

## Variable Temperature High-Resolution $^{19}\text{F}$ MAS Solid-State NMR Characterization of Fluorocarbon Rubbers

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Received April 18, 2011, Accepted May 29, 2011

Variable temperature high-resolution  $^{19}\text{F}$  magic angle spinning (MAS) solid-state NMR spectroscopy was used to characterize fluorocarbon (FKM) rubbers. The high-resolution spectra of copolymers made from two monomers, vinylidene fluoride and hexafluoropropene, and terpolymers composed of vinylidene fluoride, hexafluoropropene, and tetrafluoroethylene, were obtained using MAS speeds of up to 18 kHz combined with high temperatures of up to 200 °C at a magnetic field strength of 9.4 Tesla. From these high resolution solid-state NMR spectra, we were able to assign the spectral peaks and differentiate the copolymer FKM from the terpolymer FKM. We also determined quantitatively the monomer compositions of each FKM rubber.

**Key Words** : Fluorocarbon rubber,  $^{19}\text{F}$  NMR, Solid-state NMR

### Introduction

FKM is a representative fluorocarbon-based synthetic rubber. FKM rubber has excellent long-term swell resistance even in harsh environments, for example those involving high temperatures, ozone, acids, bases, mineral oil, fuels, hydraulic fluids, aromatics and many organic solvents and chemicals. Since FKM rubber was introduced in the late 1950's to meet the requirements of the aerospace industry for a high performance elastomer, it has been widely used as a universal sealing material in many other industries, including the automotive, chemical processing, oil and gas, and power generation industries, although its cost is higher than that of other elastomers. All FKM rubbers contain vinylidene fluoride (VF) as the monomer and they are not a single entity, but a family of fluoropolymer rubbers. FKM rubbers can be classified by their fluorine content of between 66 and 70 percent. In general, FKM rubbers having higher fluorine content have a higher fluid resistance derived from their increased fluorine level. On the basis of their chemical composition, FKM rubbers can be largely divided into two types, *viz.* copolymers and terpolymers. The standard type of FKM is a copolymer made from the two monomers, VF and hexafluoropropylene (HFP). Their fluorine content is typically around 66 weight percent and they are the most widely used FKM rubbers, showing good overall performance. The terpolymers are composed of VF, HFP, and tetrafluoroethylene (TFE). TFE is added to increase the fluorine content of the polymer to between 68 and 69 weight percent, which results in its having better chemical and heat resistance than that of the copolymers, but negatively affects the compression set and low temperature flexibility. In industry, it is very important to select the correct material for a particular application and it is also necessary to check the type and quantity of the monomer sequences in order to ensure quality control and cost saving.

The  $^{19}\text{F}$  nucleus has a natural abundance of 100 percent and a high gyromagnetic ratio, so that  $^{19}\text{F}$  NMR provides excellent detectable sensitivity. Also, having a large chemical shift range of ~400 ppm,  $^{19}\text{F}$  NMR spectroscopy is attractive in polymer studies.  $^{19}\text{F}$  NMR studies related to the determination of the type and quantity of the monomer sequences in fluoropolymers have been previously described.<sup>1-5</sup> High resolution  $^{19}\text{F}$  NMR analysis of fluoropolymers has been typically limited to solution-state NMR spectroscopy and has often involved low molecular weight polymers.<sup>6,7</sup> However, most fluoropolymers are insoluble. To obtain the spectra of insoluble polymers, such as these fluoropolymers, or to analyze their polymeric states, which are present only in the solid-state, it is necessary to employ solid-state NMR spectroscopy.

