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FERROELECTRIC TRANSITION IN 70/30 VF₂/TrFE COPOLYMER STUDIED BY DEUTERON NMR

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Deuteron pulse nuclear magnetic resonance (NMR) spectra and spin-spin (T_2) and spin-lattice (T_1) relaxation times were measured between 20 and 140°C for a 70/30 mol % random copolymer of deuterated vinylidene fluoride (VF₂) and normal trifluoroethylene (TrFE). These "powder" spectra were simulated by the Vold procedure and were dePaked to aid in studying the molecular motions. The spectra show that the ferroelectric (FE) transition occurs between 40 and 140°C with large thermal hysteresis. The dePaked spectra at 140°C are consistent with a dynamically disordered 3/1 helical structure.

INTRODUCTION

Deuteron NMR is a powerful tool for studying phase transitions because the deuteron's quadrupolar interaction with the local electric field gradient (efg) gives clues about local structure and molecular motions. We studied an unoriented copolymer sample with random chain sequences of deuterated VF₂, formula CD₂CF₂, and normal TrFE, formula CHF₂CF₂. This copolymer after annealing is 80 to 85% crystalline, the remainder being amorphous. The crystals, of size 100 to 200 Å, make a transition from an orthorhombic FE phase having a *trans* chain configuration to a hexagonal PE phase with disordered 3/1 helical chains.

Previous NMR studies in piezoelectric polymers were reviewed recently.¹ Since then, Hirschinger, Meurer, and Weill² studied proton and ¹⁹F NMR in VF₂/TrFE copolymers.

We report here the first measurements of the deuteron NMR spectrum and spin-lattice (T_1) and spin-spin (T_2) relaxation times in the family of strongly piezoelectric polymers and copolymers based on poly(vinylidene fluoride). Such measurements have proven useful in studying other polymers also.^{3,4}

EXPERIMENTAL METHOD AND RESULTS

The sample, prepared at AT&T Bell Laboratories, is a chalky-appearing solid. From the NMR standpoint it is a "powder sample" because the crystallites are randomly oriented.

We used a Chemagnetics pulse NMR spectrometer and a magnet giving a dc field H_0 of 4.7 T. We employed the quadrupolar echo sequence, consisting of a 90° pulse followed after an interval τ_2 by another 90° pulse phase shifted by 90° .³ The spectrometer Fourier-transforms the echo, which occurs at a time τ_2 after the second pulse. For obtaining NMR spectra, the shortest possible τ_2 was used. To measure T_2 , we varied τ_2 and analyzed the corresponding change in signal strength. To measure T_1 , two such pulse pairs separated by a variable time τ_1 and having minimum τ_2 were employed. Results were obtained at selected temperatures between 20 and 140°C.

Two special procedures were involved in data analysis. One was computer simulation of the Fourier-transformed pulse response, or "powder pattern," based on the Vold⁵ program. The other, called the dePakeing technique,⁶ calculates from the powder pattern the equivalent single-crystal pattern that would occur if H_0 were along the efg principal axis at each deuteron site.

Powder patterns and corresponding dePaked or simulated powder spectra are shown in Figures 1–6 for three temperatures. Figure 1 shows the powder patterns at 20°C. The crystallites are nearly all in the FE phase, giving a characteristic powder pattern corresponding to little motion and small asymmetry parameter η for the efg, because the efg is caused principally by the C to which the D is bonded and is therefore nearly axially symmetric.

At 80°C for the increasing temperature run, the powder pattern in Figure 2 shows that the FE spectrum coexists with another having one-third of the FE

FIGURE 1 Fourier transformation of ^2D quadrupolar echo at 20°C.

FIGURE 2 Fourier transformation of ^2D quadrupolar echo at 80°C , increasing temperature run.

spectrum width. This indicates that the FE and PE crystalline phases coexist at this temperature.

Figure 3 shows that at 140°C the powder pattern displays only the narrower component characteristic of the PE phase.

The 20°C dePaked spectra in Figure 4 show the splitting expected for H_0 along the C—D bond for each deuteron, with little indication of motional narrowing of the NMR spectrum.

FIGURE 3 Fourier transformation of ^2D quadrupolar echo at 140°C .

FIGURE 4 Depaked ^2D spectrum at 20°C.

At 80°C the dePaked spectrum, shown in Figure 5, has changed considerably. The existence of two separate line pairs with a 3:1 splitting ratio shows more clearly than Figure 2 the existence of a spectrum resulting from two crystalline phases. At 140°C, the dePaked spectrum (not shown) consists only of two lines having the

FIGURE 5 Depaked ^2D spectrum at 80°C, increasing temperature run.

FIGURE 6 Simulated Fourier transformation of ^2D quadrupolar echo at 140°C .

separation of the inner pair of lines in Figure 5, but stronger because all the crystallites are in the PE phase.

Figure 6 shows a Vold-program simulation of the 140°C powder pattern, taking into account structure and motions for the PE phase to be discussed in the next section.

ANALYSIS OF EXPERIMENTAL RESULTS

The narrowness of the PE phase spectrum cannot be caused by static changes in the structure, because the efg depends mostly on the C—D bond length which is not strongly affected by the phase transition. Instead, the dramatic narrowing indicates rapid motion which reorients the C—D bond direction.

