A ^{19}F NMR Signal Assignment and a Detailed Structural Study of Alternating Tetrafluoroethylene-Propylene Copolymer by High Resolution ^{19}F NMR Spectroscopy and Computational Chemistry

*By Shigeki Kuroki**

^{19}F NMR spectra of Tetrafluoroethylene-propylene(TFE-P) alternating copolymers are very complicated mainly due to $^2J_{F-F}$ couplings and an accurate signal assignment is very difficult. In the present work, simplified ^{19}F NMR spectra of TFE-P alternating copolymers are measured in solution by *J*-resolved and COSY techniques. Thus geminal fluorine nuclei on the carbon atom adjacent to CH$_2$ groups and those on the carbon atom adjacent to CHCH$_3$ groups are assigned accurately. Also the two CF$_2$-CF$_2$ pairs of connection are found and these two pairs are assigned to *meso* or *racemic* configurations, respectively. Further, the conformational exchange of TFE-P copolymers in solution is discussed in a wide temperature range on the basis of experimentally obtained ^{19}F NMR chemical shifts and theoretically calculated ^{19}F nuclear magnetic shieldings.

KEY WORDS: Tetrafluoroethylene-Propylene Copolymer / ^{19}F NMR Chemical Shift / *J*-Resolved Technique / Conformation / Configuration /

Copolymers of tetrafluoroethylene and propylene (TFE-P) (Scheme 1) are the first fluoroelastomers in which a non-fluorinated alkene comonomer was used. They are synthesized by radical copolymerization and can be cured by peroxide. TFE-P copolymers possess typical characteristics of this group of elastomers excellent heat resistance, exceptional chemical resistance especially to bases and amines, high electrical resistivity and good mechanical properties.[1,2] Basic studies on the synthesis, structure and properties of these elastomers were carried out by Japanese researchers[3–9] and they were commercialized by Asahi Glass Co. as Aflas® elastomers.

The microstructure of TFE-P copolymers has been analyzed by ^{1}H and ^{19}F NMR.[10–13] These studies were done mainly to identify characteristic signals originating from the different arrangements of P and TFE(F) units in the copolymer. Thus, the positions of the resonances were detected for eight types of sequences: FFF, PFF, FFP, PFP, FPF, FPP, PPF and PPP. The relative intensities of the signals from the different arrangements can be used to determine the copolymer microstructure precisely. From the results of these studies, it was concluded that the TFE-P copolymer, which is commercially available as Aflas® has a very highly alternating structures corresponding to head-to-tail connection of FPFP (-CF$_2$-CF$_2$-CH$_2$-CH(CH$_3$)-CF$_2$-CF$_2$-CH$_2$-CH(CH$_3$)-) sequences.

But the ^{19}F NMR spectra of the TFE-P alternating copolymers are very complicated mainly due to F-F ^2J couplings and an accurate signal assignment is very difficult.[10–13] For that reason it is difficult to discuss their configuration and conformation in the solution from the basis of ^{19}F NMR results.
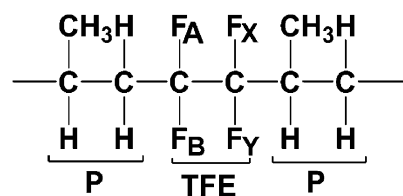
Scheme 1.

In the present work, simplified ^{19}F NMR spectra of TFE-P alternating copolymers in solution are measured by *J*-resolved and COSY techniques and signals are assigned accurately. Further, we discuss that the conformation and configuration of TFE-P copolymers in solution in a wide temperature range by experimentally obtained ^{19}F NMR chemical shifts and theoretically calculated ^{19}F nuclear magnetic shieldings. As well knowing, ^{19}F-^{1}H hetero-COSY and *J*-resolved 2D measurements are very useful and popular for charactering ^{19}F signals of fluoropolymers.[14] But we need to prepare a ^{1}H-^{19}F double tune NMR probe. For the case of ^{19}F *J*-resolved and COSY techniques, we can use standard ^{1}H single tune NMR probe which is tunable to ^{19}F frequency.