High resolution  $^{19}\text{F}$  solid-state NMR spectroscopy is a valuable tool for the analysis of the structure and dynamics of fluoropolymers.<sup>8,9</sup> However, conventional  $^{19}\text{F}$  solid-state NMR often fails to obtain useful information about the structure of fluoropolymers, due to two predominant factors, the strong homonuclear  $^{19}\text{F}$ - $^{19}\text{F}$  dipolar coupling interactions and large chemical shift anisotropies (CSA), which result in a broad and featureless spectrum. There are two effective approaches to obtain high resolution  $^{19}\text{F}$  NMR spectra. One approach is the high speed magic-angle sample spinning (MAS) method, which is achieved by spinning the sample at the magic angle of 54.74 degrees with respect to the direction of the magnetic field. The strong homonuclear dipole-dipole interaction and CSA of fluorinated polymeric solids can be effectively averaged by MAS techniques, and the broadening is substantially reduced.<sup>9,10</sup> If the spinning rate is larger than the frequency range of the orientation dependent line shape, a single narrow line at the isotropic value will result. Therefore, the rate of sample spinning must be fast in comparison to the anisotropy of the interaction being spun out. Typically, the CSA of  $^{19}\text{F}$  in fluoropolymers

is greater than 10 kHz.<sup>11–13</sup> It has been recently reported that high-speed magic-angle spinning facilitates the measurement of high resolution solid-state  $^{19}\text{F}$  NMR spectra for partially fluorinated and perfluorinated polymers.<sup>14–17</sup> The other approach is to perform a variable temperature (VT) NMR experiment. VT NMR can be carried out to evaluate the thermal behavior of the polymer in the solid state with increasing temperature. The increased molecular motion at high temperature results in peak sharpening and changes in the chemical shifts. However, it sometimes results in the degradation of the sample at very high temperature.<sup>9</sup>

In this paper, we report the high resolution solid-state  $^{19}\text{F}$  MAS NMR investigations of FKM rubbers with gradually increasing temperature. From the experiments using high speed MAS at up to 18 kHz and variable temperatures of up to 200 °C at a field strength of 9.4 Tesla, we obtained the high resolution spectra of copolymers made from the two monomers, VF and HFP, and terpolymers composed of VF, HFP, and TFE. Also, we demonstrate the results of the qualitative and quantitative analysis of these FKM rubbers. Finally, we determined the type and quantity of the monomer compositions of an unknown innate sample used in the automobile industry, which cannot easily be obtained by any other analytical method.

## Experimental

**Sample Preparation.** The samples used for the investigation were three kinds of FKM rubbers, *viz.* copolymer, terpolymer, and FKM rubbers containing an unknown sample available in the automobile industry. The copolymers were made from the two monomers, VF and HFP, and the terpolymers from VF, HFP, and TFE. All of the samples were supplied by the research and development division of Hyundai-Kia motors corporation. All samples were used without further preparation.

**$^{19}\text{F}$  Solid-state NMR Spectroscopy.** The solid-state  $^{19}\text{F}$  NMR spectra were obtained using a unity/INOVA wide-bore NMR spectrometer (Varian, USA) with a magnetic field of 9.4 Tesla operating at a  $^{19}\text{F}$  Larmor frequency of 376.24 MHz. The  $^{19}\text{F}$  NMR experiments were carried out using a 4 mm triple resonance CP/MAS probe (T3 probe Varian, USA) with pencil-type spinning module housing. All of the samples were cut into fine pieces and packed in a 4.0 mm  $\Phi$  (52  $\mu\text{L}$  sample volume) zirconium oxide rotor with Vespel end cap and drive tip. All of the spectra were recorded using a single pulse excitation without decoupling. Duration of 2.9  $\mu\text{s}$  was used for the  $\pi/2$  pulse and 4 scans were acquired with a recycle delay of 5 s. The samples were spun at the magic angle at spinning frequencies of between 0 and 18 kHz and temperatures between 25 and 200 °C using moisture free air for the drive, bearing, and VT gases. The magic angle was adjusted using the  $^{79}\text{Br}$  resonance of KBr, and the actual sample temperatures were determined using the  $^{207}\text{Pb}$  resonance of  $\text{Pb}(\text{NO}_3)_2$  for calibration.<sup>18,19</sup> Depending on the experimental spinning rate and temperature, the number of acquisition data points was varied between 128 and 5120,

