Analysis of cross-polarization dynamics between $^1$H and $^{19}$F in Viton fluoroelastomer using solid-state $^{19}$F magic angle spinning and $^1$H $\rightarrow$ $^{19}$F cross-polarization magic angle spinning NMR

Shinji Ando, Robin K. Harris,* Gustavo A. Monti and Stefan A. Reinsberg

INTRODUCTION

High-speed magic-angle spinning (MAS) and high-power proton-decoupling techniques facilitate the measurement of high-resolution solid-state $^{19}$F NMR spectra for proton-containing fluoropolymers. Several papers have reported $^{19}$F spectra for analysing chemical structures and phase structures of fluoropolymers\(^8\)–\(^7\) and other fluorine-containing solids\(^8\)–\(^10\).

In a previous paper from our laboratory, Monti and Harris\(^1\) described the study of a series of Viton-type fluoroelastomers using solid-state NMR with $^{19}$F direct-polarization MAS and $^1$H $\rightarrow$ $^{19}$F cross-polarization (CP)/MAS techniques at ambient temperature. These Viton-type elastomers are copolymers and terpolymers of vinylidene fluoride (VDF), hexafluoropropene (HFP) and tetrafluoroethylene (TFE). The authors clarified the following: (1) the resolution in the $^{19}$F spectra is not significantly improved by r.f. proton decoupling; (2) a spinning rate of 10 kHz is sufficient to average effectively ($^1$H, $^{19}$F) dipolar interactions; (3) the composition of the commercial Viton used is VDF : HFP $\approx$ 1 : 1.0 of the commercial Viton used is VDF : HFP.

ABSTRACT: The cross-polarization dynamics between $^1$H and $^{19}$F in a Viton-type fluoroelastomer were studied using $^{19}$F magic angle spinning (MAS) and $^1$H $\rightarrow$ $^{19}$F cross-polarization (CP)/MAS NMR at 188.29 MHz. The phenomenological theory of spin thermodynamics based on the spin temperature hypothesis was employed to describe the polarization transfer between the $^1$H and $^{19}$F spin baths. Simultaneous fitting of the evolution of magnetization in the standard CP and a modified CP (TORQUE) experiment, using the exact solutions of the equations for the spin thermodynamics, gave unique sets of the parameters $T_{1H}$, $T_{1F}$ and $T_{HF}$ for five separate peaks in the $^{19}$F spectra. The values of $T_{1F}$ and $T_{HF}$ obtained are consistent with those independently measured by spin-locking experiments. The true values of $T_{HF}$ are significantly larger (by a factor of ca. 4) than those derived from a simple two-parameter fit of the CP behaviour with variable contact time. The temperature dependences of $T_{HF}$ and $T_{HF}$ were measured between $-$49 and 86 $^\circ$C. The relationship between the CP dynamics parameters and the local molecular motion in the polymer chains is discussed. Copyright \(1999\) John Wiley & Sons, Ltd.

KEYWORDS: NMR; $^{19}$F NMR; $^1$H NMR; fluoropolymer; cross-polarization magic angle spinning; cross-polarization dynamics; abundant spin; relaxation parameter

(4) equal values of spin–lattice relaxation times in the laboratory frame ($T_{HF}$) were obtained for all the peaks within experimental error; (5) the CF and CF$_3$ fluorines of the HFP units showed slightly larger values of spin–lattice relaxation times in the rotating frame ($T_{1F}$) than CF$_2$ fluorines; (6) no heterogeneity in phases was observed; and (7) the evolution of $^{19}$F magnetization as a function of contact time in the $^1$H $\rightarrow$ $^{19}$F CP/MAS is well fitted by a modified expression of the usual equation, and the TORQUE (TOneRhoQUEnching)\(^1\) sequence can reveal with more detail the characteristics of the evolution. However, the parameters obtained from the fittings are not consistent with each other, or with the independently measured parameters. The last fact indicates that the CP dynamics parameters obtained from the variable contact time experiments should not be taken to represent the true values of $T_{1F}$ and the rate of polarization transfer from proton to fluorine, $T_{HF}$. The conventional method which is often used for the analyses of $^1$H $\rightarrow$ $^{13}$C CP dynamics cannot be applied without modification for CP between two abundant nuclei, i.e. for $^1$H $\rightarrow$ $^{19}$F CP, a fact that is not surprising but which appears not to have been the subject of detailed evaluation in the literature.

Recently, we have reported the characteristic features of CP dynamics between $^{19}$F and $^1$H using $^1$H $\rightarrow$ $^{19}$F CP/MAS NMR.\(^1\) The sample used was a fluorinated polyimide consisting of one fluorine spin bath and one...
homogeneous proton spin bath. The analysis was based on the phenomenological approach for the spin thermodynamics between two spin baths, but the high abundance of fluorine atoms and efficient $T_{1X}^{CP}$ process were explicitly considered. In that case, $T_{1X}$ was actually much smaller than $T^{H}_{1}$. The value of $T_{1X}$ was successfully determined by the analysis using effective CP parameters, which can be directly obtained from the CP experiments, and independently measured $T_{1X}^{CP}$ and $T_{1H}^{CP}$. All the parameters relevant to the CP dynamics showed reasonable consistency. However, the use of the relaxation parameters that had been obtained from separate experiments was essential in the analysis of the previous study.\(^{13}\)

In the present study, we developed a method to deduce true CP dynamics parameters from CP curves of a Viton fluoroelastomer in combination with TORQUE experiments without using separately measured relaxation parameters. When the assumptions and the method of analysis are appropriate, the CP dynamics parameters obtained are found to be consistent with separately measured relaxation parameters.

