensities for the two regions. Peaks due to  $\text{CF}_2$  resonances of both monomer units ( $\text{VF}_2$  and HFP) appear in the range  $-85$  to  $-118$  ppm. The number of  $\text{VF}_2$  units ( $N_{\text{VF}_2}$ ) can be determined by using the following equation.

$$N_{\text{VF}_2} = \frac{1}{2}(S_2 + S_3) - N_{\text{HFP}} \quad (2)$$

From this equation, which is similar to that used by Maciel et al., the copolymer is composed of 78.7/21.3 mol %  $\text{VF}_2$ /HFP, respectively, as presented in Table 8.<sup>5</sup> These values compare favorably to the monomer feed ratios 78.8/21.2 mol % for  $\text{VF}_2$ /HFP and the solution-state NMR values 78.1/21.9 mol % for  $\text{VF}_2$ /HFP, respectively.

**Copolymer B.** Figure 4 shows the spectrum obtained of copolymer B, which is also a copolymer of  $\text{VF}_2$  and HFP. Chemical shift assignments for each peak according to probable five-carbon sequences and integrated areas for different regions used for monomer ratio calculations are presented in Table 3.<sup>3–6,22</sup> The spectrum appears to be identical to that of copolymer A. This is not surprising, since the polymers were prepared using identical monomer feed ratios (Table 1), but the integrated areas are slightly different. Copolymer B has a small amount of curesite monomer added to promote cross-linking. Another difference between copolymer A and copolymer B can be seen by closely comparing the two spectra. Additional resonances can be seen in the spectrum of copolymer B. These resonances at  $-108.8$ ,  $-109.5$ , and  $-121.8$  through  $-124.5$  ppm are similar to those observed in the spectra of terpolymers containing  $\text{VF}_2$ /HFP/TFE such as terpolymer A and terpolymer B (vide infra). Consequently this leads us to believe that trace amounts of TFE are

**Table 3. Chemical Shifts of Copolymer B**

spectral range corresponding to area $S_n^a$	chemical shift (ppm)	fragment <sup>d</sup>	integrated area
$S_1$	$-70.3$	02420	2210.8
	$-74.0$	22402	
$S_2$	$-86.1$	20202	3638.2
	$-87.1$		
	$-88.3$		
	$-89.4$		
	$-93.1$	20200	
	$-94.2$		
$S_3$	$-100.0$	04202	3405.0
	$-101.2$		
	$-101.6$		
	$-103.8$	20242	
	$-105.4$	40224	
	$-106.4$		
	$-107.8$	20224	
	$-108.8$	22202	
	$-109.8$		
	$-110.1$	20220	
impurity <sup>b</sup>	$-111.8$		
	$-112.0$		
	$-113.3$	02200	
	$-115.0$		
	$-115.4$	02240	
	$-116.4$		
	$-116.8$		
	$-117.9$		
	$-119.5$	22222	
	$-121.8$	02222	
impurity <sup>c</sup>	$-124.5$	02220	
$S_4$	$-180.0$	242	719.5
	$-180.8$	042	

<sup>a</sup> Figure 4. <sup>b</sup> Included in integrated area. <sup>c</sup> Not included in integrated area. <sup>d</sup> 0 =  $\text{CH}_2$ ; 2 =  $\text{CF}_2$ ; 4 =  $\text{CF}_2\text{CF}_2$ .

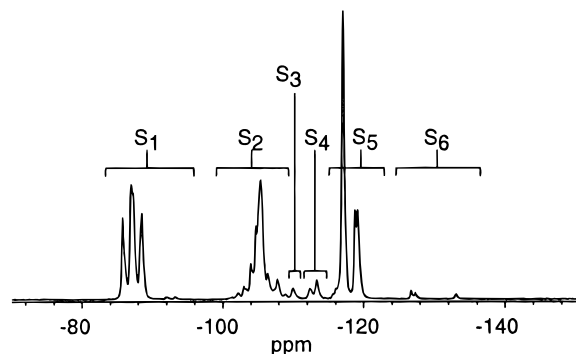
present in our sample of copolymer B. The same procedure to determine monomer ratios for copolymer A was used, but slightly different values were obtained. Using eqs 1a, 1b, and 2, the values obtained for  $N_{\text{HFP}}$  and  $N_{\text{VF}_2}$  are 20.7 and 79.3 mol %, respectively. This compares well to both the monomer feed values 21.2/78.8 and the solution-state NMR values 22.1/77.9 mol % HFP/ $\text{VF}_2$  as reported in Table 8.