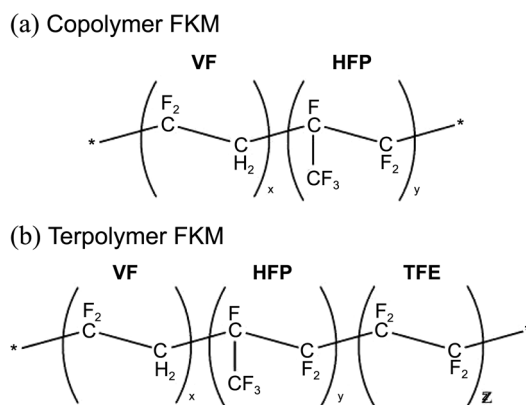
corresponding to acquisition times of between 0.85 and 34.11 ms, respectively. The  $^{19}\text{F}$  chemical shifts were referenced to polytetrafluoroethylene (PTFE), which was assigned a chemical shift of -121 ppm. All of the spectra were acquired and processed by a VNMRJ 2.1B (Varian, US). The assignments, integrations, and comparisons of all of the spectra were carried out using Topspin 2.1 (Bruker, Germany).

## Results and Discussion

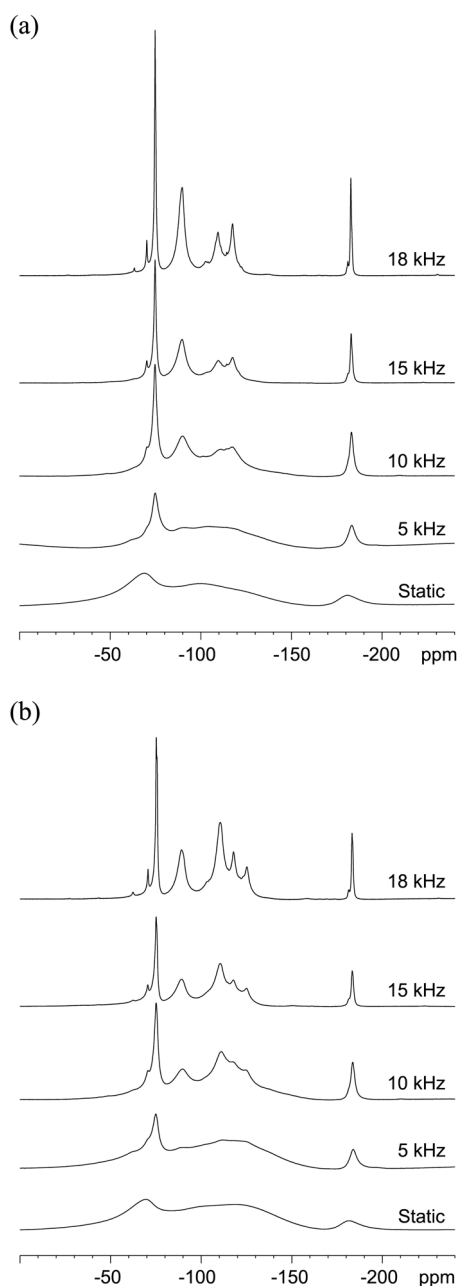
The  $^{19}\text{F}$  solid-state NMR spectra of the FKM rubbers containing the copolymer, terpolymer, and unknown sample were acquired using MAS rates of up to 18 kHz combined with temperatures of up to 200 °C. Figure 1 shows the chemical structure of the copolymer and terpolymer FKM rubbers. The copolymers (Figure 1(a)) were made from the two monomers, VF and HFP, and the terpolymers (Figure 1(b)) were composed of three monomers, VF, HFP, and TFE.