**THEORY AND CALCULATION**

In the same way as in the previous study,\(^{13}\) we employed a phenomenological spin thermodynamics theory based on the spin-temperature hypothesis. The inverse spin temperature $\beta$, which is defined as $\hbar/kT$, is proportional to the magnitude of magnetization in the case that only the Zeeman interaction is considered. The variations with time of the inverse spin temperatures, $\beta_H$ and $\beta_X$ for the H and X spin baths, are described within this framework. It is assumed that H is an abundant nucleus, whereas X can be an abundant or a rare nucleus. When there is a difference between $\beta_H$ and $\beta_X$, polarization transfer occurs between H and X spins during the contact time ($t_{CP}$) of cross-polarization (CP) and TORQUE experiments as depicted in Fig. 1(a) and (b). The rate of the polarization transfer from H to X spin baths is characterized by a time constant $T_{1X}^{CP}$. It should be noted that this notation is different from the conventional way, in which the transfer rate from $^1$H to $^{13}$C during $^1$H $\rightarrow$ $^{13}$C CP is often expressed as $T_{CH}$, not as $T_{HC}$. Under the spin-lock condition in the presence of simultaneous r.f. fields of $B_{1X}$ for X and $B_{1H}$ for H, each link between a spin bath and the lattice is characterized by spin–lattice relaxation times in the rotating frame, $T_{1X}$ for X and $T_{1H}$ for H. We assume that $\beta$ in each spin bath is immediately equilibrated. Hence we neglect oscillation of magnetization between H and X spins. Such phenomena can occur when there are strongly coupled H–X spin pairs. In addition, we consider only experimental situations where MAS does not interfere with the CP process.

Assuming first-order kinetics, the variations of $\beta_X$ and $\beta_H$ under a cross-relaxation condition can be described by the coupled differential equations\(^{14,15}\)

$$\begin{align*}
\frac{d}{dt_{CP}} \beta_X &= -\frac{1}{T_{CH}} (\beta_X - \beta_H) - \frac{1}{T_{1X}} \beta_X \\
\frac{d}{dt_{CP}} \beta_H &= \frac{\epsilon}{T_{CH}} (\beta_H - \beta_X) - \frac{1}{T_{1H}} \beta_H
\end{align*}$$

(1)

Figure 1. Pulse sequences for measuring parameters relevant to the CP dynamics between $^{19}$F and $^1$H. (a) Standard variable contact-time CP; (b) variable contact-time TORQUE; (c) variable-time $^{19}$F spin-lock; and (d) a variable-time $^1$H spin-lock followed by a short contact CP. Sequences (c) and (d) are used for the direct measurement of $T_{1X}$ and the indirect measurement of $T_{1H}$, respectively.

where $\epsilon$ is defined as

$$\epsilon = \frac{N_X (\gamma_X B_{1X})^2}{N_H (\gamma_H B_{1H})^2}$$

(2)

and $N$ and $\gamma$ are the number of spins and the gyromagnetic ratio for the indicated nuclear type, respectively. When the Hartmann–Hahn condition,

$$\gamma_H B_{1H} = \gamma_X B_{1X}$$

(3)

is achieved, $\epsilon$ is equal to $N_X/N_H$. In the case of $H$ to X cross-polarization, Eqn (1) can be straightforwardly solved under the initial conditions ($t_{CP} = 0$):

$$\beta_X = 0 \text{ and } \beta_H = \beta_{1H}$$

(4)

The dependence of $\beta_X$ on $t_{CP}$, which corresponds to an evolution of X magnetization as a function of contact time.
in the standard CP experiments (which we shall refer to as a CP curve), can be expressed as follows:\textsuperscript{14,15}:

\[
\frac{\beta_X(t)}{\beta_{BB}}_{CP} = \frac{1}{a_+ - a_-} \left[ -\exp \left( -\frac{a_-}{T_{HX} t_{CP}} \right) + \exp \left( -\frac{a_+}{T_{HX} t_{CP}} \right) \right]
\]

where

\[a_\pm = a_0 \pm \sqrt{a_0^2 - b}\]

with

\[a_0 = \frac{1}{2} \left( 1 + \varepsilon + \frac{T_{HX} T_{1p}^H}{T_{1p}^X} \right)
\]

and

\[b = T_{HX} \frac{T_{1p}^H}{T_{1p}^X} \left( 1 + \frac{T_{HX} T_{1p}^H}{T_{1p}^X} \right) + \varepsilon \frac{T_{HX} T_{1p}^H}{T_{1p}^X}
\]

In the same way, the dependence of $\beta_X$ on $t_{CP}$ in $H \rightarrow X$ TORQUE experiments (which we shall refer to as a TORQUE curve) can be expressed as\textsuperscript{12}

\[
\frac{\beta_X(t)}{\beta_{BB}}_{TOR} = \exp \left( -\frac{t_{SL}}{T_{1p}^H} \right) \left[ \frac{\beta_X(t)}{\beta_{BB}}_{CP} \right]
\]

where $t_{SL}$ is a spin-lock time for the $H$ nuclei prior to the cross-polarization to $X$ nuclei.

Figure 2 shows the calculated CP and TORQUE curves for $\varepsilon = 0.01$ and 1. The constant spin-lock time for $H$ spins, $t_{cont} = t_{SL} + t_{CP}$, in the TORQUE curves is 5.0 ms, and the values of $\beta_X$ are normalized at $t_{CP} = t_{cont}$ in order to compare the shapes of the curves. $T_{HX}$ was kept constant at 0.5 ms, and the relaxation parameters used for the various curves were used were (A) $T_{1p}^H = 2.5$ ms, $T_{1p}^N = 100$ ms, (B) $T_{1p}^H = 2.5$ ms, $T_{1p}^N = 2.5$ ms, (C) $T_{1p}^H = 5.0$ ms, $T_{1p}^N = 5.0$ ms and (D) $T_{1p}^H = 100$ ms, $T_{1p}^N = 2.5$ ms. The CP curves for $\varepsilon = 0.01$ [Fig. 2(a)] correspond to a typical case of $^{1}H \rightarrow ^{13}C$ CP, because the natural abundance of $^{13}C$ is 1% and the number of carbons is at most the same order as that of hydrogens. In this case, it is well known that the decaying slope of the CP curves in a logarithmic scale is principally determined by $-1/T_{1p}^N$ in a region of $t_{CP} \gg T_{HX}$, and the influence of $1/T_{1p}^H$ on the slope is negligible. This indicates that different $T_{1p}^N$'s can be potentially discriminated from the decaying slope of CP curves when $\varepsilon$ is much smaller than 1. Since the number of $^{13}C$ atoms is generally much smaller than that of $^{1}H$ in organic molecules unless carbons are enriched in $^{13}C$, there is no effective direct relaxation path from $^{13}C$ to the lattice. Thus, the heat capacity of the $^{13}C$ spin bath is negligibly small, and $T_{1p}$ is generally much longer than $T_{1p}^N$.