Those techniques and the information about the conformation and configuration of TFE-P copolymers in solution are very useful for characterization of newly developed fluoro-elastomers such as TFE-P-VdF(vinylidene fluoride) terpolymers.

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EXPERIMENTAL AND CALCULATIONS

Materials

Alternating TFE-P copolymer was purchased from Asahi Glass Co., Ltd. and used without further treatment. The glass transition temperature (T_g) was $-3\,°C$. The specific gravity was 1.55 and the fluorine content was 57%.[15]

NMR Measurements

^{1}H, ^{13}C and ^{19}F NMR spectra of TFE-P copolymer in THF-d_8 (internal standard TMS for ^{1}H and ^{13}C and CFCl$_3$ for ^{19}F) were measured by a Bruker Avance DSX 300 NMR spectrometer operating at 300 MHz for ^{1}H, 75.5 MHz for ^{13}C and 282.4 MHz for [19]F.

Magnetic Shielding Calculation

Geometric parameters (bond lengths and bond angles) of model compounds were optimized without any constraint using the 6-31G(d,p) level of theory and ^{19}F nuclear shieldings were calculated using the 6-31G(d,p) level of theory and gauge-including atomic orbital (GIAO) methods. The program package used was Gamess R3 program package.[16]

RESULTS AND DISCUSSION

^{1}H and ^{13}C Solution State NMR of Alternating TFE-P Copolymer

Figure 1 shows the ^{1}H solution state NMR spectrum of the alternating TFE-P copolymer in tetrahydrofuran(THF)-d_8 solution. The peak at 1.32 ppm is assigned to the CH$_3$ protons, and that at 2.13 ppm is assigned to the CH$_2$ protons. The peaks at 2.66 and 2.78 ppm are assigned to the CH protons. In ^{1}H spectra, it is possible to identify directly the triads FPF, PPF+FPP and PPP centered on the P moiety from the resonance of the CH$_3$ protons by applying the methodology of previous authors.[10–13] They reported that the PPP, FPP, PPF and FPF triads appear at 0.88, 1.02, 1.12 and 1.28 ppm,
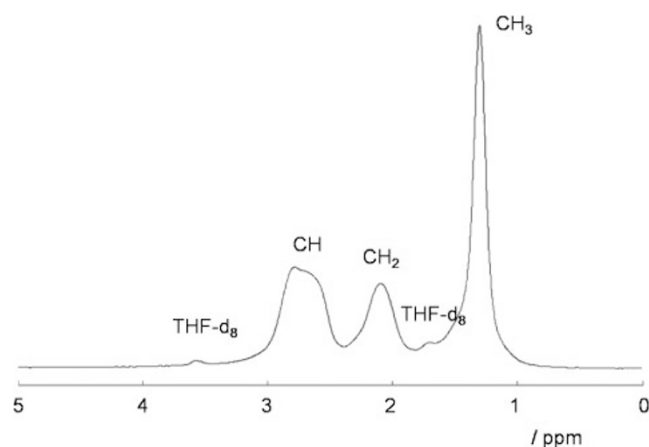
respectively. Now only a peak appears at 1.32 ppm assigned to the CH$_3$ protons. This result shows that only FPF triads exist and there are no PPP, FPP and PPF triads. This means that this TFE-P copolymer has highly alternating structures.

Figure 2 shows the [1]H-decoupled ^{13}C solution state NMR spectrum of the alternating TFE-P copolymer in THF-d_8 solution. The peaks at 14.0 and 14.4 ppm are assigned to the *meso* or *racemic* configurations of the CH$_3$ carbons. The peaks at 31.2 and 31.0 ppm are assigned to the CH and CH$_2$ carbons, respectively. These ^{13}C chemical shifts are very different from that of the usual polypropylenes.[17] These chemical shifts of (P) (CH$_2$CH(CH$_3$)) groups are the effects of the neighboring F(CF$_2$CF$_2$) groups.