**Copolymer C.** We have previously published work showing the five-carbon sequence determination and percent monomer composition of a copolymer of  $\text{VF}_2$  and CTFE at 150  $^\circ\text{C}$  and 23 kHz MAS.<sup>21</sup> Copolymer C and the compound previously published are both copolymers of  $\text{VF}_2$  and chlorotrifluoroethylene (CTFE) with similar monomer feed ratios (Table 1). In this publication we present our results when copolymer C is analyzed with 64 transients at 250  $^\circ\text{C}$  and 22 kHz MAS and acquired with 3072 data points, as shown in Figure 5 and Table 4.

Our assignments of peaks into the five-carbon sequence units shown in Table 4 are based on the assignments of Muresheva.<sup>7,8</sup> Muresheva developed the following equation for determining the monomer ratio for  $\text{VF}_2$  and CTFE copolymers.<sup>7</sup>

$$\frac{P(\text{VF}_2)}{P(\text{CTFE})} = \frac{S_1 + S_2 + 3S_3 - S_4}{S_5 + S_6 + 2(S_4 - S_3)} \cdot \frac{3}{2} \quad (3)$$

The following assumptions were used in the derivation



**Figure 5.** VT MAS  $^{19}\text{F}$  NMR spectrum of fluoropolymer copolymer C, composed of 69.0%  $\text{VF}_2$  and 31% CTFE (mole percent). The spectrum was acquired with 64 transients, 22 kHz MAS, 250  $^\circ\text{C}$ , and 3072 data points. Assignment of the resonances is given in Table 4.

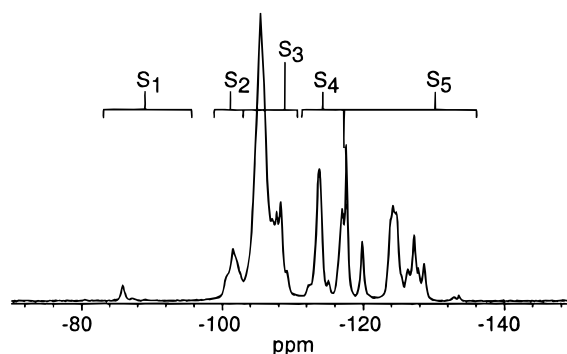
**Table 4.** Chemical Shifts of Copolymer C

spectral range corresponding to area $S_i^a$	chemical shift (ppm)	fragment <sup>b</sup>	integrated area
$S_1$	-86.6	20202	2924.1
	-88.0		
	-89.4		
	-94.0		
$S_2$	-101.9	20230	2896.8
	-102.9		
	-103.6		
	-109.3		
	-110.1		
$S_3$	-111.3	20220	126.0
	-113.6		
$S_4$	-113.6	02200	305.4
	-114.5		
$S_5$	-116.7 to -118.2	02230	3524.1
	-120.0 to -120.6		
$S_6$	-127.7	032	139.3
	-128.4		
	-134.2		
	-134.5		
	-134.5		

<sup>a</sup> Figure 5. <sup>b</sup> 0 =  $\text{CH}_2$ ; 2 =  $\text{CF}_2$ ; 3 =  $\text{CFCl}$ .

of eq 3: (1) The number of CTFE–CTFE–CTFE sequences is low compared to the number of CTFE–CTFE– $\text{VF}_2$  type sequences. (2) Thermodynamically unfavorable additions of  $\text{VF}_2$  and CTFE units need not be taken into account. (3) Head to head additions occur to the same extent in all copolymers. These assumptions are reasonable for this copolymer because, as shown in Table 1, the  $\text{VF}_2$  component is much larger than the CTFE component. The values determined from solid-state NMR using eq 3 are 68.7/31.3 mol %  $\text{VF}_2$ /CTFE monomer units in the copolymer. These values compare favorably to the monomer feed ratios 69.0/31.0 and the solution-state NMR values 67.2/32.7 mol %  $\text{VF}_2$ /CTFE, respectively, as shown in Table 8.