On the other hand, the CP curves for $\varepsilon = 1$ [Fig. 2(b)] correspond to a typical case of $^{1}H \rightarrow ^{19}F$ CP, because $^{19}F$ has 100% natural abundance, and the number of fluorines may be comparable to that of hydrogens in fluorinated organic compounds and polymers. For example, the $N_{F}/N_{H}$ of one of the most popular fluoropolymers, poly(vinylidene fluoride), is 1. These curves show significantly different behaviour from those in Fig. 2(a). In particular, no difference was observed in the curves (A), (C) and (D) in spite of their large differences in $T_{1p}^H$ and $T_{1p}^N$. This can be explained by the fact that the decaying slope is principally determined by $(1/T_{1p}^H + 1/T_{1p}^N)/2$, not by $1/T_{1p}^H$, when $\varepsilon = 1$ and $1/T_{1p}^N$ is not negligibly small. Curves (A), (C) and (D) actually involve the same value of $(1/T_{1p}^H + 1/T_{1p}^N)/2$. Consequently, a term involving $1/T_{1p}^N$ has to be explicitly incorporated into the analysis of CP dynamics between abundant nuclei. The
high natural abundance of $^{19}$F often makes $T_{1\rho}^F$ of the same order as $T_{1\rho}^H$, which is much shorter than $T_{1\rho}^H$. In addition, the heat capacity of the $^{19}$F spin bath can be comparable to that of the $^1$H spin bath when $\varepsilon$ is close to 1. Fig. 2(b) clearly indicates that CP curves cannot discriminate three cases of $T_{1\rho}^H < T_{1\rho}^F$, $T_{1\rho}^H = T_{1\rho}^F$ and $T_{1\rho}^H > T_{1\rho}^F$. This is one of the major reasons why the conventional method cannot be applied to the analysis of $^1$H $\rightarrow$ $^{19}$F CP dynamics. Furthermore, Eqn (5) can be approximated by the following equation:

$$\frac{\beta_X(t)}{\beta_{19F}}_{CP} = A \left[ - \exp \left( - \frac{t_{CP}}{T_{1H}} \right) + \exp \left( - \frac{t_{CP}}{T_{1\rho}} \right) \right]$$

(10)

where $A$ is constant in magnitude and $T_{1H}^X$ and $T_{1\rho}^X$ are effective time constants for the increase and decay of $\beta_X$. This indicates that any kind of CP curve for a homogeneous system can be well described by these two constants using the conventional expression. When $\varepsilon$ is negligibly small and $T_{1\rho}^F$ is much longer than $T_{1\rho}^H$ (e.g. $^1$H $\rightarrow$ $^{13}$C CP), $T_{1H}^X$ and $T_{1\rho}^X$ should be very close to $T_{1H}^X$ and $T_{1\rho}^X$, respectively. However, when $\varepsilon$ is not negligibly small and $T_{1\rho}^X$ is comparable to $T_{1\rho}^H$ (e.g. $^1$H $\rightarrow$ $^{19}$F CP), no simple relationship is expected between the effective parameters ($T_{1H}^X, T_{1\rho}^X$) and the true parameters for CP dynamics, $T_{1H}^X, T_{1\rho}^X$ and $T_{1\rho}^X$. In the previous study, the following expression was used to describe $^1$H $\rightarrow$ $^{19}$F CP curves for Viton:11

$$\frac{\beta_X(t)}{\beta_{19F}}_{CP} = A \left[ - \exp \left( \frac{1}{y} + \frac{1}{T_{1\rho}^X} \right) t_{CP} \right]$$

$$+ \exp \left( - \frac{t_{CP}}{x} \right)$$

(11)

In an ideal case ($T_{1H}^X \ll T_{1\rho}^X \ll T_{1\rho}^F, N_F/N_H \ll 1$), $x$ would be equal to $T_{1\rho}^X$ and $y$ to $T_{1H}^X$. This equation gave an acceptable description for all the CP curves of five separated peaks in Viton. However, as discussed in the paper, the parameters $x$ and $y$ cannot be regarded as the true values of $T_{1\rho}^X$ and $T_{1H}^X$, respectively, because the influence of $N_F/N_H$ is ignored in this equation. Accordingly, there was some discrepancy between the independently measured $T_{1\rho}^X$ data and the values of $x$ obtained from the fitting of CP curves. In a similar manner, the expression used to describe the $^1$H $\rightarrow$ $^{19}$F TORQUE curves did not give true values of CP dynamics parameters.

Figure 2(c) shows the TORQUE curves calculated for $\varepsilon = 0.01$. The decay of $\beta_X$ is effectively suppressed in all cases, indicating that it is mainly caused by $T_{1\rho}^H$. The shape of the curves is insensitive to the magnitude of $T_{1\rho}^X$. On the other hand, the TORQUE curves calculated for $\varepsilon = 1$ [Fig. 2(d)] show significantly different behaviour from those in Fig. 2(c). The decay of $\beta_X$ can be suppressed only in the cases when $T_{1\rho}^H = T_{1\rho}^F$ [(B) and (C)]. Otherwise, the slope at $t_{CP} = t_{const}$ is positive for $T_{1\rho}^H \ll T_{1\rho}^X$ (A) and negative for $T_{1\rho}^H > T_{1\rho}^X$ (D). This relationship is verified in the Appendix.

Figure 3 shows the calculated CP and TORQUE curves for $\varepsilon = 0.01$ and 1 with varying rates of polarization transfer $T_{1H}^X$. $T_{1H}^X$ was varied as (A) 0.1, (B) 0.3, (C) 0.5 and (D) 1 ms, and the same relaxation parameters, $T_{1H}^X$ and $T_{1\rho}^X$, as in Fig. 2 were used for the calculations. The CP curves for $\varepsilon = 0.01$ [Fig. 3(a)] and $\varepsilon = 1$ [Fig. 3(b)] indicate that, in the decaying region ($t_{CP} > 3$ ms), the same behaviour as in Fig. 2(a) and (b) was exhibited, although the slope in the initial region ($t_{CP} < 1$ ms) is sensitive to $T_{1H}^X$. In the same way, the TORQUE curves [Fig. 3(c) and (d)] show very similar behaviours to those in Fig. 2(c) and (d) in the decaying region. In particular, when $\varepsilon = 1$, the TORQUE curve has a positive slope at $t_{CP} = t_{const}$ when $T_{1\rho}^X > T_{1\rho}^H$ and a negative slope when $T_{1\rho}^X < T_{1\rho}^H$ regardless of the variation of $T_{1H}^X$. Although the TORQUE sequence does not quench the relaxation process with $T_{1\rho}^X$, when $\varepsilon$ is not negligibly small, this relation should be generally helpful in analysing CP dynamics between abundant nuclei.