As temperature increases, part of the crystalline region transforms to the PE phase. This contributes another pair of lines to the dePaked spectrum, with splitting approximately $1/3$ that of the first pair. The factor $1/3$ is consistent with a dynamically disordered $3/1$ -helical structure,^{7,8} shown (without disorder) in Figure 7. The kink-3-bond hindered rotation³ maintains the tetrahedral angle between the chain axis and the C—D bonds, giving an average efg with axial symmetry along the chain and $1/3$ of the static efg strength. (Hindered rotation of a *trans* chain would give $1/2$ instead of $1/3$ the static efg strength.)

At very high temperatures (above 130°C) but below the melting point, the spectrum shows only the smaller splitting. This means that at these temperatures the whole system is in the disordered 3/1 helical PE phase.

Figure 7 also shows the *c*-axis projection of the *trans* chain which occurs in the FE phase. One can see why these chains pack in an orthorhombic structure. As more and more CD₂ (or CH₂) units are replaced by CHF with increasing TrFE content, the added large fluorine ions reduce the tendency to form the orthorhombic structure, so the FE transition temperature T_c decreases with increasing TrFE content.

The height of the dePaked FE-phase NMR peaks indicates the fraction of material in the FE phase, if the NMR linewidth is independent of temperature, as appears to be the case. The measured height must be multiplied by absolute temperature T to compensate for the Boltzmann factor which governs m_l state populations. The

FIGURE 7 Projections of two chain conformations along chain axis. Top projection is of TGTGTG . . . helical chain, with C, D, and F indicating atoms in top molecular unit and all carbon atoms. Bottom projection is of all-*trans* chain. Atomic radii used are $C = 1.02 \text{ \AA}$, $D = 0.50 \text{ \AA}$, and $F = 1.36 \text{ \AA}$.

FIGURE 8 Relative intensity of signal from ferroelectric (FE) phase, obtained from dePaked signal height for increasing temperature run followed in time by decreasing temperature run.

results of this analysis appear in Figure 8. The very large thermal hysteresis with steeper slope on the decreasing temperature run has been seen in other experiments as well.^{9,10} The higher 20°C signal at the end of the cycle compared to the beginning is probably an annealing effect which increases the fraction of crystalline material at the expense of the amorphous material, as has also been seen in other experiments.¹⁰

So far we have limited relaxation-time data. We measured T_1 at 20, 80 and 130°C and T_2 at 80°C for both crystalline phases.

From the T_2 data in Figure 9, we found a value of 130 μ s in the FE phase and 118 μ s in the PE phase, both at 80°C. The very close spin-spin relaxation rates in the two phases indicates that the same mechanism is dominant in both phases.

Using least square fits to exponential decays to calculate the T_1 values at 20, 80 and 130°C, we obtain $T_1 = 0.16$ s, 0.27 s and 1.0 s at these temperatures respectively for the FE phase and $T_1 = 0.02$ s at 80°C for the PE phase. The T_1 values for the FE phase show longer T_1 at higher temperatures, consistent with our previous ^{19}F T_1 results.¹⁰ The magnetization recovery for the FE phase could be fit better with two T_1 components, as illustrated in Figure 10. The error bars on the T_1 value for the PE phase are quite large, because of the lower limit on pulse pair separation (τ_1) discussed below.

So far we have not identified a contribution to the spectra from the amorphous regions. The NMR software allowed a minimum time interval of 90 ms between solid-echo pulse pairs, so any T_1 much shorter than 90 ms could not be observed. From results for deuterated polyethylene¹¹ we expect that the spin-lattice relaxation time T_1 for this amorphous regime is much shorter than 90 ms. With such a short T_1 , the amorphous region would contribute to the spectrum. Accordingly, we believe this contribution was not seen because it is low and broad, as would be

FIGURE 9 Data for spin-spin relaxation time T_2 determination at 80°C, increasing temperature run. The circles represent the logarithm of the height of the dePaked signal for the outer pair of lines corresponding to the “low-temperature” ferroelectric phase, plotted against the interval τ_2 between the first and second pulse in the quadrupolar echo pulse pair. The squares represent the same data for the inner pair of lines corresponding to the “high-temperature” paraelectric crystalline phase.

expected if different chains in the amorphous region have different mobility and hence different degrees of motional averaging of the efg's responsible for the spectral width.

CONCLUSIONS

From these deuteron NMR measurements in a 70 mol% CD_2CF_2 , 30 mol% CHFCl_2 random copolymer, we have demonstrated the hysteresis of the ferroelectric tran-

FIGURE 10 Data for spin-lattice relaxation time T_1 determination for the ferroelectric phase at 20°C and at 80°C, increasing temperature run. The abscissa shows the time interval τ_1 between two quadrupolar echo pulse pairs. The first pair eliminates the population difference, and the second pair is used to obtain the magnetization recovery signal height “ht” of the dePaked signal. The ordinate shows the logarithm of the equilibrium (long τ_1) signal “ht_{eq}” less the signal “ht”. The data are analyzed in terms of two T_1 components, a long component T_{1l} obtained from the long τ_1 values and a short component T_{1s} obtained by subtracting the long component from the raw data.

sition and have provided strong support for the disordered helical model for the paraelectric crystalline phase. A more complete presentation of the results and their analysis will be presented elsewhere. Further measurements are planned, especially of spin-lattice relaxation time T_1 , to find the rate of motions in the paraelectric phase and to explain why there are apparently two widely different contributions to T_1 .

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