High-Resolution Variable-Temperature MAS ^{19}F NMR Spectroscopy of Fluorocarbon Polymers

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A valuable tool for the analysis of the structure of fluorocarbon polymers is ^{19}F NMR spectroscopy.[1,2] In ^{19}F NMR, neighbors of a particular fluorine nucleus can have a measurable effect on chemical shift. As a result, the type and quantity of monomer sequences can be determined in a fluorocarbon polymer.[2−4] Solution-state ^{19}F NMR spectroscopy is used quite extensively for the routine analysis of fluoropolymers, but insoluble or intractable polymers require their analysis in the solid state.

Solid-state ^{19}F NMR of fluorocarbon polymers is extremely difficult due to the strong homonuclear ^{19}F−^{19}F dipolar coupling interactions, which result in broad featureless spectra. The dipolar coupling interaction can be further complicated by ^{19}F−^{1}H dipolar interactions and ^{19}F chemical shift anisotropy (CSA). Typically, the static line width for ^{19}F in fluorinated polymeric materials is greater than 10 kHz.[5−9] Three approaches have been taken in the past to try and obtain high-resolution ^{19}F NMR spectra. One 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). The sample must be spun at a rate faster than the dipolar-broadened line width in order to obtain high-resolution ^{19}F NMR spectra. Maciel and co-workers obtained solid-state ^{19}F NMR spectra of fluoropolymers by magic-angle spinning at rates of >19 kHz.[5] Another approach is to average the static line broadening interaction in ^{19}F NMR using combined rotation and multiple pulse spectroscopy (CRAMPS).[10−12] CRAMPS is not as useful for nuclei such as ^{19}F with large CSAs, as the rotation rate is limited to <4 kHz. At these spinning speeds there would be considerable overlap of the isotropic and rotational sidebands at moderate magnetic fields. As a result, most researchers studying fluoropolymers in the solid state have generally stayed away from this technique.[9] The third technique is to heat the samples to very high temperatures (>300 °C) and acquire the spectra static, with no spinning.[13] The reported resolution for this technique appears to be comparable to that reported by Maciel.[5]

We have taken the approach of combining very high speed magic-angle spinning in conjunction with high temperatures to obtain dramatically improved resolution compared to any previous solid-state ^{19}F NMR study of fluoropolymers. By using MAS rates >25 kHz combined with temperatures >150 °C, spectra of a typical dimonomeric fluoropolymer, Kel-F 3700, were obtained with resolution superior to some previously reported *solution-state* spectra of a comparable Kel-F system.[2−4] This technique has the potential to revolutionize ^{19}F NMR fluoropolymer analysis in the solid state.

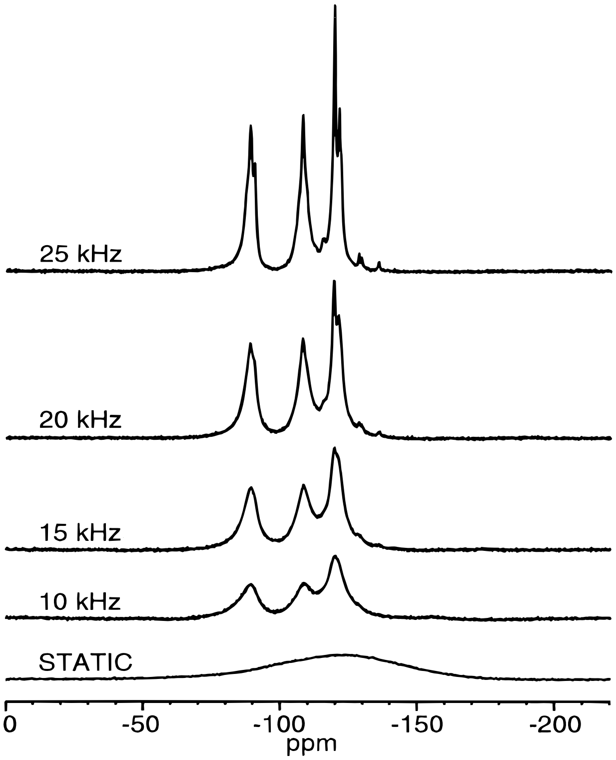

Figure 1. Variable MAS speed ^{19}F NMR spectra of Kel-F 3700. Each spectrum was acquired at room temperature (25 °C) with 64 acquisitions. The static spectrum was processed with 512 data points, while 2048 points were used for all others.