**EXPERIMENTAL**

**Sample**

A Viton fluoroelastomer of commercial origin was used as a sample. This is a random copolymer of $\text{CF}_2\text{CH}_2$—(VDF) and $\text{CF}-(\text{CF}_3)\text{CF}_2$—(HFP) components, although with a restriction that adjacent HFP repeating units are not expected. The sample was purchased from Goodfellow (Cambridge, UK). The lower working temperature of Viton as an elastomer is $-10$ to $-50^\circ$C and the upper working temperature is 220 to 300$^\circ$C. The sample was ground into a powder under liquid nitrogen, dried under vacuum at 70$^\circ$C for 8 h, and annealed at 110$^\circ$C for 72 h in order to evaporate absorbed water and volatile additives prior to being packed in the rotor.

**Nuclear magnetic resonance**

All solid-state NMR experiments were carried out on a Chemagnetics CMX-200 spectrometer operating at resonance frequencies of 188.29 MHz for fluorine and 200.13 MHz for proton nuclei. A commercial (Chemagnetics) $^1$H—$^{19}$F double-tuned APEX MAS probe.
capable of high-power heteronuclear decoupling and fitted with 4 mm o.d. zirconia Pencil rotors was used. Vespel drive tips, spacers and end-caps were utilized to avoid unwanted background signal on the fluorine channel. In order to reduce the effect of inhomogeneity in spin-locking fields, spacers 4 mm in length were added to both ends of the sample. The resulting sample length was about 3.5 mm. Samples were spun at the magic angle at a rate of 10 kHz. CP and TORQUE experiments were carried out at ambient probe temperature (the calibrated temperature inside the rotor was around 35°C). The fluorine rf field strength was equivalent to about 83 kHz. Fluorine chemical shifts are quoted with respect to CFCl₃ and were measured via replacement with a sample of liquid C₆F₁₆ (−164.3 ppm) without proton decoupling. The Bloch–Siegert effect, which is a chemical shift displacement of ca 1.4 ppm caused by the ¹H decoupling, was corrected after the measurements (using standardized calibrations).

¹⁹F MAS spectra were also recorded using direct polarization with π/2 pulses of 3 μs duration. Relaxation delays of 4 s are sufficiently long compared with the spin–lattice relaxation time in the laboratory frame of the sample (T₁F = 0.6 s, T₁H = 0.4 s) to ensure quantitative peak intensities. Higher and lower temperature ¹⁹F MAS spectra were taken by using the temperature-control unit with a nitrogen gas flow. The measurements started 15 min after the temperature at the probe-head reached the relevant set temperature. The ¹⁹F spin–lattice relaxation times in the rotating frame (T₁sr) and in the laboratory frame (T₁L) were measured at a spinning speed of 10 kHz using the H–F probe by means of the variable-time spin-lock technique [Fig. 1(c)] and the inversion–recovery technique (π–t–π/2–acq) respectively, under high-resolution conditions. Experiments for measuring T₁L and T₁sr were carried out with set temperatures between −60 and 80°C at 20°C intervals. The temperature inside the spinning rotor was corrected using a calibration curve. This curve was prepared from the temperature dependence of the frequency difference between two resonances in the ¹H spectrum of methanol absorbed on tetrakis(trimethylsilyl)silane.¹⁶ The cross-polarization dynamics between the ¹⁹F and ¹H nuclei were studied using the standard (variable contact time) CP experiment and a modified CP (TORQUE) pulse sequence developed by Tekely et al.¹² In contrast to conventional rigid fluoropolymers, the polarization transfer between ¹H and ¹⁹F is not efficient for Viton, because NH, the capacity of the magnetization source, is considerably smaller than NF and an efficient CP is moderated by vigorous molecular motion. Accordingly, 400 FID transients were accumulated for each spectrum in the CP and TORQUE experiments. The ¹H spin–lattice relaxation times in the rotating frame (T₁sr) were measured via ¹⁹F resonance by a variable ¹H spin-lock time followed by ¹H → ¹⁹F CP [Fig. 1(d)]. The use of ¹H → ¹⁹F CP was necessary in the measurement because of the strong background signal in the ¹H channel for the H–F probe. The contact time used for such experiments was 0.2 ms.

Figure 3. Evolution of βx in the standard H → X CP experiment for (a) ε = 0.01 and (b) ε = 1 and in the H → X TORQUE experiment for (c) ε = 0.01 and (d) ε = 1. The values of T₁Hx used were (A) 0.1, (B) 0.3, (C) 0.5, (D) 1.0, respectively, where the unit is ms. The relaxation parameters used were the same as for Fig. 2.
RESULTS AND DISCUSSION

Cross-polarization dynamics

Figure 4 shows a $^{19}$F MAS direct-polarization proton-decoupled NMR spectrum of commercial Viton measured at ambient probe temperature and a spinning speed of 10kHz. As reported previously, r.f. proton decoupling during acquisition does not improve the resolution at ambient temperature. However, all the free induction decays (FIDs) were acquired with $^1$H-decoupling with a magnitude of about 75kHz in this study because the resolution of the $^{19}$F spectra was improved by decoupling at lower temperatures (see below). The major sequence of repeating units and the peak assignments are shown in Fig. 5. The spectral resolution indicates that F–F homonuclear dipolar interactions are moderately efficiently averaged under this measuring condition, but the narrower signals obtained at higher temperatures (see below) show that the dipolar interactions are not completely averaged at ambient temperature. Although more than seven signals are observed in the spectrum, which arise from variations in the regioregularity (head-to-head and tail-to-tail structures) in the polymer sequence, we analysed the CP dynamics for five major peaks only. The relevant peaks, at $-75$, $-90$, $-110$, $-118$ and $-184$ ppm, were assigned to the fluorines of $^{19}$F(HFP), $^{19}$F(VDF), $^{19}$F(VDF), $^{19}$F(HFP) and $^{19}$F(HFP) groups, respectively. The $^{19}$F(VDF) is the $^{19}$F group directly bonded to $^{19}$F(HFP). The $N_f/N_{HF}$ ratio in this sample of commercial Viton can be straightforwardly calculated from the previously reported monomer composition as $\varepsilon = 1.85,11$ This indicates that the magnitude of the H spin bath, which is the source of magnetization in $^1$H $\rightarrow$ $^{19}$F CP, is considerably smaller than the magnitude of the F spin bath. In a sense, this is a case of CP from a relatively rare spin to an abundant spin. The CP dynamics behaviour under such an unusual condition has never, to our knowledge, been analysed in detail.

