A Nuclear Magnetic Resonance Study of Poled Vinylidene Fluoride/Trifluoroethylene Copolymer

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ABSTRACT: Because poly(vinylidene fluoride) can have large piezoelectric and pyroelectric coefficients, it has been the object of many experiments designed to determine the structures and molecular dynamics associated with the formation and decay of the piezoelectric activity. There is a body of evidence that is consistent with the existence of a ferroelectric phase which, unfortunately, is terminated by a melting rather than a Curie transition. In contrast, vinylidene/trifluoroethylene copolymers exhibit a transition at temperatures well below melting that terminates the polar phase and thereby offers the possibility of better characterization of the ferroelectric phase in a polymer. NMR relaxation data are reported for poled vinylidene/trifluoroethylene copolymer (52/48 mol %). Interpretation of these data in conjuction with comparable results for the unpoled material leads to the following conclusions. The shift to higher temperatures by 10–15 °C of the "ferroelectric" transition upon poling is confirmed. There is improved crystallographic packing in the ordered regions of the poled sample and there is an indication that poling induces an increase in the size of the ordered regions, for which an estimate is made. Molecular motion in the amorphous regions is more constrained in the poled material below the "ferroelectric" transition. The data are consistent with the onset of chain rotation with increase in temperature which may be intimately associated with the "ferroelectric" transition.

Introduction

An earlier report[1] on unpoled and undrawn PVDF/TrFE (52/48 mol %) is the forerunner to this paper, which presents comparable NMR measurements on the drawn and poled version of the copolymer. Special interest centers on the transition at ~70 °C, to which ferroelectric character has been assigned by some authors.[2,3] NMR data on the unpoled copolymer reveal that both amorphous and crystalline regions participate in this transition and the earlier paper speculates first on the degree of stabilization of the ordered state induced by internal electric fields created in the poling process and second on whether or not the induced stability remains after the external field has been removed. This notion of lattice stabilization is supported in X-ray measurements,[3,4] which reveal in lucid fashion the conformational changes that take place as the transition temperature, T, is traversed. In the unpoled material below T, two disordered crystalline phases in trans-planar and 3/1-helical conformations are proposed, which contrast with the one well-ordered trans phase of much reduced spacing (reflecting a much tighter structure) observed in the poled and drawn copolymer. Above T (70 °C for the former and ≃85 °C for the latter) all conformations transform into the 3/1-helical structure characteristic of TrFE. The spacing of the disordered 3/1-helical conformation in the copolymer below T is less than the comparable spacing for neat TrFE, indicating a closer packing of this component in the copolymer. The compact trans-planar conformation in the poled and drawn material survives electrical depoling but reverts to the two disordered crystalline phases following thermal depoling at ~100 °C. In both cases molecular orientation is preserved.[3,4]

Molecular anisotropy can be usefully explored by NMR[5,6] and this additional facility will be exploited in the NMR data to be presented below on the drawn and poled copolymer.

Experimental Section

The essential characteristics of the vinylidene fluoride/trifluoroethylene (52/48 mol %) copolymer, obtained from Daikin Kogyo Co. Ltd., have been listed in earlier reports.[1-4] A sample, coated with Au electrodes, was poled at 25 °C using an electric field of 700 kV/cm. Transmission X-ray photographs revealed modest c-axis orientation in both poled and unpoled films as received. An oriented sample suitable for NMR study was prepared by stacking strips of film, 2.0 × 0.4 cm^2, to a thickness of 0.25 cm in a Kel-F holder attached to a goniometer which monitored the angle, γ, between the preferred c-axis direction and the magnetic field H_0.

The solid echo sequence provided proton free induction decays from which T_2 was obtained on the assumption that the line shape was Gaussian. The second, long, component in two-component decays was Lorentzian. This analysis represents a departure from the procedure used in the first paper where both components were presumed to be Lorentzian. The earlier data have been reanalyzed in those cases where comparisons are drawn with the present measurements. T_1 and $T_{1\rho}$ (H_1 = 10 G) were recorded in the manner described previously.[1] With the exception of studies on the orientation dependence of T_2, all data were recorded for orientation angle $\gamma = 90°$. Signal averaging was effected by means of a Commodore PET computer interfaced to the spectrometer via a Biomation digitizer.