The Kel-F sample was obtained from 3M Specialty Adhesives and Chemicals Division. The nominal composition was based on anticipated monomer feed ratios of 69.0/31.0 mol % of vinylidene fluoride (VF_2) and chlorotrifluoroethylene (ClF_3E) monomer units, designated as Kel-F 3700. The glass transition of the sample was −15 °C. The sample was liquid nitrogen ground into a powder. No further preparation was performed on the sample.

All NMR spectra were acquired using a Chemagnetics CMX 300 MHz spectrometer operating at 282.2 MHz for ^{19}F. Single pulse excitation ($\pi/2 = 2\ \mu$s) without ^{1}H decoupling or background suppression techniques was used. Samples were spun at the magic angle at rates between 0 and 25 kHz and at temperatures between 20 and 150 °C with moisture free air for the drive, bearing, and VT gases. A Chemagnetics double-resonance ^{1}H/^{19}F probe with a Vespel spinning module housing, 3.2 mm (16.2 mm^3 sample size) zirconia rotor, and Vespel endcaps and drive tip were used. Depending on sample conditions, between 512 and 5120 data points were acquired with a spectral width of 150 kHz, corresponding to acquisition times of 3.4 and 34 ms, respectively. A total of 64 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 poly(tetrafluoroethylene) (Teflon), which was assigned a chemical shift of −122 ppm. Five-carbon sequences were assigned to particular resonances on the basis of solution-state studies of similar compounds.[2−4]

Figure 1 shows solid-state ^{19}F MAS NMR spectra of Kel-F 3700 at 25 °C and multiple spinning speeds. The static spectrum was processed with only 512 data points and gives a single broad featureless peak, with the

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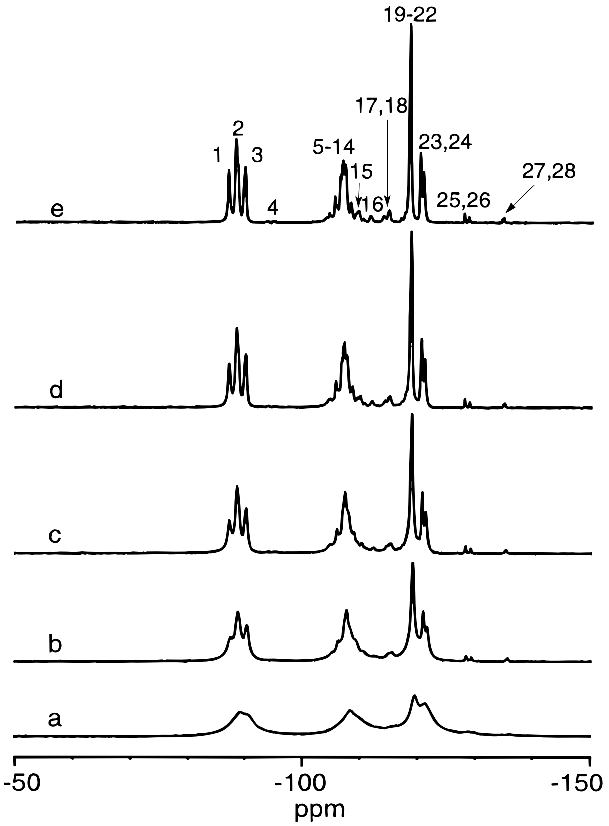

Figure 2. Variable-temperature ^{19}F NMR spectra of Kel-F 3700. Each spectrum was obtained with 64 acquisitions at spinning speeds of 23 kHz: (a) 25 °C and 3072 data points; (b) 75 °C and 3072 points; (c) 100 °C and 4096 points; (d) 125 °C and 4096 points; (e) 150 °C with 5120 points. Assignment of the resonances is presented in Table 1.