Figure 2 shows the solid-state  $^{19}\text{F}$  MAS NMR spectra of the copolymer and terpolymer FKM rubbers measured by single pulse excitation with spinning rates ranging from 0 to 18 kHz at 25 °C. The very broad peaks in the static spectra arise from the homonuclear  $^{19}\text{F}$ - $^{19}\text{F}$ ,  $^1\text{H}$ - $^{19}\text{F}$  dipolar interactions and chemical shift anisotropies. From these spectra, it was impossible to interpret the chemical structure or to differentiate the type of polymers. Figure 2 shows a substantial improvement in the resolution as the MAS rate is increased to 18 kHz in order to average the dipolar interactions. The spectra of the copolymer and terpolymer FKM rubbers at 5 kHz were very broad, and both spectral patterns were quite similar, so it was difficult to differentiate them. The spectra of the copolymer and terpolymer FKM at 10 kHz and above have somewhat different patterns between -120 and -100 ppm. At 18 kHz, the resolution was significantly better than that observed at lower spinning speeds. However, it is still necessary to obtain higher resolution spectra for the sake of peak assignment and the interpretation of the possible structures.

Figure 3 shows the solid-state  $^{19}\text{F}$  MAS NMR spectra of the copolymer and terpolymer FKM rubbers measured by

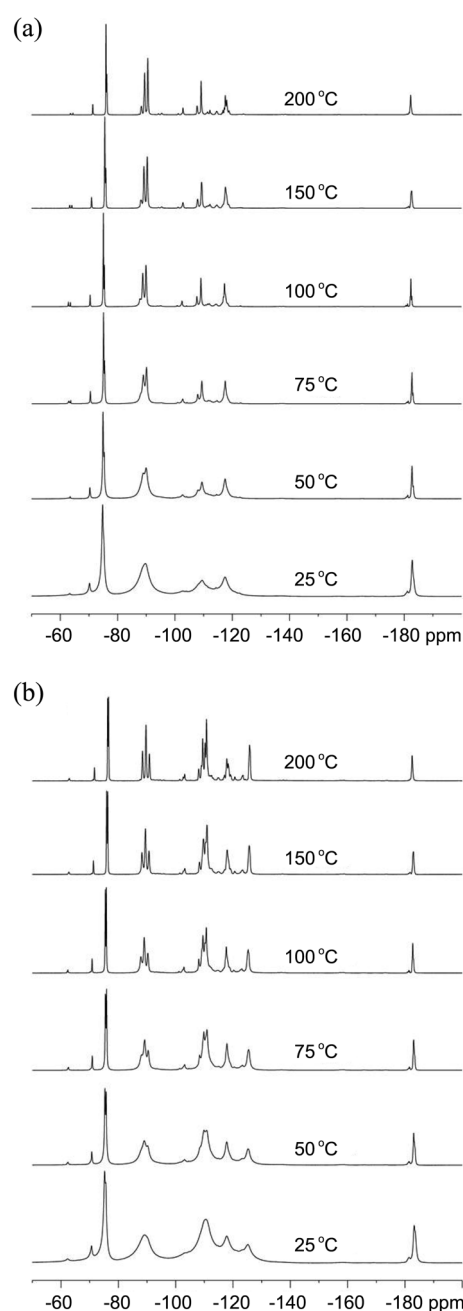


**Figure 1.** Chemical structures of (a) copolymer and (b) terpolymer FKM rubbers.



**Figure 2.**  $^{19}\text{F}$  solid-state MAS NMR spectra of (a) copolymer and (b) terpolymer FKM rubbers as a function of MAS rate from 0 to 18 kHz. All spectra were acquired with four transients at 25 °C. Depending on the MAS rate, the number of acquisition data points was adjusted between 128 and 2048, corresponding to acquisition times of between 0.85 and 13.64 ms, respectively.