The peaks at about 120 ppm are assigned to the CF$_2$ carbons. The integral ratio of resonant areas assigned to tetrafluoroethylene (F) (CF$_2$CF$_2$) and propylene (P) (CH$_2$CH(CH$_3$)) is 1.00:1.60 and the ratio of F:P is 1:1.07. The integral values include 5 to 10% experimental error because [13]C{[1]H} signal intensities are modulated by NOE. This result said this TFE-P copolymer has highly alternating structures which is obtained from ^{1}H NMR observation.

The peaks assigned to the CF$_2$ carbons show the J multiplets with fluorines. There exist two kinds of CF$_2$ carbon and their NMR parameters are $\delta = 119.4$ ppm, $^1J_{CF} = 254.4$ Hz, $^2J_{CF} = 32.0$ Hz, and $\delta = 120.8$ ppm, $^1J_{CF} = 254.3$ Hz, $^2J_{CF} = 35.8$ Hz. These two peaks are assigned to the CF$_2$ carbons bonded with CH$_2$ and CH(CH$_3$) groups, respectively. The integral ratio of these two resonants is about 1.0:1.0. This results show us highly alternating structures corresponding to head-to-tail connection of FPFP (-CF$_2$-CF$_2$-CH$_2$-CH(CH$_3$)-CF$_2$-CF$_2$-CH$_2$-CH(CH$_3$)-) sequences. The peaks at around at 112 ppm are assigned to the CF$_2$ carbons of FF sequences.

^{19}F Solution State NMR of Alternating TFE-P Copolymer

Figure 3(a) shows the ^{19}F solution state NMR spectrum of the alternating TFE-P copolymer in THF-d_8 solution at room temperature recorded by a simple single pulse experiment. This spectrum appears complicated mainly by splitting of geminal $^2J_{FF}$ coupling and an accurate signal assignment is very difficult. The ^{19}F homonuclear J-resolved 2D NMR spectrum measured at room temperature is shown in Figure 4. The J-resolved 1D ^{19}F spectrum appears on the horizontal axis and the information about J couplings of each signal appears on the vertical axis. Figure 3(b) shows the 1D J-resolved ^{19}F solution state NMR spectrum obtained from 2D experiment of the alternating TFE-P copolymer in THF-d_8 solution at room temperature. Compared with Figure 3(a), 1D J-resolved ^{19}F NMR spectrum is very simple and it is easy to assign every peak accurately. The main large peaks are numbered as 1 to 8 (-110.3(1), -112.6(2), -113.1(3), -115.2(4), -116.0(5), -119.5(6), -119.9(7), -120.4(8) ppm) from the higher frequency to lower frequency as shown in Figure 3(b).

In this paper, geminal fluorine nuclei on the carbon atom adjacent to CH$_2$ groups and those on the carbon atom adjacent to CHCH$_3$ groups are indicated AB and XY as a letter, respectively, regardless of their steric configurations. Ishigure