Table 1. Chemical Shifts of Kel-F 3700

spectral range corresponding to area S_n	line[a]	chemical shift (ppm)	fragment[b]	integrated area
S_1	1	−86.6	2 0 2 0 2	
	2	−88.0	3 0 2 0 2	818.7
	3	−89.4	3 0 2 0 3	
	4	−94.0	2 0 2 0 0	
S_2	5−14	−103.6, −109.3	2 0 2 2 3	827.8
	15	−110.1	2 3 2 3 0	
S_3	16	−111.3	2 0 2 2 0	28.7
S_4	17	−113.6	0 2 2 0 0	81.2
	18	−114.5	0 2 2 3 2	
S_5	19−22	−116.7, −118.2	0 2 2 3 0	1000
	23, 24	−120.0, −120.6	2 2 3 0 2	
S_6	25, 26	−127.7, −128.4	0 3 2	34.6
	27, 28	−134.2, −134.5	0 2 3 2 0	

[a] Figure 2. [b] 0 = $-CH_2-$; 2 = $-CF_2-$; 3 = $-CFCl-$.

broadening due primarily to homonuclear $^{19}F-^{19}F$ dipolar interactions and shielding anisotropies. When the MAS rate was increased to 10 kHz, three regions become apparent as the dipolar interactions are partially averaged. At 20 kHz the resolution is similar to the best resolution observed by Maciel *et al.* for a similar sample of Kel-F 3700.[5] At 25 kHz the resolution reported is significantly better than was observed at 20 kHz.

Figure 2 shows the dramatic improvement in resolution possible when the temperature is increased for the same sample of Kel-F 3700 while spinning at 23 kHz. This increase in resolution is caused by molecular motion further averaging the dipolar interactions. Table 1 shows the five-carbon sequences for each resonance for the spectrum at 150 °C in Figure 2. The assignments of the peaks are based on solution-state NMR studies.[3] Murasheva *et al.* developed a method for determining the ratio of vinylidene fluoride to chlorotrifluoroethylene from the relative intensities of the S_1-S_6 sets of resonances.[4] They were able to derive a relationship between vinylidene fluoride $P(VF_2)$ and chlorotrifluoroethylene $P(ClF_3E)$.

$$\frac{P(\mathrm{VF_2})}{P(\mathrm{ClF_2E})} = \frac{S_1 + S_2 + 3S_3 - S_4}{S_5 + S_6 + 3(S_4 - S_3)}\,\frac{3}{2}$$

The integrated area of these sets could be measured easily and accurately from the solid-state spectrum. Applying this technique to our solid-state NMR results of Kel-F 3700, we obtain a ratio of $PVF_2/PClF_3E$ of 68.6/31.4 mol %. The corresponding ratios determined from solution-state NMR are 67.2/32.8 mol %. The target ratio for the monomer feed ratios is 69.0/31.0 mol %. It is obvious that the solid-state NMR results are very close to both the solution state results and the anticipated monomer feed ratios. It should be noted that the ratio of 75/25 mol % provided to Maciel and co-workers by 3M for the composition of Kel-F 3700 was incorrect and should have been the same value as reported here. This actually increases the accuracy of the number reported by Maciel.

We have shown that a combination of high MAS rates and high temperature results in solid-state ^{19}F NMR spectra of comparable resolution to solution-state ^{19}F NMR spectra. This appears to be a promising technique for routine qualitative and accurate quantitative analysis of intractable fluoropolymer materials which cannot be easily analyzed by other methods. Although not presented here, we have also obtained spectra of intractable polymers that show resolution comparable to that reported here.

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