**Copolymer D.** Copolymer D is made from monomer feed ratios consisting of 24.3/75.7 mol %  $\text{VF}_2$ /CTFE monomer units. The spectrum of copolymer D is presented in Figure 6 with peak assignments given in Table 5. Assignments are based on solution-state NMR studies of similar compounds.<sup>7–10</sup> The high concentration of CTFE results in additional peaks in the spectrum compared to the spectra of previous polymers because of meso or racemic stereochemistry. We used definitions



**Figure 6.** VT MAS  $^{19}\text{F}$  NMR spectrum of fluoropolymer copolymer D, composed of 24.3%  $\text{VF}_2$  and 75.7% CTFE (mole percent). The spectrum was acquired with 64 transients, 21 kHz MAS, 250  $^\circ\text{C}$ , and 3072 data points. Assignment of the resonances is given in Table 5.

**Table 5.** Chemical Shifts of Copolymer D

spectral range corresponding to area $S_n^a$	chemical shift (ppm)	fragment <sup>b</sup>	integrated area	
$S_1$	−86.6 −88.0 −89.4	20 <u>2</u> 02	100.7	
$S_2$	−101.2 −102.3	23 <u>2</u> 32 meso	5561.4	
$S_3$	−106.1 −107.8 −108.4 −109.0 −109.9	23 <u>2</u> 32 racemic		
$S_4$	113.0 −114.5 −115.8 −117.7	02 <u>2</u> 00 02 <u>2</u> 32 02 <u>2</u> 30		1619.2
$S_5$	−118.4 −120.6 −124.6 −124.9 −125.2 −125.4 −126.1 −127.0 −127.9 −128.6 −129.4 −133.5 −134.2	02 <u>3</u> 02 22 <u>3</u> 02 32 <u>3</u> 23 racemic–racemic 32 <u>3</u> 23 meso–racemic 32 <u>3</u> 23 meso–meso 02 <u>3</u> 20		2736.4

<sup>a</sup> Figure 6. <sup>b</sup> 0 =  $\text{CH}_2$ ; 2 =  $\text{CF}_2$ ; 3 =  $\text{CFCl}$ .

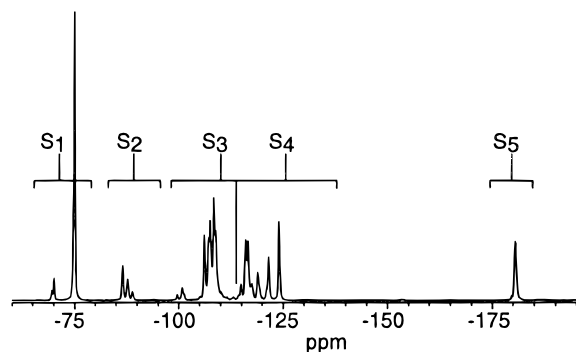
of meso and racemic as defined by Cais<sup>9</sup> and by Bovey<sup>10</sup> for similar systems. On the basis of assignments of similar systems in the literature, it was found that resonances below -118.0 ppm are due to  $\text{CFCl}$ . As a result we determined the number of CTFE units ( $N_{\text{CTFE}}$ ) by using eq 4.

$$N_{\text{CTFE}} = S_5 \quad (4)$$

$S_5$  is the integrated area due to the  $\text{CFCl}$ . To determine the amount of  $\text{VF}_2$  the difference was taken from the  $\text{CF}_2$  region as described in eq 5

$$N_{\text{VF}_2} = 1/2(S_1 + S_2 + S_3 + S_4) - N_{\text{CTFE}} \quad (5)$$

Using these equations we obtained values of 24.8/75.2



**Figure 7.** VT MAS  $^{19}\text{F}$  NMR spectrum of fluoropolymer terpolymer A, composed of 50.5%  $\text{VF}_2$ , 26.7% HFP, and 22.8% TFE (mole percent). The spectrum was acquired with 64 transients, 22 kHz MAS, 250  $^\circ\text{C}$ , and 3072 data points. Assignment of the resonances is given in Table 6.

mol %  $\text{VF}_2/\text{CTFE}$ , respectively. These values, as determined from solid-state NMR, compare favorably to the monomer feed ratio 24.3/75.7 and solution-state NMR results 25.0/75.0 mol %  $\text{VF}_2/\text{CTFE}$ , respectively, as shown in Table 8.