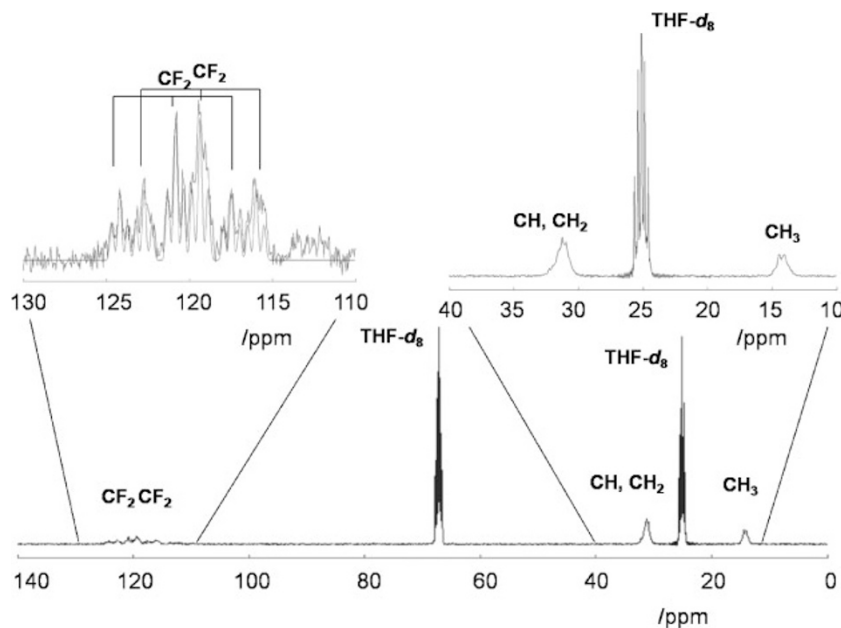**Figure 1.** ^{1}H solution state NMR spectrum of alternating TFE-P copolymer in tetrahydrofuran(THF)-d_8 solution at room temperature.

Figure 2. ^{1}H-decoupled ^{13}C solution state NMR spectrum of alternating TFE-P copolymer in THF-d_8 solution at room temperature.

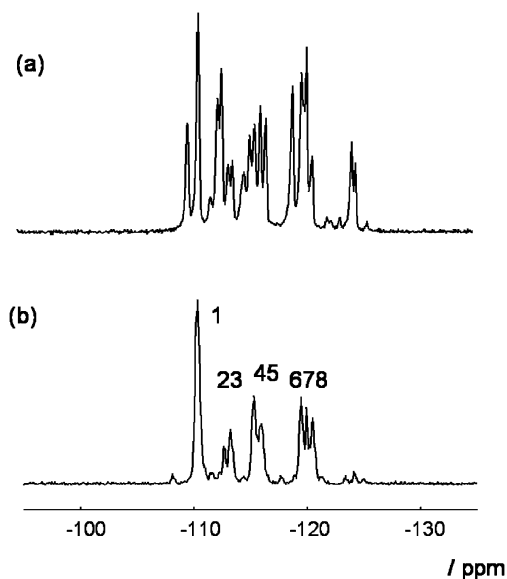**Figure 3.** (a) ^{19}F solution state NMR spectrum of alternating TFE-P copolymer in THF-d_8 solution at room temperature by a simple single pulse experiment, and (b) 1D J-resolved ^{19}F solution state NMR spectrum of alternating TFE-P copolymer in THF-d_8 solution at room temperature.

Figure 4. ^{19}F homonuclear J-resolved 2D NMR spectrum at room temperature.

et al. reported that $^2J_{AB} = 263$ Hz and $^2J_{XY} = 271$ Hz.[10] The J splittings shown in Figure 4 are $^2J_{1,2,3} = 265$ Hz and $^2J_{4,5,6,8} = 270$ Hz, respectively. From these results, the peaks of 1–3 are assigned to AB fluorines and those of 4–6 and 8 are assigned to XY fluorines. Every signal is a doublet which corresponded to the vicinal coupling $^3J_{AB\text{-}XY}$. The peak of 7 has a very small J coupling, so this peak is assigned to fluorines of TFE-TFE sequences.