Results and Discussion

T_1, T_2, and $T_{1\rho}$ data (Figure 1) for the poled (and drawn) material differ from the results for the unpoled sample in a number of respects. These differences are illustrated in Figure 2, where T_2 magnitudes and intensities are compared for the poled and unpoled samples. The principal, "ferroelectric", transition temperature T which is manifest in both short (T_{2S}) and long (T_{2L}) components shifts by ~10–15 °C to higher temperatures. In addition, the transition in T_{2S}(poled) is much sharper than T_{2S}(unpoled). At temperatures above T, both sets of data become comparable. Upon decreasing the temperature after thermal depoling this comparability is broadly sustained. The observation that T_2(poled < T_2(unpoled) at temperatures below T is consistent with a tighter crystallographic structure in the poled material but the alternative possibility that the difference may be in part due to anisotropy in T_2 as a function of orientation angle γ must be borne in mind. In any event, the change in T_2 is almost certainly a manifestation of the remaining order noted in the earlier X-ray work for the case of thermally depoled material.[3,4]

The temperature dependence of T_1 and $T_{1\rho}$ in the region of the principal transition lends general support to the conclusions outlined above. Note that a third $T_{1\rho}$ component of magnitude ~5 × 10^{-3} s is resolved for the poled

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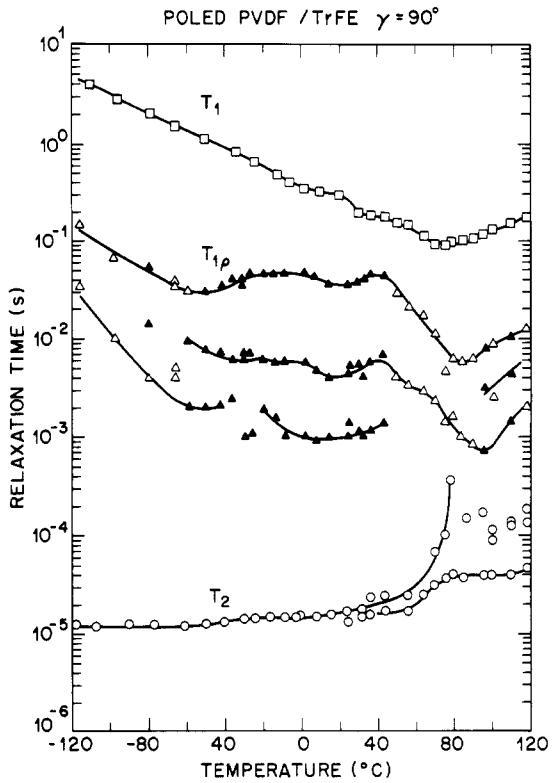

Figure 1. T_1 (60 MHz) (□), $T_{1\rho}$ (H_1 = 10 G) (△, ▲), and T_2 (○) data for poled PVDF/TrFE (52/48 mol %) copolymer. The filled triangles correspond to the case where three components can be resolved. The orientation angle γ = 90° throughout.

