



# Deuteron NMR Study of Ferroelectric Transition in VF<sub>2</sub>/TrFE Copolymer

Authors: V. Hugo Schmidt, Carole Perry, Edward A. Dratz, and Yong Ke

This is an Accepted Manuscript of an article published in [Ferroelectrics](#) on May 2011, available online: <http://www.tandfonline.com/10.1080/00150199108222412>.

Schmidt, V. Hugo, Carole Perry, Edward A. Dratz, and Yong Ke. " Deuteron NMR Study of Ferroelectric Transition in VF<sub>2</sub> /TrFE Copolymer ." *Ferroelectrics* 117, no. 1 (May 1991): 149–155. doi:10.1080/00150199108222412.

Made available through Montana State University's [ScholarWorks](#)  
[scholarworks.montana.edu](http://scholarworks.montana.edu)

DEUTERON NMR STUDY OF FERROELECTRIC TRANSITION IN VF<sub>2</sub>/TrFE COPOLYMER

V. HUGO SCHMIDT<sup>1</sup>, CAROLE PERRY<sup>2</sup>, EDWARD A. DRATZ<sup>2</sup>, and YONG KE<sup>1</sup>  
Montana State University, Bozeman, MT 59717

<sup>1</sup>Department of Physics

<sup>2</sup>Department of Chemistry

(Received July 24, 1989; in final form October 16, 1989)

**abstract** - Deuteron NMR results on a 70/30 mole % random copolymer of deuterated vinylidene fluoride and normal trifluoroethylene are reviewed, for temperatures on both sides of the ferroelectric-paraelectric phase transition of the crystalline portion of the copolymer. A calculation is presented for the deuteron quadrupolar NMR spin-lattice relaxation caused by kink-3-bond motions along disordered helical chains in the paraelectric phase.

Poly(vinylidene fluoride), formula (CH<sub>2</sub>CF<sub>2</sub>)<sub>n</sub>, abbreviated PVF<sub>2</sub>, is a polymer which exhibits a strong and commercially important piezoelectric effect.<sup>1-3</sup> The crystals formed from the melt are in the antiferroelectric  $\alpha$  phase, and the polymer must be stretched and poled to convert these crystals to the piezoelectric and ferroelectric  $\beta$  phase. The  $\beta$  phase has a trans configuration of the C-C- chains, with protons on one side and fluorines on the other. This arrangement provides a large spontaneous polarization which is significantly altered by stress and which can be reversed by a strong electric field. Therefore it is piezoelectric and ferroelectric. It exhibits no transition to a nonferroelectric state because it melts near 180 °C before such a state is reached.

Polytrifluoroethylene (PTrFE), formula (CHF<sub>2</sub>CF<sub>2</sub>)<sub>n</sub>, has a structure which is still controversial. Kolda and Lando<sup>4</sup> proposed a 3/1 helix with a pitch distance 6.75 Å. Later, Tashiro *et al.*<sup>5</sup> claimed it has a trans configuration, although their phase diagram shows above 50 °C a "gauche" phase described (for their 55/45 VF<sub>2</sub>/TrFE copolymer) as a mixture of T<sub>3</sub>G, TG, T<sub>3</sub>G\*, and TG\* sequences with average fiber period 4.60 Å. Both the 3/1 helix and the gauche structures are not piezoelectric.

When random copolymers of VF<sub>2</sub> and TrFE are made, the TrFE imparts desirable properties to the copolymer. First, the copolymer with over 15 mole % TrFE crystallizes into the  $\beta$  phase directly,<sup>6-8</sup> without stretching, so only poling is needed to make it macroscopically piezoelectric. Second, a higher degree of crystallinity can be obtained,<sup>9</sup> and it is the crystalline portion which is piezoelectric. Third, the ferroelectric transition is accessible for study because it falls below the melting point for over 15 mole % TrFE.<sup>10</sup>

The structure of the high-temperature (paraelectric) phase of

these copolymers is believed to be disordered hexagonal, thereby showing some similarity to the hexagonal structure of pure PTrFE polymer. Studies of the ferroelectric-paraelectric (FE-PE) transition by various experimental methods show that the transition occurs over a wide temperature range and also exhibits a large thermal hysteresis.