**Terpolymer A.** In Figure 7 the 22 kHz and 250  $^\circ\text{C}$   $^{19}\text{F}$  MAS NMR spectrum of the sample terpolymer A acquired with 64 transients and 3072 data points is shown. Terpolymer A is produced with the typical monomer feed ratios 50.5/26.7/22.8 mol %  $\text{VF}_2/\text{HFP}/\text{TFE}$ , respectively. Structural assignments were based on solution-state studies and are presented in Table 6.<sup>3,5</sup> The monomer composition of this terpolymer is normally calculated by solution-state NMR using  $\text{CF}$  ( $\sim -180$  ppm) and  $\text{CF}_3$  ( $\sim -75$  ppm) resonances of HFP to give the composition of that monomer. The  $\text{CF}_2$  ( $-85$  to  $-135$  ppm) region contains components of all monomers. Assuming that the HFP is the only source of  $\text{CF}_3$  and  $\text{CF}$  groups, which have unique resonances under areas  $S_1$  and  $S_5$ , respectively,  $N_{\text{HFP}}$  can be calculated using

$$N_{\text{HFP}} = \frac{1}{3}(S_1) \quad (6a)$$

$$N_{\text{HFP}} = S_5 \quad (6b)$$

The results were averaged to minimize error in integration of these regions. The  $\text{CF}_2$  region ( $-85$  to  $-135$  ppm) contains resonances due to all monomers. Distinct regions can be labeled as a particular three-carbon sequence. For example,  $S_2$  is 020 where 0 =  $\text{CH}_2$  and 2 =  $\text{CF}_2$ , which can only be caused by two neighboring vinylidene fluoride units. There are several resonances that can result from the combination of more than one pair of monomer units. For example, a 022 resonance could result from a combination of either  $\text{VF}_2$  and TFE or  $\text{VF}_2$  and HFP. From the monomer ratios it was apparent that the concentration of TFE was less than that of  $\text{VF}_2$ ; we therefore assumed that the majority of the TFE concentration is in the 224 and 222 three-carbon sequence regions under  $S_4$ . Using eq 7 we obtained the number of TFE units ( $N_{\text{TFE}}$ ).

$$N_{\text{TFE}} = \frac{1}{2}(S_4) - N_{\text{HFP}} \quad (7)$$

The number of  $\text{VF}_2$  monomers was determined by eq 8

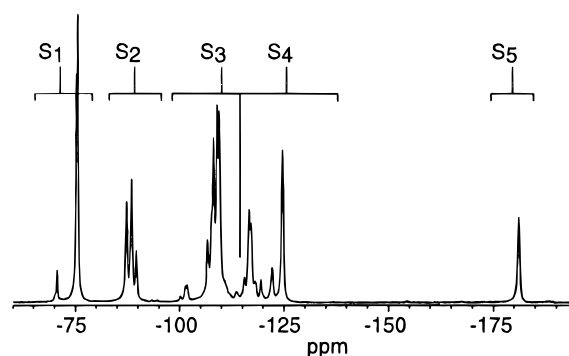
$$N_{\text{VF}_2} = \frac{1}{2}(S_2 + S_3 + S_4) - N_{\text{HFP}} - 2N_{\text{TFE}} \quad (8)$$

where the  $\text{CF}_2$  region of the spectrum is  $S_2 + S_3 + S_4$ .