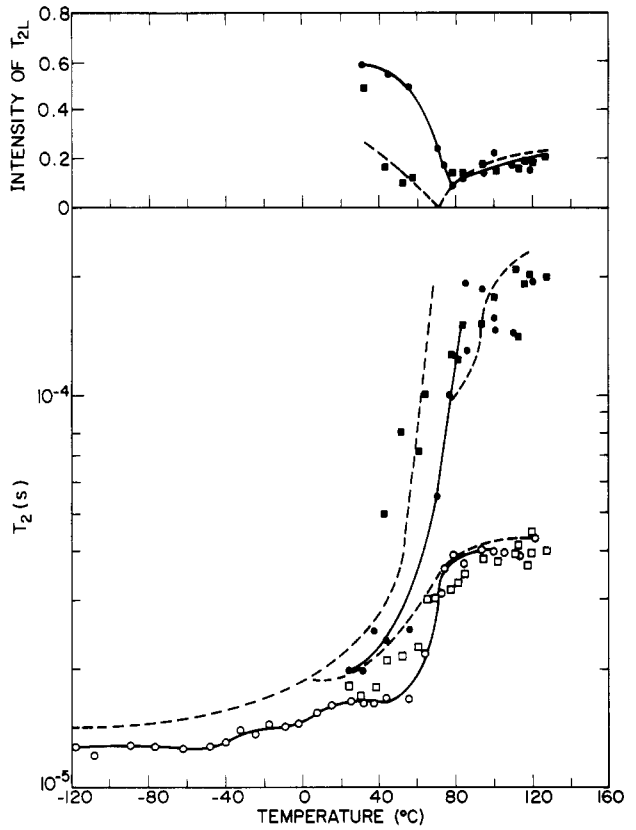

Figure 2. T_2 data for the poled film (○, ●) where unfilled and filled circles denote T_{2S} and T_{2L}, respectively. Corresponding data for the thermally depoled film are denoted by unfilled and filled squares, respectively. The dashed lines correspond to T_2 obtained earlier[1] for the unpoled and undrawn copolymer. T_{2L} intensity data are included.

and drawn material between +40 °C and −40 °C. Consider also the dependence of $T_{1\rho}$ on γ as shown in Figure 3. $T_{1\rho}$

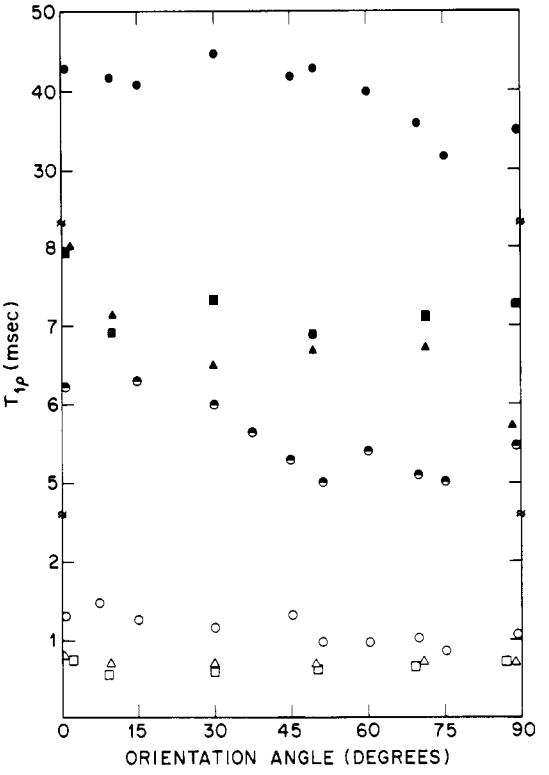

Figure 3. $T_{1\rho}$ data as a function of sample orientation γ in the magnetic field H_0. Unpoled film: $T_{1\rho L}$ (▲); poled film: $T_{1\rho L}$ (●), $T_{1\rho I}$ (◒), $T_{1\rho S}$ (○); Initially poled sample, after successive temperature cycling to +120 and +140 °C: $T_{1\rho L}$ (■), $T_{1\rho S}$ (□). All data were recorded at +25 °C.

for the poled and drawn copolymer exhibits anisotropy in the form of a modest decrease in the magnitude of all three components as γ approaches 90°. The effect is most pronounced for the intermediate component. This anisotropy becomes much less pronounced and virtually disappears after heating to ±140 °C and $T_{1\rho}$ reverts to the two-component decay observed in the unpoled but drawn material as received for which data are also presented in Figure 3. The $T_{1\rho}(\gamma)$ anisotropy observed in the copolymer contrasts with the lack of anisotropy in poled PVDF homopolymer.[8] There are two possible reasons underlying these observations. First, the additional spatial anisotropy accompanying the preferred alignment of b axes in the copolymer may well be reflected in the $T_{1\rho}$ data. Second, spin diffusion may be less effective in averaging regions that are relaxing at different rates on the $T_{1\rho}$ time scale.[6,7] One possibility is that ordered regions *of greater size* are created in the drawn copolymer, particularly when poled. Taking the time scale to be that of the intermediate component, $\sim 5.5 \times 10^{-3}$ s, the effects of spin diffusion would decrease rapidly for linear domain dimensions in excess of ~1.8 nm. The absence of anisotropy in T_1 data and the observation of exponential decay place an upper limit of ~13 nm on domain sizes in the poled and drawn sample.