The decays of $^{19}$F magnetization observed in the standard variable $^{19}$F spin-lock and the variable $^1$H spin-lock followed by $^1$H $\rightarrow$ $^{19}$F CP experiments are shown in Fig. 6 as a function of the spin-lock time, $t_{SL}$. All the curves were fitted by single exponential functions, and the directly measured $T_{1F}^p$ and the indirectly measured $T_{1F}^\vartheta$ (via $^{19}$F resonance) results thus obtained are summarized in Table 1. In Fig. 6(a), the decay curves of $^{19}$F and $^{19}$H are well described by single-exponential functions, although all three types of $^{19}$F fluorines (of VDF and HFP units) have small contributions from long $T_{1F}^p$ components. According to the results of double exponential fitting, the $^{19}$F resonances contain long $T_{1F}^p$ ($4 \pm 1$ ms) components with contents of 5–7%.

Viton fluoroelastomer should be, in principle, highly amorphous. However, Latour and co-workers have reported that the copolymers of VDF and HFP can show some degree of crystallinity, and the crystallinity is decreased as the amount of HFP in the copolymer is increased.17,18 These long $T_{1F}^p$ components suggest the existence of crystalline regions. In the previous study, no crystalline component was observed from $T_{1F}^p$ measurements and two-dimensional WISE experiments. We suspect that some degree of crystallization may have been induced by the annealing at 110°C in this study. Nevertheless, this component will be neglected in the following analyses because of its small amount.

The $^{19}$F and $^{19}$H in HFP units exhibit very similar $T_{1F}^p$ and $T_{1F}^\vartheta$ and these values are about twice as long as for $^{19}$F in VDF and HFP units. The long $T_{1F}^p$ of $^{19}$F was explained11 in terms of the rapid internal rotation of $^{19}$F group and the number of geminal F–F interactions. In addition, 2D $^{19}$F–$^{19}$F exchange experiments show noticeable correlation between the $^{19}$F and $^{19}$F fluorines even for short mixing times ($\sim 0.8$ ms),11 which gives support for the similar $T_{1F}^p$ values of the CF and $^{19}$F fluorines. It is also reasonable that $^{19}$F(HFP) show similar $T_{1F}^p$ because they have similar molecular structures and are bonded to each other. The fact that fluorines...
lock conditions is not efficient on the time-scale of several to several tens of milliseconds, presumably because of the fluorine spin-diffusion between those groups under spin-in CF(HFP), CF₃(HFP), CF₂(VDF) and CF(HFP) signals (although T₁F should be identical for all the cases from the molecular structure) may cause the apparent difference in the efficiencies of ¹H → ¹⁹F CP. A relatively long t_{cpr} of 0.2 ms was used for the indirect measurement of T₁H because the CP is inherently inefficient in Viton. The results show that CF₁ and CF resonances have longer T₁F than T₁H, although all CF₂ resonances have shorter T₁F than T₁H. The mean T₁F is longer than the T₁H averaged over all fluorines. The T₁H and T₁F measured in this study are proportionally larger than those of the previous study. This systematic difference was caused by the distribution of the B₁ field along the spinning axis of a sample rotor, which was measured using the Bloch–Siegert shift and indicated that a homogeneous r.f. field (±3%) is generated only for 3–4 mm near the coil centre. It is apparent that the more homogeneous and stronger B₁ field attained by the confinement of sample in the experiments reported here caused the increase in the measured value of T₁F.

The evolutions of the ¹⁹F magnetization obtained from the standard CP and TORQUE experiments (CP curves and TORQUE curves) at the exact Hartmann–Hahn match are shown in Fig. 7 as a function of the contact time, t_{cpr}. Although the CP curves shown in Fig. 7(a) are essentially identical with those reported previously, more points of t_{cpr} were taken for a precise fitting (38 points for CP and 34 points for TORQUE). In the TORQUE experiments, a constant spin-lock time for H spins, t_{const} of 5 ms was used, which is longer than for the previous study (3 ms), because t_{const} should be sufficiently longer than T₁H. Owing to its rubbery nature, Viton should have considerably longer values of T₁H than conventional rigid polymers.

![Graph of spin-lock time dependence of ¹⁹F signal intensities for five major peaks of Viton measured using the pulse sequences in Fig. 1(c) and (d). The plots were fitted by single exponential functions, and the T₁F and T₁H obtained are summarized in Table 1. Spectrometer operating conditions are the same as in Fig. 4. A contact-time of 0.2 ms and 400 transients were used for the indirect measurement of T₁H. Proton spins were decoupled by an irradiating r.f. field during acquisition.](image)

**Table 1. Comparison of CP dynamics parameters for Viton**

<table>
<thead>
<tr>
<th>Chemical shift, δF (ppm)</th>
<th>Peak assignment</th>
<th>Independently measured values</th>
<th>Conventional fit of CP curve [Eqn (10)]</th>
<th>Simultaneous fit of CP and TORQUE curves [Eqns (5) and (9)]</th>
</tr>
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<tbody>
<tr>
<td>-75 CF₃(HFP)</td>
<td>2.13 &gt; 1.65</td>
<td>0.60 2.25</td>
<td>2.54 2.70 1.61</td>
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<tr>
<td>-90 CF₃(VDF)</td>
<td>1.17 &lt; 1.79</td>
<td>0.54 1.38</td>
<td>2.25 1.29 1.73</td>
<td></td>
</tr>
<tr>
<td>-110 CF₂(VDF)</td>
<td>0.94 &lt; 1.52</td>
<td>0.37 1.17</td>
<td>1.42 1.07 1.53</td>
<td></td>
</tr>
<tr>
<td>-118 CF₃(HFP)</td>
<td>0.99 &lt; 1.45</td>
<td>0.38 1.09</td>
<td>1.54 1.00 1.39</td>
<td></td>
</tr>
<tr>
<td>-184 CF(HFP)</td>
<td>2.21 &gt; 1.69</td>
<td>0.62 1.76</td>
<td>2.74 1.93 1.54</td>
<td></td>
</tr>
</tbody>
</table>

*Individually measured proton and fluorine spin–lattice relaxation times in the rotating frame (T₁F, T₁H), effective time constants for cross-polarization (T₁HF) and relaxation to the lattice (T₁p) by conventional fitting, and T₁H, T₁F and T₁HF obtained by the simultaneous fitting of CP and TORQUE curves are given. Units = ms.
through isotropic spin diffusion. Hence we did not introduce the two-stage process of polarization transfer into the analyses.