**Table 6. Chemical Shifts of Terpolymer A**

spectral range corresponding to area $S_n^a$	chemical shift (ppm)	fragment <sup>b</sup>	integrated area
$S_1$	-70.1	02420	2247.5
	-70.7		
	-75.3	22402	
	-75.6		
	-75.6		
$S_2$	-87.1	20202	620.9
	-88.3		
	-89.4		
	-93.1	20200	
	-94.4		
$S_3$	-100.1	04202	3586.2
	-101.3	20242	
	-102.9		
	-105.6	40224	
	-106.6		
	-107.6	20224	
	-108.0		
	-108.9	22202	
	-109.3		
	-109.9		
$S_4$	-110.7	20220	2879.8
	-112.1		
	-113.6	02200	
	-114.8		
	-115.4 to -118.1	224	
	-119.4	22222	
	-119.8		
$S_5$	-121.5	02222	699.9
	-122.0		
	-124.5	02220	
	-180.9	042	
	-180.9	242	

<sup>a</sup> Figure 7. <sup>b</sup> 0 =  $\text{CH}_2$ ; 2 =  $\text{CF}_2$ ; 4 =  $\text{CFCF}_3$ .



**Figure 8.** VT MAS  $^{19}\text{F}$  NMR spectrum of fluoropolymer terpolymer B, composed of 61.1%  $\text{VF}_2$ , 18.0% HFP, and 20.9% TFE (mole percent). The spectrum was acquired with 64 transients, 22 kHz MAS, 250  $^\circ\text{C}$ , and 3072 data points. Assignment of the resonances is given in Table 7.

The  $N_{\text{TFE}}$  value has to be doubled in eq 8 because it has two  $\text{CF}_2$  groups for each monomer, whereas HFP and  $\text{VF}_2$  only have one. Using these equations we obtained values of 49.1/25.6/25.3 mol %  $\text{VF}_2/\text{HFP}/\text{TFE}$ , respectively. This compares favorably to the typical monomer feeds 50.5/26.6/22.8 and solution-state NMR results 52.6/25.9/21.5 mol %  $\text{VF}_2/\text{HFP}/\text{TFE}$  as reported in Table 8.

**Terpolymer B.** In Figure 8 the  $^{19}\text{F}$  MAS NMR spectrum of the sample terpolymer B is shown. Ter-

Table 7. Chemical Shifts of Terpolymer B

spectral range corresponding to area $S_n^a$	chemical shift (ppm)	fragment <sup>b</sup>	integrated area
$S_1$	-70.1	02420	1803.6
	-70.6		
	-75.3	22402	
	-75.6		
$S_2$	-87.2	20202	1532.5
	-88.4		
	-89.6		
	-93.2	20200	
	-94.5		
$S_3$	-100.0	04202	3739.3
	-101.3	20242	
	-101.7		
	-106.6	40224	
	-107.5	20224	
	-108.8	22202	
	-109.4		
	-110.6	20220	
	-111.1		
	-113.5	02200	
$S_4$	-115.4	224	2401.1
	-116.5		
	-117.0		
	-118.0		
	-119.3	22222	
	-122.0	02222	
$S_5$	-124.5	02220	550.9
	-180.9	042	
		242	

<sup>a</sup> Figure 8. <sup>b</sup> 0 = CH<sub>2</sub>; 2 = CF<sub>2</sub>; 4 = CF<sub>2</sub>CF<sub>3</sub>.

polymer B, according to typical monomer feed ratios, is a terpolymer of 61.1/18.0/20.9 mol % VF<sub>2</sub>/HFP/TFE. Structural assignments were based on solution-state studies and are presented in Table 7. Calculations similar to that of terpolymer A were used to determine monomer composition. These calculations gave values of 62.6/17.9/19.5 mol % VF<sub>2</sub>/HFP/TFE, respectively. This compares favorably to the typical monomer feeds 61.1/18.0/20.9 and solution-state NMR results 62.0/18.9/19.1 mol % VF<sub>2</sub>/HFP/TFE as reported in Table 8.

## Discussion

**Assignment of <sup>19</sup>F Peaks.** For all the polymers studied the assignments of peaks were based primarily on previously published work. In some cases higher resolution was obtained than that for the solution-state NMR spectra found in the literature. There are two potential explanations for our improved spectral resolution. One is that many of the reported spectra were acquired using low-field ( $\leq 2.35$  T) NMR spectrometers and that at 7.05 T our resolution is significantly improved. The second explanation is that even when fluoropolymers can be dissolved, there may still be limited mobility. In this case, <sup>19</sup>F–<sup>19</sup>F dipolar couplings may not be totally averaged, resulting in line broadening. Because of the poorer resolution in solution, the assignment of some of the peaks was based on observed trends rather than on literature assignments.