Figures 4 and 5 portray the anisotropy in T_2 as a function of γ for unpoled and poled samples. It is recalled that both are modestly drawn. The general character of the three sets of data for the unpoled material are consistent with the onset of chain rotation in the crystalline regions as the temperature is raised. This is evident if one assumes that *intra* interactions dominate, in which case T_{2S} is least at γ = 0° and maximum at $\gamma \approx 54°$; for a chain rotating about its long axis the relaxation rate of the transverse component of the magnetization is roughly proportional to $3\cos^2\gamma - 1$, giving $T_{2S} \propto [3\cos^2\gamma - 1]^{-1}$. (The increase in X-ray spacing at T will cause a significant reduction in

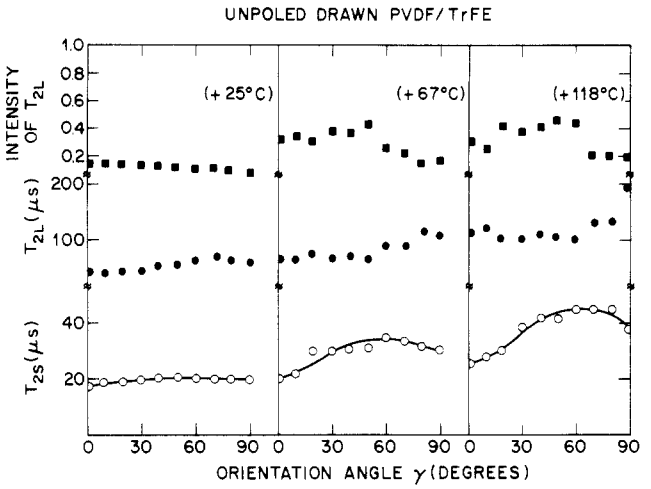

Figure 4. T_2 magnitudes (○, ●) and intensity of long component (■) as a function of sample orientation γ in the magnetic field H_0 for the unpoled drawn PVDF/TrFE (52/48 mol %) copolymer at 25, 67, and 118 °C.

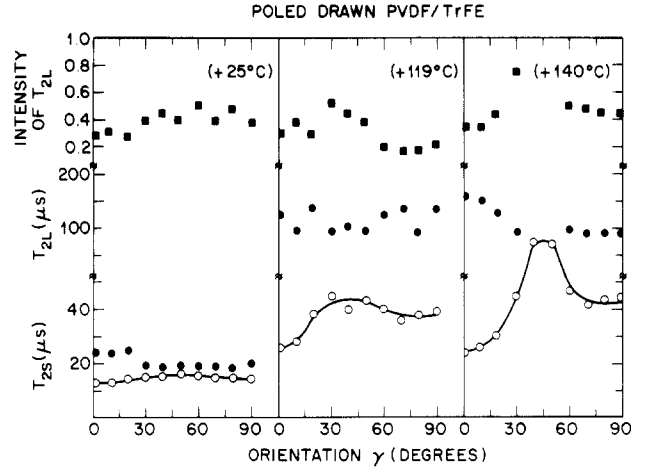

Figure 5. T_2 magnitudes (○, ●) and intensity of long component (■) as a function of sample orientation γ in the magnetic field H_0 for poled and drawn PVDF/TrFE (52/48 mol %) copolymer at +25, +119, and +140 °C.

the *inter* contribution to T_2, thereby enhancing the dominance of *intra* interactions.) Within the constraints of imperfect *c*-axis alignment, which tends to average out the anisotropy in T_2, this expression can adequately describe the observed anisotropy in T_{2S}. It is difficult to ascertain whether or not there is anisotropy in the long, amorphous, T_2 in view of the inaccuracy associated with the decomposition procedures. The probability, for example, that $T_{2L}(90°)$ in the 118 °C data is overestimated is borne out in the correspondingly reduced intensity of T_{2L}. The anisotropy in T_{2S} remains essentially unaltered following heating to +120 °C although it is somewhat more difficult to resolve T_{2L}, which becomes marginally shorter and of slightly lower intensity. This change in T_{2L} is an entirely plausible consequence of thermal annealing.