The $T_{1p}^H$ s obtained are between the independently measured $T_{1p}^F$ s and $T_{1p}^H$ s except for CF$_3$(HFP). The $T_{1p}^H$ s are longer than $T_{1p}^H$ for CF$_3$ and CF but shorter for CF$_2$ fluorines. In Fig. 7(a), the maximum intensities are reached for $t_{CP}$ between 0.6 and 1.0 ms, and all the $T_{1p}^H$ s are relatively short (0.37–0.62 ms). However, this does not mean an efficient polarization transfer of $^1$H $\rightarrow$ $^{19}$F; the true $T_{1p}^F$ values for Viton are actually mostly longer than the $T_{1p}^H$ s (see below). This means that CP may appear to be much more efficient than it is in fact, since the contact time dependence of the fluorine magnetization is generated from a compensation of unusually long $T_{1p}^F$ together with comparable values of $T_{1p}^F$ and $T_{1p}^H$. However, this means that, although the maximum in the CP curve occurs at a relatively short $t_{CP}$, the signal intensity at the maximum is relatively low. The TORQUE curves in Fig. 7(b) clearly indicate that the peaks of CF$_3$(HFP) and CF(HFP) have positive slopes at $t_{CP}$ $>$ 2 ms, although the other peaks of CF$_2$ have almost zero slopes. From the considerations in the theory and calculation, these positive slopes coincide with the fact that CF$_3$ and CF(HFP) have larger $T_{1p}^H$ s than the respective $T_{1p}^F$ s.

As was explained above, one cannot deduce true CP parameters ($T_{1p}^F$, $T_{1p}^H$, $T_{1p}^{HF}$) directly from the experimental $^1$H $\rightarrow$ $^{19}$F CP and TORQUE curves separately, although these two curves show very different features depending on the magnitudes of the CP parameters. In particular, this situation is pronounced when $\epsilon$ is not negligibly small. For applying spin thermodynamics theory based on the spin temperature hypothesis to Viton, we assume the following: (1) Fluorine spins of each functional group [CF$_3$(HFP), CF$_2$(VDF), CF$_3$(VDF), CF$_3$(HFP) and CF(HFP)] form their own spin baths. These spin baths are not connected to each other during spin-lock or CP because fluorine spin diffusion between different groups is efficiently suppressed by the substantial molecular motion and the macroscopic rotation at 10 kHz as described above. This is attested by the different values of $T_{1p}^F$ found for each site. Efficient spin diffusion between the sites is inhibited by the resonance energy differences (we deliberately avoided rotational resonances). (2) Proton spins form one spin bath since there is only one site of protons [CH$_2$(VDF)] in Viton. This bath is connected to all the fluorine baths during CP. (3) Fast magnetization transfer, which is mediated by the residual F–F homonuclear dipolar interactions, occurs within each spin bath during spin-lock or CP. This condition is necessary to fulfill the fast-correlation assumption of the spin temperature approximation. It should be noted that our CP operation has always involved the centred triple band matching condition. If the thermodynamic model for two spin baths is appropriate for the CP dynamics analysis of Viton, CP and TORQUE curves should be simultaneously described with a unique set of CP parameters. As shown in Fig. 8, the $^1$H $\rightarrow$ $^{19}$F CP and TORQUE curves associated with each peak were simultaneously fitted by an independent variation of the three relevant CP
T, which is the sole source of magnetization, is connected to all fluorine baths during CP. Moreover, it was difficult in practice to determine individual values of $\varepsilon$ from curve fitting, since $\varepsilon$ was not sensitive to the obtained CP parameters within the range of $\pm 0.3$.

The most striking feature of the results from simultaneous fitting is the large difference between true $T_{HF}$s and effective $T_{HF}$s for all the peaks; the former are about four times as large as the latter, and in fact $T_{HF}$s are comparable to or larger than $T_{HF}$s and $T_{HF}$s (rendering CP relatively inefficient, as is expected for an elastomer). The $T_{HF}$s obtained from the fitting agree very well with the independently measured $T_{HF}$s. In addition, the $T_{HF}$s obtained from the fitting agree well with the independently measured $T_{HF}$s for CF$_3$(VDF), CF$_2$(VDF) and CF$_2$(HFP), although slight discrepancies are observed for those of CF$_3$(HFP) and CF(HFP). As described above, the similar values of $T_{HF}$s for CF$_3$ and CF of HFP units may be caused by the efficient spin diffusion among these spins. This may arise from the spatial proximity of these groups in the polymer chain although the signals are far apart in the spectrum. However, under the spin-lock conditions of CP and TORQUE experiments, the $^1$H $\rightarrow$ $^{19}$F polarization transfer might interfere with spin diffusion between CF and CF$_3$.