For the purpose of assigning AB-XY connections, the ^{19}F COSY experiment was performed. The ^{19}F COSY NMR

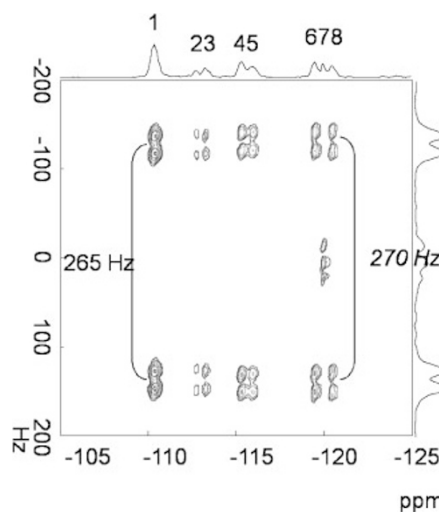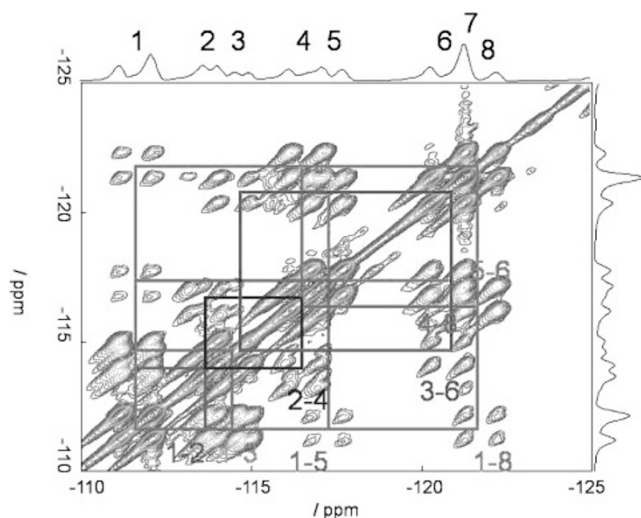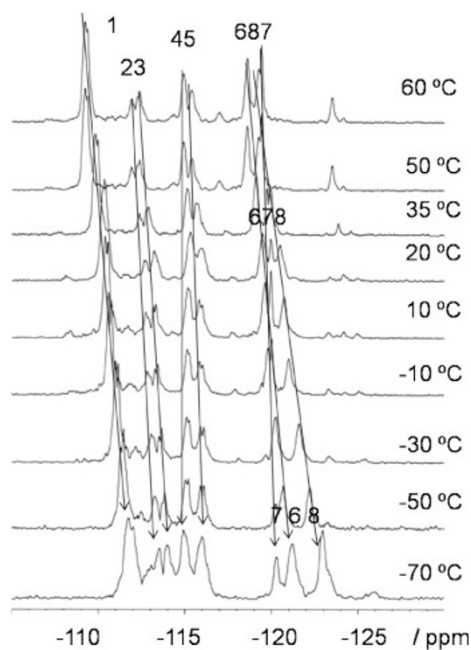spectrum of the TFE-P alternating copolymer at room temperature is shown in Figure 5. Large cross peaks between 1 and 2 (AB pair), between 1 and 3 (AB pair), between 4 and 8 (XY pair) and between 5 and 6 (XY pair) exist. These cross peaks come from the $^2J_{AB}$ and $^2J_{XY}$ couplings. And also small cross peaks between 1 and 5, 1 and 8, 2 and 4, 3 and 6 exist. These cross peaks come from the ^3J couplings between AB and XY pairs. Consequently, two (AB-XY) pairs which are (1,2-4,8) and (1,3-5,6) exist. These two (AB-XY) pairs are assigned to *meso* or *racemic* configurations, respectively.

Temperature Dependence of ^{19}F Chemical Shifts of Alternating TFE-P Copolymer

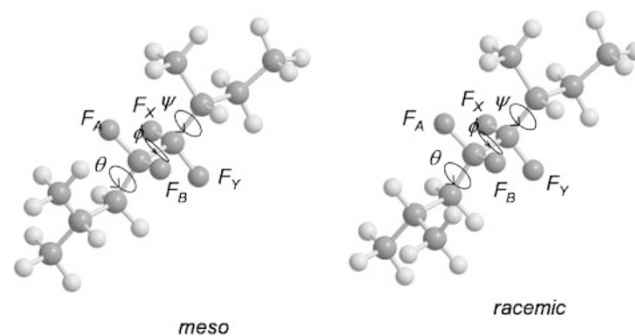Figure 6 shows the 1D J-resolved ^{19}F solution state NMR

Figure 5. ^{19}F COSY NMR spectrum of TFE-P alternating copolymer at room temperature.