A number of nuclear magnetic resonance (NMR) studies have been made of PVF<sub>2</sub> and its copolymers.<sup>11</sup> Most of these measurements have been made on the abundant spin 1/2 nuclei in these materials, namely <sup>1</sup>H and <sup>19</sup>F. However, nuclei with quadrupole moments (such as the deuteron, <sup>2</sup>H or D, spin 1) yield much structural and dynamic information which is difficult to obtain with spin 1/2 nuclei. For this reason we performed a deuteron NMR study<sup>12</sup> of a 70/30 mole % random copolymer of fully deuterated VF<sub>2</sub> (CD<sub>2</sub>CF<sub>2</sub> monomer) and ordinary TrFE (CHF<sub>2</sub>CF<sub>2</sub> monomer). This work complemented <sup>1</sup>H and <sup>19</sup>F NMR studies on the undeuterated 70/30 copolymer made by us<sup>9</sup> and by Hirschinger, Meurer, and Weill.<sup>8</sup>

The deuterated sample was prepared by Janet Kometani and R. E. Cais at ATT-Bell Labs at Murray Hill. We used a Chemagnetics NMR system operating at a deuteron resonant frequency of about 30 MHz, with 90° pulse time of 2.8 microseconds. We used a 90x-90y quadrupolar echo technique to find the spectra and spin-spin relaxation time T<sub>2</sub>. We employed a sequence of such pulse pairs to find the spin-lattice relaxation time T<sub>1</sub>. Unfortunately, the software limited the pulse pair repetition time to 90 milliseconds or longer. At 90 msec separation no saturation could be observed for the paraelectric phase signal, so we were unable to determine T<sub>1</sub>, other than to note that it must be shorter than about 30 milliseconds.

The most striking feature of our results was that, while the ferroelectric crystalline phase showed a static "Pake doublet" powder pattern, the paraelectric crystalline phase showed a pattern of similar shape but 1/3 as wide. This was interpreted as resulting from motional narrowing caused by C-D bonds making tetrahedral angles with the chain axis at all times, but rotating about that axis so as to average the electric field gradient tensor components perpendicular to the chain axis. The structure most likely to give such a spectrum is a disordered helical chain, with kink-3-bond defects<sup>13</sup> running up and down the chain and thereby rotating the C-D bonds by 120° steps about the chain.

To study the dynamics of the paraelectric phase, we are making deuteron T<sub>1</sub> measurements in that phase and will compare these results with predictions of an analytic model presented below. We plan to make Monte Carlo simulations of the chain dynamics to look for deviations from this simple dynamic model.

For a model of the polymer chain in the paraelectric phase, we believe as discussed above that there are short helical chain

segments connected by mobile kink-3-bond defects. As illustrated in Fig. 1, the defect can move to a new location, thereby shortening one (say clockwise) chain segment by one turn and lengthening an adjacent (counterclockwise) segment by one turn. At the boundary, according to the chain-axis projection in Fig. 1, the chain center would move from the center of one equilateral triangle to an adjacent triangle. Because of the constraints of neighboring chains, the chain axis would relax in one or two lattice spaces back to the average position midway between the two triangle centers. These constraints make it unlikely that two kinks will get so close together that in the projection shown in Fig. 1, two adjacent bond projections will lie along the same line. The chain conformation rule then becomes: at every vertex of the chain projection, the chain must either turn through  $120^\circ$  and continue its previous helix, or it must turn through  $120^\circ$  in the opposite sense and begin a new helix wound in the opposite sense.