For copolymer D, assignments were difficult because of the high concentration of CTFE. The CTFE monomer has a chiral center after polymerization. The chirality

Table 8. Polymer Composition Determined by Monomer Feed Ratio, Solution NMR, and Solid-State NMR

polymer	monomer feed <sup>a</sup>	solution-state NMR ( $\pm 0.1\%$ ) <sup>b</sup>	solid-state NMR ( $\pm 0.3\%$ )
copolymer A	78.8% VF <sub>2</sub>	78.1% VF <sub>2</sub>	78.7% VF <sub>2</sub>
	21.2% HFP	21.9% HFP	21.3% HFP
copolymer B	78.8% VF <sub>2</sub>	77.9% VF <sub>2</sub>	79.3% VF <sub>2</sub>
	21.2% HFP	22.1% HFP	20.7% HFP
copolymer C	69.0% VF <sub>2</sub>	67.3% VF <sub>2</sub>	68.7% VF <sub>2</sub>
	31.0% CTFE	32.7% CTFE	31.3% CTFE
copolymer D	24.3% VF <sub>2</sub>	25.0% VF <sub>2</sub>	24.8% VF <sub>2</sub>
	75.7% CTFE	75.0% CTFE	75.2% CTFE
terpolymer A	50.5% VF <sub>2</sub>	52.6% VF <sub>2</sub>	49.1% VF <sub>2</sub>
	26.7% HFP	25.9% HFP	25.6% HFP
	22.8% TFE	21.5% TFE	25.3% TFE
terpolymer B	61.1% VF <sub>2</sub>	62.0% VF <sub>2</sub>	62.6% VF <sub>2</sub>
	18.0% HFP	18.9% HFP	17.9% HFP
	20.9% TFE	19.1% TFE	19.5% TFE

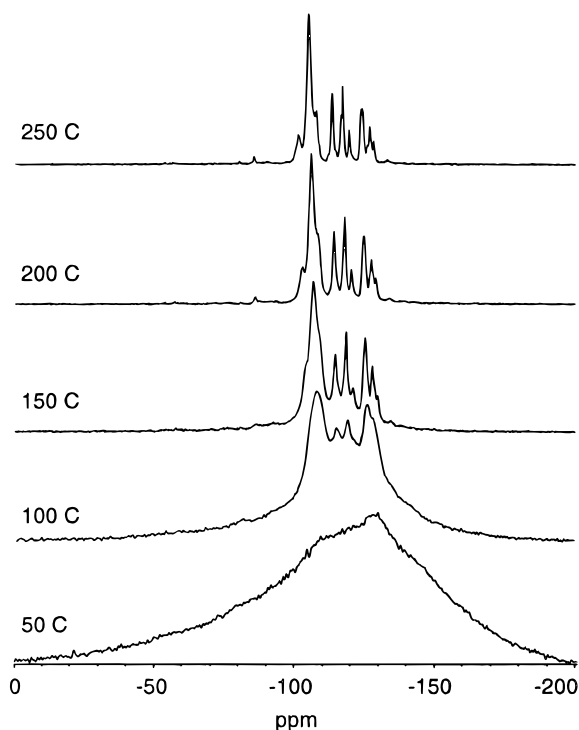
<sup>a</sup> The monomer composition of each polymer is given in mole percent. <sup>b</sup> Solution-state results supplied by Dyneon LLC (<sup>1</sup>H/<sup>19</sup>F).<sup>23</sup>

can be observed in NMR through geminal fluorine–fluorine spin–spin coupling of roughly 300 Hz, making assignment of peaks difficult. The CF<sub>2</sub> groups not surrounded by the chiral centers CFCl were mainly due to VF<sub>2</sub>, but CH<sub>2</sub>–CFCl–CF<sub>2</sub> (032) type sequences are also found in this region. We based our assignment of these peaks on VF<sub>2</sub>/CTFE copolymer studies by Murasheva<sup>7</sup> and CTFE homopolymer studies by Cais<sup>9</sup> and Bovey.<sup>10</sup>