Figure 6. 1D *J*-resolved ^{19}F solution state NMR spectrum of alternating TFE-P copolymer in THF-d_8 solution at various temperatures from -70 to 60 °C.

Scheme 2.

Table I. The relative energy on the basis of *ttt* conformers calculated for both *meso* and *racemic* configurations, when one of the three internal torsion angles (θ, ϕ or ψ) becomes *gauche* conformation from *trans* conformation

configuration	conformation (θ, ϕ, ψ)	energy difference (*kJ/mol*)
meso	*ttt*	0
	tgt	+18.3
	gtt	+7.3
	ttg	+1.8
	gtg	+4.5
racemic	*ttt*	0
	tgt	+11.0
	gtt	+2.7
	ttg	+3.1
	gtg	+7.0

spectrum obtained from 2D experiment of the alternating TFE-P copolymer in THF-d_8 solution at various temperatures at -70 to 60 °C. As Ishigure *et al.* have already mentioned, the spectra of these copolymers are remarkably temperature dependent.[10] A decrease in temperature leads to a large low frequency shift especially of peaks 1, 2, 3, 6 and 8. These remarkable temperature dependences of chemical shifts may be closely related to the conformation of the copolymers and arise from the temperature dependence of the populations of the conformers. On the other hand, the ^{19}F chemical shift variation of peaks 4 and 5 is small within the temperature range. In next section, we will discuss the temperature dependence of the conformation of TFE-P copolymer combined with quantum chemical calculations.

Analysis of ^{19}F Nuclear Magnetic Shieldings by *Ab Initio* MO Calculation

To examine the effects of main chain configuration and conformation on ^{19}F chemical shift, total energies and nuclear magnetic shieldings of fluorine nuclei are calculated using the 6-31G(d,p) GIAO method. The structures of model compounds used for the calculations are *meso* and *racemic* CH$_3$-CH(CH$_3$)-CH$_2$-CF$_{AB2}$-CF$_{XY2}$-CH(CH$_3$)-CH$_3$ (Scheme 2). Some conformers are generated by rotating the three internal torsion angles defining the conformation of the central TFE units, θ, ϕ and ψ. The internal torsion angles are constrained at *trans* or *gauche* positions under geometry optimization.

The differences of the total energy are calculated for both *meso* and *racemic* configurations, when one of the three internal torsion angles (θ, ϕ or ψ) becomes *gauche* conformation from *trans* conformation. The relative energy values on the basis of *ttt* conformers are shown in Table I. When the internal torsion angle ϕ between CF$_{AB2}$ and CF$_{XY2}$ becomes *gauche* conformation from *trans* conformation, the relative energy on the basis of *ttt* conformers becomes very large, which are $+18.3$ kJ/mol for *meso* and $+11.0$ kJ/mol for *racemic*, respectively. When the other torsion angles (θ or ψ) become

Table II. Calculated nuclear magnetic shieldings of fluorine nuclei in the central TFE unit in various conformations