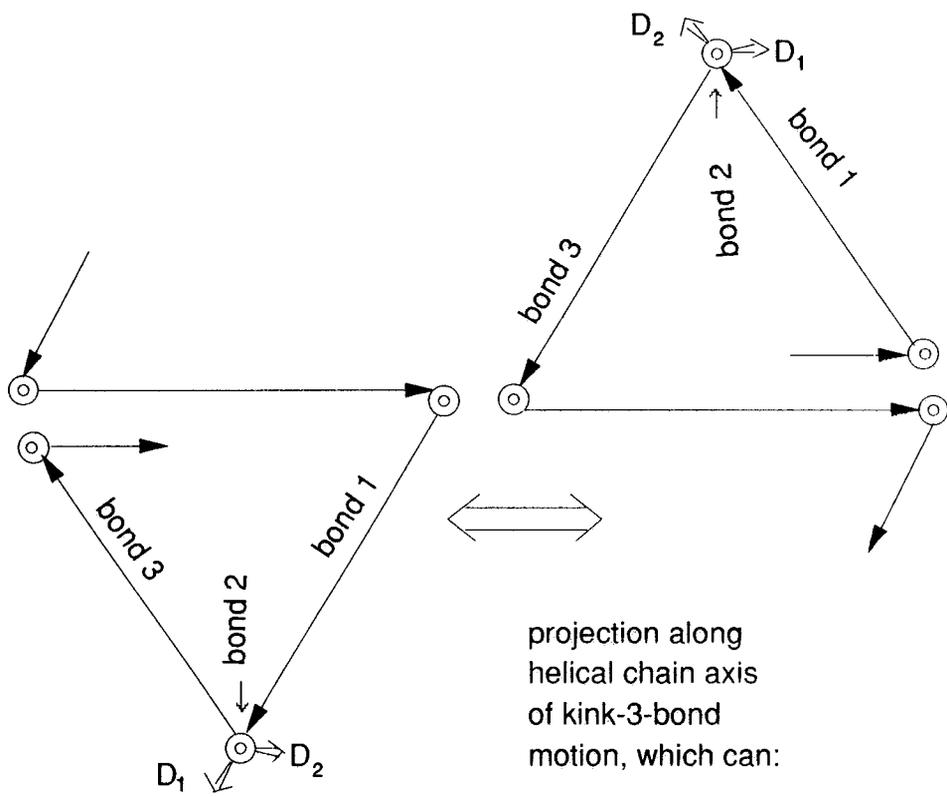
The statistical analysis of the chain static conformation subject to the above rule is quite simple. Each C-C bond having a nonzero projection component in Fig. 1 (in other words, every other C-C bond) can either be in the interior of a helix at zero energy, or can be the boundary between a clockwise and counterclockwise segment at positive creation energy  $\epsilon_c$ . Then each such bond has probability  $[1+\exp(\beta\epsilon_c)]^{-1}$  of constituting a boundary, where  $\beta=1/kT$ .

The dynamic behavior is more complex. A boundary moves by 3 projected bonds (six C-C bonds) during one kink-3-bond displacement, but can only do this if there are no intervening boundaries. If there are two boundaries 3 projected bonds (one turn) apart, they can annihilate and liberate energy  $2\epsilon_c$ . In helix segments long enough to contain four or more zero-energy adjacent projected bonds, it is possible to create a new segment inside this segment of length one turn, at a cost of energy  $2\epsilon_c$ . Because there is considerable distortion involved in moving a kink-3-bond defect one step along a chain, we assume that such motion requires surmounting a diffusion barrier of height  $\epsilon_d$ , with attempt frequency  $f$ .

The analysis becomes simpler if we assume  $\beta\epsilon_c \gg 1$  and  $\beta\epsilon_d \gg 1$ . Then the fraction of boundary-type projected bonds is  $\exp(-\beta\epsilon_c)$ , twice that fraction of C-D bonds reorient by a projected angle of  $120^\circ$  if all these boundaries move one helix turn, and the probability of such motion per unit time is  $f \cdot \exp(-\beta\epsilon_d)$ . Thus the probability  $w$  per unit time that a given C-D bond reorients in a given direction is

$$w = f \cdot \exp[-\beta(\epsilon_c + \epsilon_d)]. \quad (1)$$

The above expression for  $w$  is the starting point of our analysis for spin-lattice relaxation time in the paraelectric phase. The important type of average needed in this calculation is  $\langle V(0)V(t) \rangle$ , where  $V$  represents a component (subscripts omitted



- 1) Move *cw-ccw* boundary up or down 1 turn, as shown;
- 2) Create or destroy pair of boundaries;
- 3) Average  $^2D$  efg components perpendicular to chain.