The terpolymers of VF<sub>2</sub>/HFP/TFE were difficult to assign due to many peaks which overlap in the CF<sub>2</sub> region. All three monomers have CF<sub>2</sub> groups. Sequences such as CH<sub>2</sub>–CF<sub>2</sub>–CF<sub>2</sub> (022), CF<sub>2</sub>–CF<sub>2</sub>–CF<sub>2</sub>CF<sub>3</sub> (224), and CH<sub>2</sub>–CF<sub>2</sub>–CF<sub>2</sub>CF<sub>3</sub> (024) contain two different monomers. We made an assumption that the central CF<sub>2</sub> in CH<sub>2</sub>–CF<sub>2</sub>–CF<sub>2</sub> (022) peaks and in CH<sub>2</sub>–CF<sub>2</sub>–CF<sub>2</sub>CF<sub>3</sub> (024) peaks was due exclusively to VF<sub>2</sub>. In the future we would like to incorporate a <sup>1</sup>H/<sup>19</sup>F cross integration standard into this system, as is done in solution NMR studies to determine the amount of VF<sub>2</sub> through <sup>1</sup>H NMR. Quantifying the amount of VF<sub>2</sub> using cross integration would allow the monomer ratios to be determined without making assumptions about the source of CF<sub>2</sub> in the central monomer unit.

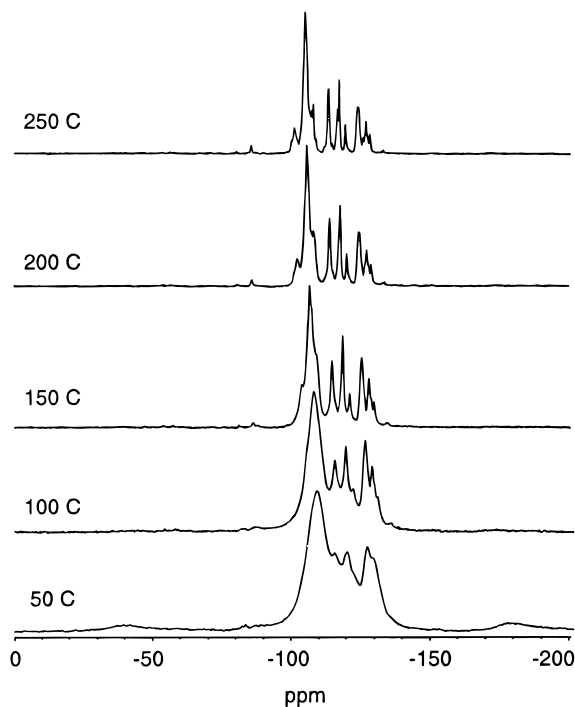
**Effect of MAS on Motionally-Averaged Fluoropolymers.** At room temperature all of the polymers studied here are well above their *T*<sub>g</sub> values, and there is considerable molecular motion present. The use of MAS to narrow lines in motionally-averaged fluoropolymers is well-known. One of the earliest examples of MAS in motionally-averaged systems is a <sup>19</sup>F NMR study of polytetrafluoroethylene (PTFE).<sup>24</sup> The line width at room temperature of PTFE is already narrowed to about 30% of its line width in the absence of molecular motion, and a significant increase in resolution is possible with MAS. Andrew and co-workers have discussed the effect of magic-angle spinning on the spectra of samples that have been substantially narrowed by molecular motion.<sup>25</sup> They determined that MAS can result in narrow lines, provided that the molecular motion is due to rapid but restricted molecular motion, as would be anticipated for a polymer. This was demonstrated by Benoit and Rabii, who showed that the <sup>19</sup>F NMR spectrum of a viscous solution of a vinylidene fluoride/hexafluoropropylene copolymer in ethyl acetate could be narrowed using MAS.<sup>26</sup>





**Figure 9.** VT  $^{19}\text{F}$  NMR spectra at 4 kHz MAS of copolymer D, composed of 24.3% CTFE and 75.7 mole percent  $\text{VF}_2$ . Each spectrum was acquired with 64 transients and 3072 data points.