**Variable-temperature studies**

In order to relate the CP dynamics parameters obtained to the molecular motion of Viton, variable-temperature measurements of the relaxation parameters should be useful. Figure 9 shows $^{19}$F MAS direct-polarization proton-decoupled spectra of Viton at different temperatures between $-49$ and $84^\circ$C at about $20^\circ$C intervals. As the temperature is decreased, the resonances become broader and spinning side bands more intense [Fig. 9(a)]. The peaks at $-110$ and $-118$ ppm are not separately resolved at $8^\circ$C. Moreover, the peak at $-90$ ppm is strongly affected by decreasing temperature. This peak, which corresponds to CF$_3$(VDF), showed a significant broadening between $8$ and $-11^\circ$C and became almost beyond detection at $-49^\circ$C. This is probably because VDF units are gradually undergoing a phase transition to the glassy state. Although the $T_{HF}$ values of poly(vinylidene fluoride) and poly(hexafluoropropylene) are reported as ca $-50$ and $152^\circ$C, respectively, Viton is unlikely to show a discrete glass transition because this is a cured polymer containing a variety of additives. Compared with non-decoupled spectra (not shown), proton decoupling during acquisition became more effective as the temperature was decreased. This was most noticeable for the CF$_3$ peaks. In contrast, the peaks originated from HFP units, which have a minor composition of 22% in Viton, are still pronounced at $-49^\circ$C. This indicates that there is a significant difference in mobility between VDF and HFP units at lower temperatures. On the other hand, as the temperature is increased, the resonances become sharper and spinning side bands weaker [Fig. 9(b)]. The very high resolution of the spectrum at $84^\circ$C corresponds to that measured at a spinning rate of $15$ kHz at ambient temperature. It should be noted that, even at $84^\circ$C, the peaks associated with VDF units show larger linewidths than those with HFP units.
Figure 9. Fluorine-19 MAS direct-polarization proton-decoupled spectra of Viton at different temperatures. Temperatures inside the rotor were calibrated via replacement with a sample of methanol absorbed on tetrakis(trimethylsilyl)silane at the same spinning rate. Experimental conditions are the same as for Fig. 4. Peaks corresponding to spinning side bands at lower temperatures are indicated by asterisks.

Figure 10 shows the temperature dependence of $T_{1\rho}$ and $T_{1p}$ for five major peaks of Viton. Both relaxation parameters are expressed on a logarithmic scale. As seen in Fig. 10(a), $T_{1\rho}$ is systematically increased as the temperature decreased. In particular, the $T_{1\rho}$ increases monotonically with the inverse of temperature between $-11$ and $27^\circ$C. Assuming the Arrhenius law, activation energies between 10 and 13 kJ mol$^{-1}$ were obtained from the slopes of the plots for different fluorine peaks. All the resonances associated with CF$_2$ groups show identical $T_{1\rho}$ at each temperature over the entire range of measurement, but CF(HFP) shows significantly larger $T_{1\rho}$ at temperatures below 46 $^\circ$C and CF$_3$(HFP) units also show larger $T_{1\rho}$ below $-11^\circ$C. This supports the fact that VDF and HFP units have different modes of mobility at lower temperatures. On the other hand, the values of $T_{1p}$ for different peaks show distinct valleys in their temperature dependence, which have minima between 8 and 46 $^\circ$C [Fig. 10(b)]. The characteristic behaviour of $T_{1p}$ can be classified into three regions. First, Viton exhibits a solid-like behaviour in $T_{1p}$ below $8^\circ$C. $T_{1p}$ increases as the temperature decreases, which indicates that immobile components show longer $T_{1p}$s than those of mobile components. It should be noted that CF$_3$(HFP) shows a significantly smaller slope than the other fluorines in this region. This suggests that CF$_3$ keeps its mobile character even at lower temperatures, which may be related to fast rotation of the CF$_3$ group. A small value of $T_{1p}$ for CF$_3$ can also be explained by the same reason. Since Viton has an almost homogeneous phase structure, it is surprising that there are four different $T_{1p}$s in the same polymer chain. This suggests that the mobility of each type of fluorine is not correlated with each other, and there is little spectral spin

diffusion between fluorines despite the significant overlap of the resonances. In particular, different values of $T_{1p}^F$ between CF$_3$ and CF in HFP units show the absence of efficient spin diffusion between these fluorines at lower temperatures. Second, Viton exhibits a liquid- or solution-like behaviour in $T_{1p}^F$ at temperatures above 46 °C. $T_{1p}^F$ increases as the temperature increases, and mobile components show longer $T_{1p}^F$.s. The reason why CF$_3$(HFP) shows longer $T_{1p}^F$ than the CF$_2$ fluorines has been explained in terms of the rapid internal motion of CF$_3$ group and the number of geminal F–F interactions. This is convincing at temperatures above 46 °C. Moreover, the cooperative behaviour in $T_{1p}^F$ for CF$_3$ and CF in HFP indicates a significant correlation between their mobility, which suggests vigorous molecular motion of CF$_3$(HFP) as a unit at higher temperatures. All other CF$_2$ groups, including CF$_2$(HFP) units, seem to compose another set having a different mode of mobility from CF$_2$(CF$_3$). The CF$_2$ fluorines also show identical $T_{1p}^F$ values at each temperature. Third, the temperature dependence of $T_{1p}^F$ between 8 and 46 °C is not clear, and it is not easy to relate $T_{1p}^F$ to molecular motion. For example, the relationship between $T_{1p}^F$ of CF$_2$(VDF), which is most likely in an immobile component at lower temperatures, and those of CF$_2$(VDF) and CF$_2$(HFP) is reversed at 27 °C. In addition, the valley temperatures of $T_{1p}^F$s for CF$_3$ and CF of HFP units are displaced to lower values than those for CF$_2$ fluorines. According to BPP theory, the time constant of the autocorrelation function, $\tau_c$, can be estimated as $2 \mu s (\gamma B/2\pi \approx 83 kHz)$ in this temperature range, because then the frequency of molecular motion in the polymer chains of Viton is of a similar order of magnitude to that of the $B_1$ field used for spin-locking. This is a major reason that Viton shows relatively short values of $T_{1p}^F$.

From the comparison between Figs 4 and 9, the CP dynamics parameters of Viton were measured at an inside rotor temperature of around 35 °C. Although Viton does not show a simple behaviour in $T_{1p}^F$ at this temperature, this situation should be similar to that in the high-temperature region. Hence the relatively large values of $T_{1p}^F$ observed for CF$_3$, and CF of HFP units might indicate a higher mobility of these fluorines than the CF$_2$ fluorines in VDF and HFP units. In addition, the large values of $T_{HF}^F$ for CF$_3$ and CF of HFP, which straightforwardly indicate inefficiency in cross-polarization between H and F, can also be indicative of higher mobility for these groups. The proportionality between $T_{HF}^F$ and $T_{1p}^F$ supports this view (see Table 1). The considerably smaller values of $T_{1p}^F$ for CF$_3$(VDF) and CF$_2$(HFP) than those of CF$_2$(VDF) may originate from the slightly higher mobility of the VDF unit, although this situation is reversed at lower temperatures. This suggests that the CF$_3$(VDF)–CF$_2$(HFP) sequence forms a relatively rigid local structure in the polymer chain compared with the consecutive VDF sequence at ambient temperature. Moreover, the small values of $T_{HF}^F$ for CF$_3$(VDF) and CF$_2$(HFP) indicate that the high density of fluorine atoms in the VDF–HFP sequence does not interfere with the polarization transfer from protons to fluorines. This fact may support the structural rigidity of this sequence.