Figure 1

here) of the electric field gradient (efg) tensor at a typical deuteron site. A given deuteron is assumed to spend equal time at three sites at which  $V=V_1, V_2,$  and  $V_3$ . For finding  $T_1$  we need only consider deviations from the time-averaged value of  $V$ , so  $\Sigma V_i=0$ .

To find the autocorrelation function for  $V$ , we consider the three differential equations for the probability  $P_i(V_i, t)$  that  $V$  has the value  $V_i$  at time  $t$ . These three equations are

$$dP_1/dt = -2wP_1 + w(P_2 + P_3) \quad (2)$$

and two similar equations formed by cyclic permutation of the subscripts. For boundary conditions  $V_1(0)=1, V_2(0)=V_3(0)=0$  the solutions are

$$P_1(t) = [1 + 2\exp(-3wt)]/3, \quad P_2(t) = P_3(t) = [1 - \exp(-3wt)]/3. \quad (3)$$

We use these solutions, and two others obtained for the cases  $P_2(0)=1$  and  $P_3(0)=1$  by cyclic permutation of subscripts in Eq. (3), to evaluate the autocorrelation function:

$$\begin{aligned} \langle V(0)V(t) \rangle &= (1/3)V_1 P_1(0) \Sigma V_i P_i(t) + (2 \text{ corresponding terms}) \quad (4) \\ &= (2/9)(V_1^2 + V_2^2 + V_3^2 - V_1 V_2 - V_2 V_3 - V_3 V_1) \exp(-3wt) \\ &= (2/3)[(V_1 + V_2)^2 - V_1 V_2] \exp(-3wt). \end{aligned}$$

The last expression is obtained by substituting  $V_3 = -V_1 - V_2$ .

To find the efg tensor components in a reference frame in which  $V_{zz}$  is along the static magnetic field  $H_0$ , as required for quadrupole-perturbed NMR, we assume the efg is axially symmetric ( $\eta=0$ ) with its principal axis along the C-D bond which is assumed to make the tetrahedral angle ( $\cos\alpha = -1/3$ ) with the chain axis. If  $H_0$  is along this bond axis,  $eQV_{zz}/h$  (the quadrupolar coupling constant) is 156.7 kHz, which for the  $I=1$  deuteron is 2/3 of the maximum splitting 235.1 kHz of the resonance lines for the deuteron powder pattern. Here  $e$  is proton charge,  $Q$  is deuteron electric quadrupole moment, and  $h$  is Planck's constant.

For arbitrary  $H_0$  direction, it is necessary to rotate the coordinate system from  $z$  along the bond axis through the tetrahedral angle so that  $z$  is along the chain axis. Next the coordinate system must be rotated about the chain axis until the  $y$  axis lies along the projection of  $H_0$  onto a plane perpendicular to the chain axis. Finally the  $z$  axis must be rotated until it is along  $H_0$ . The efg tensor, which starts in a simple diagonal representation, must be transformed by these rotations until it is in the  $H_0$  frame. If  $\theta$  is the polar angle of  $H_0$  relative to the chain axis, and  $\phi$  is the angle between the projections of  $H_0$  and the bond onto a plane perpendicular to the chain axis, the efg components (less their average values) in the  $H_0$  frame are

$$V_{xx} = -(2/3) \cos 2\theta, \quad (5)$$

$$V_{yy} = (1/3) (1 + \cos 2\theta) \cos 2\theta - (2^{1/2}/3) \sin 2\theta \cos \theta,$$

$$V_{zz} = (1/3) (1 - \cos 2\theta) \cos 2\theta + (2^{1/2}/3) \sin 2\theta \cos \theta,$$

$$V_{xy} = (2/3) \cos \theta \sin 2\theta - (2^{1/2}/3) \sin \theta \sin \theta,$$

$$V_{xz} = -(2/3) \sin \theta \sin 2\theta - (2^{1/2}/3) \cos \theta \sin \theta,$$

$$V_{yz} = -(1/3) \sin 2\theta \cos 2\theta - (2^{1/2}/3) \cos 2\theta \cos \theta.$$