configuration	conformation (θ, ϕ, ψ) (energy difference/kJ mol^{-1})	calculating nuclear shieldings/ppm			
		F_A	F_B	F_x	F_Y
meso	*ttt* (0)	364.12	368.30	362.64	378.40
	ttg (+1.8)	363.34	365.26	365.50	365.92
	gtt (+7.3)	348.98	362.84	362.40	376.39
	gtg (+4.5)	354.34	355.57	362.16	363.64
racemic	*ttt* (0)	361.82	364.42	378.26	364.02
	ttg (+3.1)	359.84	367.64	364.24	367.02
	gtt (+2.7)	356.17	354.76	373.92	362.05
	gtg (+7.0)	353.44	356.93	361.27	367.02
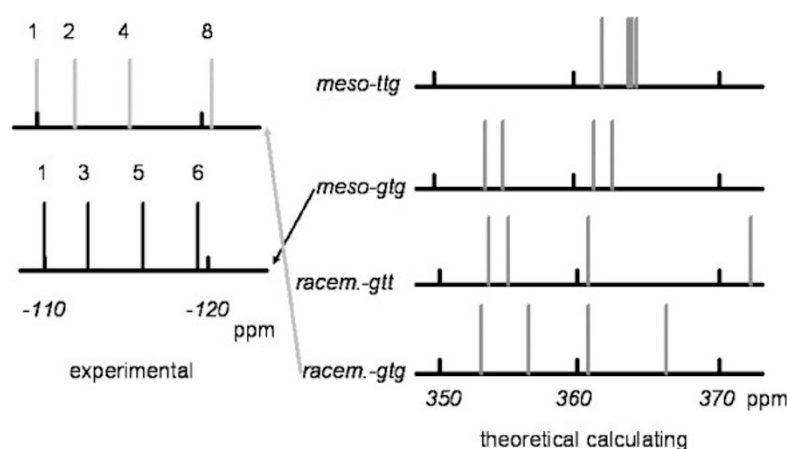
Figure 7. Stick spectra produced from experimentally observed ^{19}F chemical shifts at room temperature and from the calculated ^{19}F magnetic shieldings of four fluorine atoms of the model compounds of *ttg* and *gtg* conformers for *meso* and *gtt* and *gtg* conformers for *racemic*.

gauche conformation from *trans* conformation, the relative energies on the basis of *ttt* conformers are very small. From these results, we can understand that the internal torsion angle ϕ between CF$_{AB2}$ and CF$_{XY2}$ is fixed in the *trans* conformation and the other torsion angles (θ or ψ) take *trans* or *gauche* conformations. Therefore we will consider the four conformers such as *ttt*, *ttg*, *gtt* and *gtg* for the calculations of nuclear magnetic shieldings of fluorine nuclei.

Table II shows the calculated nuclear magnetic shieldings of fluorine nuclei at the central TFE unit in various conformations. Note that the positive sign for the calculated shielding denotes shielding in contrast to the negative sign of the experimental chemical shift values. The experimental data shows that the peaks of F$_{AB}$ fluorines appear always at a higher frequency than those of F$_{XY}$ fluorines. This tendency agrees with the results of *ttg* and *gtg* conformers for *meso* and the results of *gtt* and *gtg* conformers for *racemic* by the theoretical calculation. Figure 7 shows the stick spectra produced from experimentally observed ^{19}F chemical shifts at room temperature and from the calculated ^{19}F magnetic shieldings of four fluorine atoms of the model compounds of *ttg* and *gtg* conformers for *meso*, and *gtt* and *gtg* conformers for *racemic*. The theoretical calculated peak positions of *gtg* conformer well explain the experimentally obtained peak positions for both *meso* and *racemic* configurations. Compared with theoretically calculated and experimentally obtained peak positions, the

signals of (1,2-4,8) are assigned to the *gtg* conformer of *racemic* configurations and the signals of (1,3-5,6) are assigned to the *gtg* conformer of *meso* configurations. Consequently, the population of the *gtg* conformer is larger than that of the other conformers for both *meso* and *racemic* configurations at room temperature.