**CONCLUSIONS**

A phenomenological theory of spin thermodynamics based on the spin temperature hypothesis was employed to describe CP dynamics between $^1$H and $^{19}$F spin baths. Characteristic features of evolutions of magnetization in the standard $^1$H → $^{19}$F CP and a modified CP (TORQUE) experiment were investigated from calculations using the exact solutions of the spin thermodynamics equations. In the calculation, the high-abundance and efficient $T_{1p}^F$ processes were explicitly considered. It was shown theoretically that the decays of fluorine signals in TORQUE can be used to discriminate the cases of $T_{1p}^F > T_{1p}^H$, $T_{1p}^F = T_{1p}^H$ and $T_{1p}^F < T_{1p}^H$ when the number of fluorines is not negligible compared with that of protons. The standard CP experiment cannot discriminate those cases in principle. A Viton fluoroelastomer was subjected to solid-state NMR measurements with $^{19}$F direct polarization MAS and $^1$H → $^{19}$F CP/MAS techniques. Although the effect of homonuclear spin diffusion between fluorines in different units was not included in the analysis, simultaneous fitting of the evolution of magnetization in the CP and TORQUE experiments gave unique sets of parameters of $T_{HF}^F$, $T_{1p}^F$, $T_{1p}^H$ and $T_{HF}^H$ for five separate peaks of the $^{19}$F spectra without the aid of separate experiments. The $T_{1p}^H$ and $T_{HF}^H$ obtained from the simultaneous fitting were consistent with the respective values independently measured by spin-locking experiments. This indicates that the theory used and the method developed in this study are appropriate for analysing the CP dynamics behaviour between fluorines and protons in fluoropolymers that contain considerable amounts of fluorine. Variable-temperature measurements of $T_{1p}^F$, $T_{HF}^F$ and $T_{1p}^H$ were performed between −49 and 86 °C, and the relationship between the relaxation parameters and the local molecular motion in the polymer chains was discussed. The relatively large values of $T_{1p}^F$ and $T_{HF}^F$ observed for CF$_3$, and CF in HFP units might indicate higher mobility of these fluorines than for those of CF$_2$ in VDF and HFP units.

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**REFERENCES**

One can examine the signs of each term at \( t = t_{CP} \) over cross-polarization time \( t_{CP} \) can be calculated as follows:

\[
\frac{\partial \beta_{s}(t)/\beta_{b}}{\partial t_{CP}} = \frac{1}{a_{s} - a_{-}} \exp \left( \frac{-t_{SL}}{T_{1p}} \right) \times \left( \frac{1}{T_{1p}} - \frac{a_{s}}{T_{HX}} \right) \exp \left( \frac{-a_{-}}{T_{HX}} t_{CP} \right) - \left( \frac{1}{T_{1p}} - \frac{a_{s}}{T_{HX}} \right) \exp \left( \frac{-a_{-}}{T_{HX}} t_{CP} \right)
\]

\[= BC[(D_{0} - D_{1})a^{2} - (D_{0} - D_{2})a^{2}] \]

One can examine the signs of each term at \( t_{CP} = t_{const} \) (\( t_{SL} = 0 \)) as follows:

\[B = \frac{1}{a_{s} - a_{-}} = \frac{1}{2 \sqrt{a_{s}^{2} - b}} \]

is always positive.

\[C = \exp \left( \frac{-t_{SL}}{T_{1p}} \right) \]

is unity at \( t_{SL} = 0 \).

\[D_{1} = \frac{a_{s}}{T_{HX}} \]

is always positive.

\[D_{0} = \frac{a_{0} - \sqrt{a_{0}^{2} - b}}{T_{HX}} = C_{s} - \sqrt{C_{s}^{2} - C_{b}} \]

where

\[C_{s} = \frac{a_{0}}{T_{HX}} = \frac{1}{2} \left( 1 + \varepsilon \right) \frac{T_{HX}}{T_{1p}^{H}} + \frac{1}{T_{1p}^{X}} \]

and

\[C_{b} = \frac{b}{T_{HX}} = \frac{1}{2} \left( \frac{1 + \varepsilon}{T_{1p}^{H}} \right) \left( T_{HX} \frac{1}{T_{1p}^{H}} + \frac{1}{T_{1p}^{X}} \right) \]

Then,

\[D_{0} - D_{1} = \frac{1}{T_{1p}^{H}} - \frac{a_{-}}{T_{HX}} \exp \left( \frac{1}{T_{1p}^{H}} - \frac{1}{T_{1p}^{X}} \right) \]

is always positive and not negligibly small at \( t_{SL} = 0 \).

\[A^{+} = \exp \left( \frac{-a_{-}}{T_{HX}} t_{CP} \right) \]

is always positive, but is negligibly small at \( t_{SL} = 0 \) when \( t_{const} \) is much larger than \( T_{HX} \). As a result, the sign of the slope of the TORQUE curve where \( t_{CP} = t_{const} \) (\( t_{SL} = 0 \)) is eventually determined by the sign of the term \( D_{0} - D_{1} \). When \( \varepsilon \) is negligibly small (e.g. \(^{1}H \to ^{13}C \) CP), this term straightforwardly converges to zero, corresponding to the conventional TORQUE experiments. However, when \( \varepsilon \) is not negligibly small, the TORQUE curve has a positive slope at \( t_{CP} = t_{const} \) when \( T_{1p}^{X} > T_{1p}^{H} \) and a negative slope at \( t_{CP} = t_{const} \) when \( T_{1p}^{X} < T_{1p}^{H} \) provided the term

\[\alpha = (1 + \varepsilon) \frac{1}{T_{HX}} - \left( \frac{1}{T_{1p}^{H}} - \frac{1}{T_{1p}^{X}} \right) \]

is positive. Hence one can infer the relationship between \( T_{1p}^{H} \) and \( T_{1p}^{X} \) from the slope of the TORQUE curve at \( t_{CP} = t_{const} \), at least when it is likely that.

\[\frac{1}{T_{HX}} > \left( \frac{1}{T_{1p}^{H}} - \frac{1}{T_{1p}^{X}} \right) \]