For I=1 nuclei in the fast motion regime, the spin-lattice relaxation due to efg fluctuations is

$$1/T_1 = (\pi^2/3w) (eQ/h)^2 \{ V_{zz}^2 + V_{zz}^2 + (V_{xx} - V_{yy})^2 + 4V_{xy}^2 \}. \quad (6)$$

Here  $V_{zz}^2$ , for instance, signifies the square bracket in the last expression of Eq. (4), namely

$$V_{zz}^2 = [V_{xz}(\theta, \theta) + V_{xz}(\theta, \theta + 120^\circ)]^2 - V_{xz}(\theta, \theta) V_{xz}(\theta, \theta + 120^\circ). \quad (7)$$

For a powder sample like ours, Eq. (6) should be averaged over solid angle to account for the various orientations of the crystal axes relative to  $H_0$ . For symmetry reasons, the integration over  $\theta$  need be carried out only from  $0^\circ$  to  $60^\circ$ .

We have not yet performed this integration, but for a rough idea of its value, we evaluate  $T_1$  at the middle of the integration range, namely  $\theta = 90^\circ$ ,  $\phi = 30^\circ$ . We obtain

$$w = 5.68 \times 10^{10} T_1 / \text{sec}^2. \quad (8)$$

So far, we only know that  $T_1 < 30$  msec, so if in Eq. (1) we assume  $f_0 = k\theta_D/h$ , and assume Debye temperature  $\theta_D$  of 300 K, then at our highest temperature of measurement,  $140^\circ \text{C}$ , we have a lower limit on the activation energy sum of

$$(\epsilon_c + \epsilon_d)/k > 3390 \text{ K}. \quad (9)$$

Measurements of the deuteron  $T_1$  in the paraelectric phase are in progress.

This work was supported in part by Department of Energy Grant No. DE-FG06-87ER45292.

## REFERENCES

1. R. G. Kepler and R. A. Anderson, CRC Critical Reviews in Solid State and Materials Science, Nov. 1980, p. 399.
2. M. A. Marcus, Ferroelectrics 40, 29 (1982).
3. A. J. Lovinger, in 'Developments in Crystalline Polymers', (Ed. D.C. Bassett), Applied Science, London, 1981, p. 195.

4. R. R. Kolda and J. B. Lando, *J. Macromol. Sci.*
5. K. Tashiro, K. Takano, M. Kobayashi, Y. Chatani, and H. Tadokoro, *Ferroelectrics* 57, 297 (1984).
6. A. J. Lovinger, T. Furukawa, G. T. Davis, and M. Broadhurst, *Polymer* 24, 1225 (1983).
7. T. Yagi, M. Tatemoto, and J. I. Sako, *Polym. J.* 12, 209 (1980).
8. J. Hirschinger, B. Meurer, and G. Weill, *Polymer* 28, 721 (1987).
9. J. F. Legrand, P. J. Schuele, V. H. Schmidt, and M. Minier, *Polymer* 26, 1683 (1985).
10. T. Yamada and T. J. Kitayama, *Appl. Phys.* 52, 6859 (1981).
11. V. H. Schmidt, *Ferroelectrics* 73, 333 (1987).
12. C. Perry, E. A. Dratz, Y. Ke, V. H. Schmidt, J. M. Kometani, and R. E. Cais, to appear in *Ferroelectrics*.
13. H. W. Spiess, *Colloid and Polym. Sci.* 261, 193 (1983).