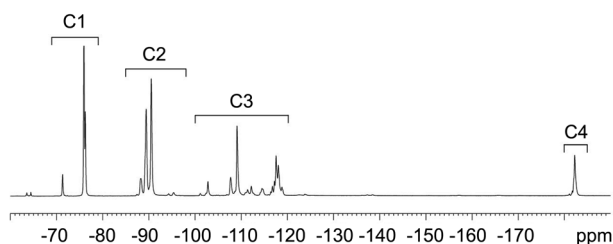
single pulse excitation with gradually increasing temperature from 25 °C to 200 °C at a spinning rate of 18 kHz. The changes in the chemical shifts arising from the variation in the temperature were calibrated with respect to the spectra of PTFE measured at each temperature. As the sample temperature was increased in the 18 kHz high speed MAS spectra, the spectral resolutions were gradually enhanced, due to the increased molecular motion resulting in the further averaging of the dipolar interactions. Depending on the temperature, the number of acquisition data points was adjusted



**Figure 3.**  $^{19}\text{F}$  solid-state MAS NMR spectra of (a) copolymer and (b) terpolymer FKM rubbers over the temperature range of 25 °C to 200 °C. All spectra were acquired with four transients at a MAS rate of 18 kHz. Depending on the temperature, the number of acquisition data points was adjusted between 2048 and 5120, corresponding to acquisition times of between 13.64 and 34.11 ms, respectively.

between 2048 and 5120, corresponding to acquisition times of between 13.64 and 34.11 ms, respectively. The best resolution spectra were achieved at 200 °C with a MAS speed of 18 kHz. The high resolution  $^{19}\text{F}$  VT MAS solid-state NMR spectra allow us to analyze the fine structure and determine the monomer ratios of each FKM rubber.

Figure 4 shows the high resolution spectrum of the copolymer FKM acquired with 4 transients using a MAS



**Figure 4.**  $^{19}\text{F}$  solid-state MAS NMR spectra of copolymer FKM rubbers acquired with 4 transients, a MAS speed of 18 kHz, and 200 °C. The resonance assignments and integrated areas are given in Table 1.

speed of 18 kHz and 200 °C. The resonances were divided into four regions according to the contributing source of the monomer unit; C1 (−69 to −79 ppm), C2 (−85 to −98 ppm), C3 (−100 to −120 ppm), C4 (−180 to −185 ppm). The resonances in the C1 and C4 regions originated from the  $\text{CF}_3$  and CF groups of HFP, respectively, and those in the C2 and C3 regions originated from the  $\text{CF}_2$  groups of VF and HFP. The possible carbon structures were assigned by comparing the spectra with the solution and solid-state  $^{19}\text{F}$  NMR spectra of similar polymers.<sup>9,20–23</sup> The chemical shift for each assigned peak and relative integrated area of each region are presented in Table 1. Based on the integrated areas of each region in Table 1, we were able to calculate the monomer ratio of the copolymer FKM as follows.

Because the  $\text{CF}_3$  groups and CF groups are the single sources of the copolymer FKM from HFP, the fractional number of HFP ( $\text{CF}_3\text{CF}=\text{CF}_2$ ) monomer units ( $N_{\text{HFP}}$ ) in the polymer can be determined by using their integrated areas, as shown in the following equations.

$$N_{\text{HFP}} = \text{C4} \quad (1)$$

$$N_{\text{HFP}} = 1/3 (\text{C1}) \quad (2)$$

From Eqs. (1) and (2), it is found that the integrated area of the C1 region is three times larger than that of the C4 region. The integrated areas of C1 and C4 in Table 1 were almost in agreement with these equations. On the other hand, the fractional number of VF ( $\text{CH}_2=\text{CF}_2$ ) monomer units ( $N_{\text{VF}}$ ) in the polymer can be determined from the integrated areas of the C2 and C3 regions. Because all of the resonances in the C2 and C3 regions have contributions from the  $\text{CF}_2$  groups of both monomer units, VF and HFP,  $N_{\text{VF}}$  can be inferred by the following equation.

$$N_{\text{VF}} = 1/2 (\text{C2} + \text{C3}) - N_{\text{HFP}} \quad (3)$$

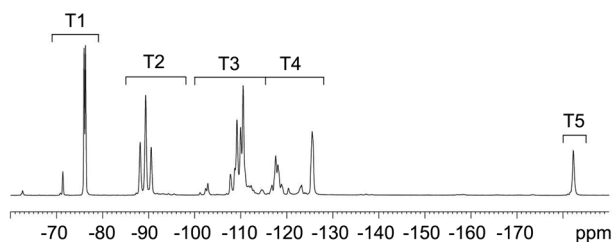
In this equation, the value of  $N_{\text{HFP}}$  used was the average value obtained from Eqs. (1) and (2). From Eqs. (1), (2) and (3), the monomer ratio of copolymer FKM used in this solid-state NMR experiment was found to be 79.1/20.9 mol % VF/HFP monomer units.