Turning to the results for the poled and drawn sample (Figure 5), it is first noted that T_{2S} is shorter at all temperatures and angles than in the unpoled material and T_{2L} is shorter at 25 °C. This may result from closer packing in the crystalline regions, as discussed earlier, or more constrained motions in the amorphous regions, or a combined effect of these two reasons. As the temperature is increased through the principal transition temperature, T, the shape of the T_2 vs. γ curve again follows the behavior expected for the onset of crystalline chain rotation about the *c* axis. The fact that the T_{2S} vs. γ peaks at different

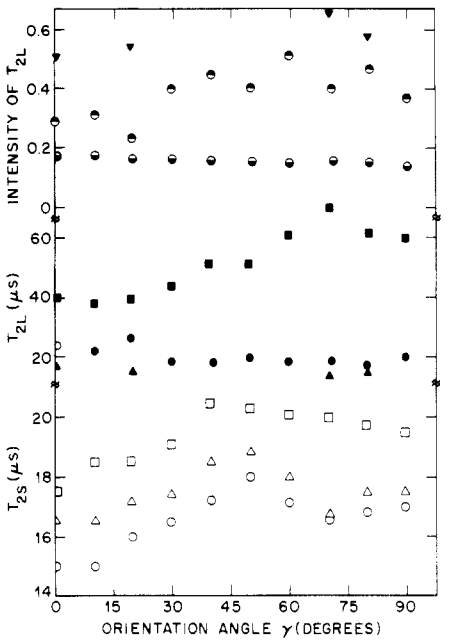

Figure 6. T_2(25 °C) recorded as a function of orientation angle γ for poled and drawn PVDF/TrFE (52/48 mol %) (○, ●), for the poled material after thermal cycling to +120 °C (△, ▲), and for unpoled and drawn copolymer (□, ■). The corresponding intensity data are denoted (◓), (▼), and (◒), respectively.

values of γ for poled and unpoled samples at comparable temperatures (~118 °C) is reminiscent of the way in which anisotropy in $T_2(\gamma)$ manifests different *b*-axis distributions.[8] Unfortunately, the copolymer crystal structure is not simple enough to permit detailed analysis of T_2 in terms of this distribution. Anisotropy in $T_2(\gamma)$ for the poled samples survives heating to temperatures well above T but below the melting point of the copolymer (Figure 6). Thus, thermal depoling effected in this way does not destroy the *c*-axis alignment that is largely responsible for the observed anisotropy in $T_2(\gamma)$. It is doubtful whether changes in the spatial distribution of *b* axis associated with the crystallographic modification accompanying thermal depoling observed in X-ray data[3,4] would have much bearing on the modest anisotropy in $T_2(\gamma)$ at 25 °C. However, it is interesting to note that $T_2(\gamma)$ data for the thermally depoled sample do not revert exactly to the $T_2(\gamma)$ response for the unpoled drawn material as anticipated on the basis of X-ray results. The small discrepancy may be due to a change in the relative amounts of disordered 3/1 helix and trans-planar material in the thermally depoled sample compared with the unpoled drawn sample. Although the two disordered phases have observably different T_2's, they are not sufficiently different as to be accurately resolved. Thus T_{2S} represents a weighted mean and if there is somewhat more of the trans-planar component with the shorter T_2 in the thermally depoled sample, this will lead to an overall reduced T_{2S} compared to T_{2S} for the unpoled drawn sample.

The depoling processes need not involve any change in that part of the distribution of *b* axes viewed by NMR. If one visualizes the poled material in terms of a preferred alignment of dipoles (*b* axes) along the direction of the applied poling field, depoling can proceed through equalization of dipole populations aligned with and against the poling field without change in the *c*- or *b*-axis spatial distribution. Recalling that NMR provides no direct information on the odd moments of the *b*-axis distribution[8,9] (in other words, cannot distinguish up from down), one notes that the technique is totally insensitive to such a change in population. It is again difficult to decide

whether the observed anisotropy in T_{2L} for the poled material is real or whether it is an artifact of the decomposition procedure.

To summarize, NMR data for poled PVDF/TrFE (52/48 mol %) taken in conjunction with earlier results for the poled material give rise to the following conclusions:

(a) The shift to higher temperatures by 10–15 °C of the "ferroelectric" transition upon poling is confirmed. Additionally, the transition becomes sharper.