Next we discuss the temperature dependence of the populations of the conformers of TFE-P copolymers shown in Figure 6. When the torsion angle ψ takes *trans* conformation, F$_Y$ fluorine of *meso* and F$_x$ fluorine of *racemic* have a very large magnetic shielding shown in Table II. This is because of the well known γ-*gauche* effect on ^{13}C chemical shifts.[18] Figure 8 shows the schematic view of ψ taking *trans or gauche* conformations for *meso*. When ψ takes *trans* conformation, one CH$_2$ group and one CH$_3$ group are in the *gauche* positions with respect to F$_Y$ fluorine, so F$_Y$ fluorine is influenced two γ-*gauche* effects. Accordingly, F$_Y$ fluorine has a very large magnetic shielding. On the other hand, when ψ takes *gauche* conformation, a CH$_2$ group is the gauche positions for F$_X$ fluorine and one CH$_3$ group is in the gauche positions with respect to F$_Y$ fluorine. Therefore, both F$_X$ and F$_Y$ fluorine are influenced one γ-*gauche* effect and both have almost the same magnetic shieldings. For the *racemic* case, this rule holds in the same way just replacing F$_X$ and F$_Y$ fluorines.

A decrease of temperature leads to a large low frequency shift especially for signals 1, 2 and 3 which are assigned to F$_{AB}$
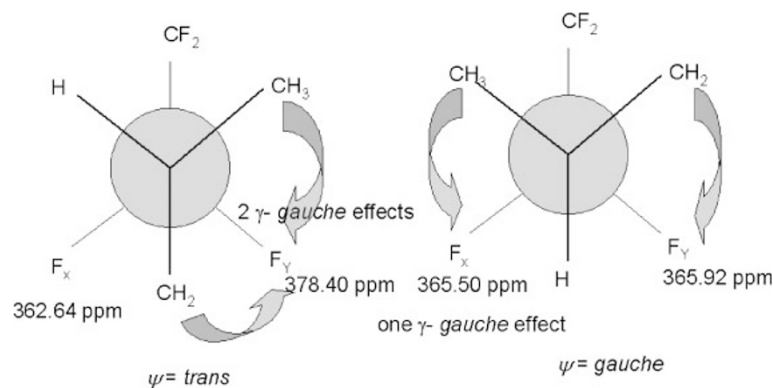
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Figure 8. A schematic view of ψ taking in *trans or gauche* conformations for *meso*.

and of signals 6 and 8 which are assigned to F_{XorY}. The chemical shift variation of signals 4 and 5 which are assigned to F_{XorY} is small as shown in Figure 6. The theoretical nuclear magnetic shielding calculation results for the *gtg* conformer are in good agreement with the experimentally obtained ^{19}F chemical shift values above 20 °C, as mentioned before. As shown in Table II, the *gtg* conformation becomes the *ttt* conformation, the theoretically calculated nuclear magnetic shieldings of F_A, F_B and F_Y (for *meso*) or F_x (for *racemic*) fluorines increase (an increment of nuclear magnetic shielding means low frequency shift) and the variation of them of F_x (for *meso*) or F_Y (for *racemic*) fluorines are very small. These results well explain the experimental obtained ^{19}F chemical shift variation. Consequently, the population of the *gtg* conformer is very large at higher temperature above 20 °C and the population of the *ttt* conformer becomes larger with a decrease in temperature.

CONCLUSIONS

Simplified ^{19}F NMR spectra of TFE-P alternating copolymers in solution are measured by *J*-resolved and COSY techniques and geminal fluorine nuclei on the carbon atom adjacent to CH_2 groups and those on the carbon atom adjacent to $CHCH_3$ groups are assigned accurately. Also the two pairs of connection between CF_{AB2}-CF_{XY2} are found and these two pairs are assigned to *meso* or *racemic* configurations, respectively.

Further, the conformation of TFE-P alternating copolymers in solution in a wide temperature range are determined by combining with quantum chemical calculations. When the three internal torsion angles (θ, ϕ and ψ) are defined for the conformation of the central TFE units, the population of the *gtg* conformer is very large above 20 °C and the population of the *ttt* conformer become larger with a decrease of temperature.

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454 ©2009 The Society of Polymer Science, Japan

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