Figure 5 shows the high resolution spectrum of the terpolymer FKM acquired with 4 transients using a MAS speed of 18 kHz and 200 °C. The spectral assignments and quantification of the terpolymer FKM were obtained by a similar procedure to that used for the copolymer FKM, but considering the additional TFE monomer unit. The resonances were divided into five regions according to the contributing source of the monomer unit; T1 (−69 to −79 ppm), T2 (−85 to −98 ppm), T3 (−100 to −115.5 ppm), T4 (−115.5 to −128 ppm), and T5 (−180 to −185 ppm). The resonances in the T1 and T5 regions originated from the  $\text{CF}_3$  and CF groups of HFP, respectively, and those in the T2 and T3 regions originated from the  $\text{CF}_2$  groups of VF and HFP. The resonances in the T4 region originated from the  $\text{CF}_2$  groups of HFP and TFE. The chemical shift for each assigned peak and relative integrated area of each region are presented in Table 2. Based on the integrated areas of each region in Table 2, we were able to calculate the monomer ratio of the terpolymer FKM as follows.

**Table 1.**  $^{19}\text{F}$  chemical shift assignments and integrated areas of copolymer FKM

Spectral region	Chemical shift (ppm) <sup>a</sup>	Integrated area	Structural assignments
C1	−71.3	22.5	−CH <sub>2</sub> −CF <sub>2</sub> −CF(CF <sub>3</sub> *)−CF <sub>2</sub> −CH <sub>2</sub> −
	−75.9, −76.2		−CF <sub>2</sub> −CF <sub>2</sub> −CF(CF <sub>3</sub> *)−CH <sub>2</sub> −CF <sub>2</sub> −
C2	−87.4, −88.3, −89.4, −90.5	35.0	−CF <sub>2</sub> −CH <sub>2</sub> −CF <sub>2</sub> *−CH <sub>2</sub> −CF <sub>2</sub> −
	−94.3, −95.4		−CF <sub>2</sub> −CH <sub>2</sub> −CF <sub>2</sub> *−CH <sub>2</sub> −CH <sub>2</sub> −
C3	−101.1	35.3	−CH <sub>2</sub> −CF(CF <sub>3</sub> )−CF <sub>2</sub> *−CH <sub>2</sub> −CF <sub>2</sub> −
	−102.8		−CF <sub>2</sub> −CH <sub>2</sub> −CF <sub>2</sub> *−CF(CF <sub>3</sub> )−CF <sub>2</sub> −
	−107.7		−CF(CF <sub>3</sub> )−CH <sub>2</sub> −CF <sub>2</sub> *−CF <sub>2</sub> −CF(CF <sub>3</sub> )−
	−109.1		−CF <sub>2</sub> −CH <sub>2</sub> −CF <sub>2</sub> *−CF <sub>2</sub> −CF(CF <sub>3</sub> )−
	−111.4, −112.2		−CF <sub>2</sub> −CH <sub>2</sub> −CF <sub>2</sub> *−CF <sub>2</sub> −CH <sub>2</sub> −
	−114.5		−CH <sub>2</sub> −CF <sub>2</sub> −CF <sub>2</sub> *−CH <sub>2</sub> −CH <sub>2</sub> −
	−116.8, −117.6, −118.1, −118.8		−CH <sub>2</sub> −CF <sub>2</sub> −CF <sub>2</sub> *−CF(CF <sub>3</sub> )−CH <sub>2</sub> −
C4	−182.2	7.2	−CH <sub>2</sub> −CF*(CF <sub>3</sub> )−CF <sub>2</sub> −
			−CF <sub>2</sub> −CF*(CF <sub>3</sub> )−CF <sub>2</sub> −

<sup>a</sup>The chemical shifts were referenced to PTFE (−121 ppm). \*Asterisk indicates relevant moiety.