(b) In the poled material there is improved crystallographic packing in the ordered regions and there is a weak indication that the average ordered domain size is greater. These observations are consistent with the simple notion that the more compact structures are stabilized upon poling.

(c) Molecular motions in the amorphous regions are probably more constrained below the "ferroelectric" transition temperature in the poled sample.

(d) Chain rotation in the ordered regions is activated as the temperature is increased and this may be intimately associated with the onset of the "ferroelectric" transition.

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Registry No. (Vinylidene fluoride)·(trifluoroethylene) (copolymer), 28960-88-5.

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ESR Study on Local Conformations of Polystyrene Spin Adducts Produced by Chlorinated Nitrosobenzene as a Chain-Scission Inducer

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ABSTRACT: Polystyrene (PSt) free radicals were produced in benzene solution by addition of 2,4,6-trichloronitrosobenzene (TCNB) followed by slight warming to 35 °C, and the radicals were trapped by TCNB to form spin adducts, from which ESR spectra were observed. On the basis of analysis of the observed ESR spectra, the spin adducts of three different species of PSt radicals, (A) $\sim CH_2-\dot{C}PhCH_2\sim$, (B) $\sim CHPh-\dot{C}H-CHPh\sim$, and (C) $\sim CH_2-\dot{C}HPh$, were identified. The assignments were confirmed by experiments using α-deuterated PSt. A spectral component observed as a double triplet was attributed to the spin adduct of the radical species B and the component was clearly split further into a quintet with small separation of 0.63 G. This quintet was assigned to the coupling with two meta protons in the trichlorobenzene and two additional δ-protons bonded to the carbon separated by three chemical bonds from the nitrogen having the unpaired electron. That is, long-range coupling was demonstrated in this spin adduct. It was found that an oligomer of styrene (St) showed a spectrum which lacked one component and had a different value for the long-range coupling. On the basis of both the McConnell equation and the Barfield equation for the δ-proton coupling, the local conformation of the spin adduct of the radical B, $\sim CHPh-\dot{C}H-CHPh\sim$, is discussed. It is concluded from the analysis of the observed quintet caused by the long-range coupling that the conformation of the TCNB referred to the main chain was fixed but the δ-protons as well as the main-chain carbon at the δ-site undergo hindered rotation among the three fixed positions.

Introduction

It was found recently that 2,4,6-trichloronitrosobenzene (TCNB) as a radical generator induced main-chain scission of poly(methyl methacrylate) (PMMA) in solution.[1] TCNB has two interesting functions; one is homolytic scission of its C–N bond caused by slight warming to produce a chlorinated phenyl radical, which abstracts a hydrogen from a molecule nearby, and the other is to serve as a spin-trapping reagent, which traps radicals to form nitroxide radicals as spin adducts. In the case of PMMA the spin adduct from primary carbon radical, $\cdot CH_2-C(CH_3)(COOCH)_3CH_2\sim$, was identified. This spectral assignment was confirmed by using α-methyl and ester methyl deuterated PMMA and with the aid of computer simulation. The evidence of main-chain scission of PMMA was provided by the observed decrease of molecular weight after addition of TCNB to the PMMA benzene solution. These facts mean that under relatively mild condition, around 40 °C, chemical degradation is induced by the addition of TCNB to break the main chain of polymers in solution to a substantial extent.

Polystyrene (PSt) is a particularly interesting polymer since it is known to undergo typical cross-linking, unlike PMMA, when γ-irradiated;[2] this is important from the viewpoint of industrial application. Therefore, it is worthwhile to investigate the degradation of PSt induced by addition of TCNB in comparison with degradation of PMMA by identifying the species of radicals produced. Analysis of the ESR spectra observed after the addition of TCNB to PSt in benzene solution provided positive evidence for formation of nitroxide radicals (spin adducts) of PSt radicals, (A) $\sim CH_2-\dot{C}Ph-CH_2\sim$, (B) $\sim CHPh-\dot{C}H-CHPh\sim$, and (C) $\sim\dot{C}HPh$.[3] Formation of radicals A and B, which are not direct products of main-chain scis-

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