**Effect of Temperature and Spinning Speed on Resolution.** Although all of the spectra in this paper were acquired with both high-speed MAS and high temperatures, for some of the polymers equivalent resolution could have been obtained by using slower MAS rates and/or lower temperatures. We performed an experiment to evaluate the effect of averaging by molecular motion compared to averaging by MAS. Figure 9 shows the  $^{19}\text{F}$  MAS NMR spectra of copolymer D spinning at 4 kHz and various indicated temperatures between 50 and 250  $^{\circ}\text{C}$ , and Figure 10 shows spectra of the same sample acquired under identical conditions except spinning at 19 kHz. The actual temperature of the sample spinning at 19 kHz is probably 20  $^{\circ}\text{C}$  higher than the indicated temperature. At 50  $^{\circ}\text{C}$ , the difference in resolution between the spectra acquired at 4 and 19 kHz is dramatic. As the temperature is increased, the faster spinning speed results in comparatively less improvement in resolution. A comparison of the spectra in Figures 9 and 10 shows that equivalent resolution is observed if the spectrum acquired at 19 kHz is compared to the spectrum acquired at 4 kHz and a 50  $^{\circ}\text{C}$  higher temperature. For example, the spectrum acquired at 19 kHz and 150  $^{\circ}\text{C}$  is roughly equivalent to the spectrum acquired at 4 kHz and 200  $^{\circ}\text{C}$ . Once a minimum line width is reached, the resolution does not improve, even with faster spinning speeds. The resolution of the spectra for terpolymer D obtained at 250  $^{\circ}\text{C}$  and MAS rates of 4 and 18 kHz is essentially the same (spectra not shown). This is not surprising, as the line width difference between the spectra at 150 and 250  $^{\circ}\text{C}$  in Figure 2 is very small. From this study we can evaluate the relative advantages and disadvantages of using high-speed MAS coupled with high temperatures. For many samples it may be more desirable to increase the sample temperature compared to increasing spinning speed. The primary advantage is that a higher signal-



**Figure 10.** VT  $^{19}\text{F}$  NMR spectra at 19 kHz MAS of copolymer D, composed of 24.3% CTFE and 75.7 mole percent  $\text{VF}_2$ . Each spectrum was acquired with 64 transients and 3072 data points.

to-noise ratio can be obtained if a larger sample volume can be used. Also, this permits the analysis of fluoropolymers using MAS probes that spin significantly slower than 25 kHz. This method would be particularly useful for analyzing samples that contain small amounts of fluoropolymers as additives. The disadvantage of using slower MAS rates is that the indicated sample temperature must be 50  $^{\circ}\text{C}$  higher. For some samples heating an additional 50  $^{\circ}\text{C}$  may not be possible, or the probe conditions may restrict the available temperature range. The use of higher spinning speeds will be most critical when broad lines are obtained even at high temperatures because the molecular motion of the polymer is restricted.

## Conclusion

The combination of high MAS rates and high temperature enables solid-state  $^{19}\text{F}$  NMR spectra of comparable resolution to that of solution-state  $^{19}\text{F}$  NMR spectra to be obtained. The results of the quantitative analysis of fluoropolymers studied by solid-state NMR were nearly equivalent to the results obtained for the same compounds studied by solution-state  $^{19}\text{F}$  NMR. In this paper we have demonstrated that VT high-speed MAS  $^{19}\text{F}$  NMR is a valuable technique for routine qualitative and accurate quantitative analysis of fluoropolymer materials which cannot be easily analyzed by other methods. We anticipate that this technique can easily be expanded for the qualitative and quantitative analyses of intractable fluoropolymer materials and other intractable matrixes which contain fluoropolymers as minor components. Some of the materials that may be amenable to study using this technique include the following: (1) perfluorinated elastomers and plastics, (2) unfilled but cross-linked hydrogen-containing fluoropolymers, (3) cured fluoropolymer end-use production parts (e.g., O-rings, gaskets, seals, tubes, hoses, etc.)



that are filled with carbon black and/or other inorganic fillers, (4) hydrogen-containing fluorinated elastomers and plastics, and (5) low-level fluoropolymer materials entrained in intractable hydrocarbon polymer matrixes.

**Acknowledgment.** The authors thank the Dyneon LLC for funds used to purchase the  $^{19}\text{F}/^1\text{H}$  probe. We also thank Dr. Allan T. Worm of Dyneon LLC and Dr. Khalid Thakur of Cargill for helpful comments.

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MA980745D