**Figure 5.**  $^{19}\text{F}$  solid-state MAS NMR spectra of terpolymer FKM rubbers acquired with 4 transients, a MAS speed of 18 kHz, and 200 °C. The resonance assignments and integrated areas are given in Table 2.

Because the  $\text{CF}_3$  groups and CF groups are the single sources of terpolymer FKM from HFP, the fractional number of HFP ( $\text{CF}_3\text{CF}=\text{CF}_2$ ) monomer units ( $N_{\text{HFP}}$ ) in the polymer can be determined by means of their integrated areas using the following equations.

$$N_{\text{HFP}} = \text{T5} \quad (4)$$

$$N_{\text{HFP}} = 1/3 (\text{T1}) \quad (5)$$

From Eqs. (4) and (5), the integrated area of the T1 region is three times larger than that of the T5 region. The integrated areas of T1 and T5 in Table 2 were almost in agreement with those obtained using these equations. The fractional number of TFE ( $\text{CF}_2=\text{CF}_2$ ) monomer units ( $N_{\text{TFE}}$ ) in the polymer can be determined from the integrated areas of the T4 region. Because all of the resonances in the T4 region have contributions from the  $\text{CF}_2$  groups of both monomer units, HFP and TFE,  $N_{\text{VF}}$  can be determined by the following

equation.

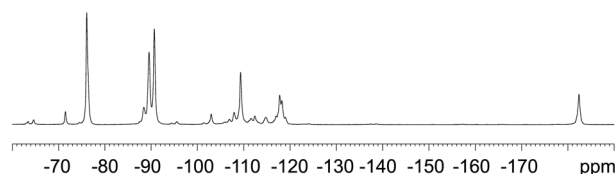
$$N_{\text{TFE}} = 1/2 (\text{T4}) - N_{\text{HFP}} \quad (6)$$

Finally, the fractional number of VF ( $\text{CH}_2=\text{CF}_2$ ) monomer units ( $N_{\text{VF}}$ ) in the polymer can be determined from the integrated areas of the T2, T3, and T4 regions due to the  $\text{CF}_2$  groups of all of the monomers as follows.

$$N_{\text{VF}} = 1/2 (\text{T2} + \text{T3} + \text{T4}) - N_{\text{HFP}} - 2 N_{\text{TFE}} \quad (7)$$

In Eqs. (6) and (7), the value of  $N_{\text{HFP}}$  used was the average value obtained from Eqs. (4) and (5). From Eqs. (5), (6) and (7), the monomer ratio of the terpolymer FKM used in this solid-state NMR experiment was 66.1/17.3/16.6 mol % VF/HFP/TFE monomer units.

Figure 6 shows the high resolution spectrum of the FKM containing the unknown sample used in the automobile industry acquired with 4 transients using a MAS speed of 18 kHz and 200 °C. From this spectrum, we determined the type and quantity of the monomer compositions of the



**Figure 6.**  $^{19}\text{F}$  solid-state MAS NMR spectra of FKM containing unknown sample used in the automobile industry acquired with 4 transients, a MAS speed of 18 kHz, and 200 °C.

**Table 2.**  $^{19}\text{F}$  chemical shift assignments and integrated areas of terpolymer FKM

Spectral region	Chemical shift (ppm) <sup>a</sup>	Integrated area	Structural assignments
T1	-70.8, -71.4	16.8	$-\text{CH}_2-\text{CF}_2-\text{CF}(\text{CF}_3^*)-\text{CF}_2-\text{CH}_2-$
	-76.0, -76.3		$-\text{CF}_2-\text{CF}_2-\text{CF}(\text{CF}_3^*)-\text{CH}_2-\text{CF}_2-$
T2	-87.3, -88.2, -89.3, -90.5	20.6	$-\text{CF}_2-\text{CH}_2-\text{CF}_2^*-\text{CH}_2-\text{CF}_2-$
	-94.3, -95.5		$-\text{CF}_2-\text{CH}_2-\text{CF}_2^*-\text{CH}_2-\text{CH}_2-$
	-101.2		$-\text{CH}_2-\text{CF}(\text{CF}_3)-\text{CF}_2^*-\text{CH}_2-\text{CF}_2-$
	-102.3, -102.8		$-\text{CF}_2-\text{CH}_2-\text{CF}_2^*-\text{CF}(\text{CF}_3)-\text{CF}_2-$
T3	-107.7	34.2	$-\text{CF}(\text{CF}_3)-\text{CH}_2-\text{CF}_2^*-\text{CF}_2-\text{CF}(\text{CF}_3)-$
	-108.6, -109.1		$-\text{CF}_2-\text{CH}_2-\text{CF}_2^*-\text{CF}_2-\text{CF}(\text{CF}_3)-$
	-109.9, -110.5		$-\text{CF}_2-\text{CH}_2-\text{CF}_2^*-\text{CF}_2-\text{CH}_2-$
	-112.2		$-\text{CH}_2-\text{CF}_2-\text{CF}_2^*-\text{CH}_2-\text{CH}_2-$
	-114.5		$-\text{CH}_2-\text{CF}_2-\text{CF}_2^*-\text{CF}(\text{CF}_3)-\text{CH}_2-$
T4	-116.8, -117.6, -118.1, -118.8	22.5	$-\text{CF}_2-\text{CF}_2^*-\text{CF}(\text{CF}_3)-$
	-120.3		$-\text{CF}_2-\text{CF}_2-\text{CF}_2^*-\text{CF}_2-\text{CF}_2-$
	-123.1		$-\text{CH}_2-\text{CF}_2-\text{CF}_2^*-\text{CF}_2-\text{CF}_2-$
	-125.5		$-\text{CH}_2-\text{CF}_2-\text{CF}_2^*-\text{CF}_2-\text{CH}_2-$
T5	-182.2	5.9	$-\text{CH}_2-\text{CF}^*(\text{CF}_3)-\text{CF}_2-$
			$-\text{CF}_2-\text{CF}^*(\text{CF}_3)-\text{CF}_2-$

<sup>a</sup>The chemical shifts were referenced to PTFE (-121 ppm). \*Asterisk indicates relevant moiety.

unknown innate sample. Although the resonances were somewhat broad due to the presence of additives, the spectral pattern of the unknown sample was apparently the same as that of the copolymer FKM. The monomer ratio of the unknown sample was 79.1/20.9 mol % VF/HFP monomer units.

### Conclusion

The high resolution  $^{19}\text{F}$  solid-state NMR spectra of FKM rubbers were obtained using high temperature and high speed MAS. Copolymer FKM rubbers can be differentiated from terpolymer FKM rubbers by using a MAS rate of more than 15 kHz at 25 °C or a MAS rate of more than 5 kHz at 50 °C. At temperatures above 75 °C without spinning, the two FKM rubbers can be differentiated by the presence or absence of resonances at  $-120$  to  $-130$  ppm. The high resolution  $^{19}\text{F}$  VT MAS solid-state NMR spectra allow us to analyze the fine structure and determine the monomer ratios of the copolymer and terpolymer FKM rubbers. Finally, we determined the type and quantity of the monomer compositions of an unknown innate sample from its high resolution  $^{19}\text{F}$  MAS solid-state NMR spectra.

**Acknowledgments.** This work was supported by the HUFS Res. Fund of 2011 and the GRRRC Program of Gyeonggi Province [GRRRC HUFS 2011-B01]. And authors want to thank Hyundai-kia Motors for the samples.

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