Polarization and Structural Transitions of Irradiated Vinylidene Fluoride-Trifluoroethylene Copolymer

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Abstract

The structure and polarization of the vinylidene fluoride-trifluoroethylene copolymer (50/50 mass ratio), a composition in the range that was first reported to show giant electrostriction after electron irradiation, has been studied by neutron scattering under an electric field. In addition, nonirradiated and irradiated samples were studied by thermal analysis and by the thermal pulse method. Both irradiation-induced melting-point and Curie-point depression and broadening were observed, but no field-induced reversible crystal-crystal conversion was observed in the irradiated specimens.

Introduction

It has been reported recently that electron beam irradiated copolymers of vinylidene fluoride and trifluoroethylene [P(VDF-TrFE)] of 50/50 mole ratio VDF/TrFE show an electrostrictive strain in the thickness direction up to 4% [1]. In order to explain this large electric field induced strain it has been hypothesized that the electric field induces a reversible crystalline conversion between crystal phases of different lattice spacings. This copolymer with a composition around 50/50 mass ratio (56/44 mol ratio) differs structurally from the neat PVDF and the copolymers with greater VDF content as it contains two coexisting crystalline phases when melt crystallized [2,3]. One phase is analogous to the trans conformation of the ferroelectric phase of PVDF; the other contains trans and also trans gauche (tg+, tg-) sequences which form a 3/1-helix and has structural properties similar to that of the paraelectric phase. Electron-beam irradiation at around room temperature has been reported to transform the trans phase to a helical crystalline phase similar to the helical paraelectric phase [2]. Irradiation above the Curie temperature has been reported to stabilize the paraelectric phase upon cooling through the Curie temperature of the unirradiated copolymer [1]. The effect of an applied electric field on this paraelectric phase at room temperature has been thought to convert reversibly some of this phase to a more compact phase, presumed to be a trans-like but non-ferroelectric phase, and thus to yield a lattice contraction associated with the electrostriction.

The neutron scattering investigation reported here establishes the temperature dependence of the lattice spacings and diffraction intensities of the phases present in the nonirradiated and irradiated copolymer over a range that includes the amorphous glass transition around -40 °C and the crystalline Curie transition around 70 °C for the ferroelectric phase of the nonirradiated...
copolymers. Neutron scattering measurements on samples under an applied electric field also establishes limits for any field effect on the d-spacing and on the integrated intensity of the diffraction peaks.

**Experimental**

**Materials:** The P(VDF-TrFE) copolymer was received in the form of pellets of irregular sizes and shapes. Each film was made from approximately 3 g of pellet material. The pellets were packed together and pressed between two teflon-coated aluminum foils held to a minimum spacing of approximately 50 μm (0.002 in) by steel spacers, in a hydraulic press with temperature-controlled plattens. The nominal pressing temperature and pressure of 210 °C and 7 MPa respectively were held for about 15 min after which time the hot pressed films were quenched in either ambient air, or in cold water or left in the press to cool to ambient. This yielded films varying in crystallinity that were evaluated for ease of use. Prior to irradiation, 100 nm aluminum electrodes were deposited on both surfaces by vacuum evaporation.

**Irradiation:** Samples were irradiated, in stacks containing up to 10 samples, in a nitrogen-flushed aluminum chamber with a polyimide window. The chamber was placed in the path of a 1 MeV electron beam coming out of a van de Graaf accelerator through an aluminum window, traveling 10 cm through atmospheric air, then passing through an aluminum scattering foil that both expanded and homogenized the beam spatially, then traveling another 40 cm in atmospheric air before entering the sample chamber. The forward scattering by the window and foil and the back-scattering from the bottom of the aluminum chamber contributed some secondary irradiation with an energy distribution below 1 MeV. Small pieces of radiation-sensitive dosimetry film were used to measure the dose absorbed by each sample in the stack during the first three minutes of irradiation. During this time, the dose remained in the linear range of the dosimetry film. Higher desired doses were obtained by continuing the irradiation for an additional time (typically between 30 min and one hour) calculated under the assumption that dose was proportional to irradiation time under fixed irradiation conditions. The investigated dose range was from 20 Mrads to 140 Mrads and the irradiation temperature range was from around 30 °C to around 110 °C. The doses used typically produced a temperature rise of around 5 °C.

**Thermal analysis:** Pieces of the irradiated films were prepared into 12 mg samples and thermally analyzed by modulated dynamic scanning calorimetry (MDSC) at 1°C/min for three heating-and-cooling cycles from −70 °C to 200 °C. Thus relaxations for the glass transition, the ferroelectric transition and crystalline melting could be compared in sequential cycles until equilibrium or reproducible cycles were obtained.

**Neutron scattering:** The neutron scattering experiments were done at the NIST Center for Neutron Research using neutrons of 2.350 Å wavelength. Diffracted intensity in counts vs angle data were collected in both reflection and transmission and were fit by one or two curves, as appropriate for each sample, to estimate the best-fitting intermolecular lattice d-spacings. The angular resolution was ±0.1° and the intensity uncertainty was ±50 counts. Pairs of samples in contact, each 50 μm thick with a beam-exposed cross-sectional area of around 10 cm², were used to obtain diffraction scans with the sample under field (65 V/μm max). This allowed for applying a high voltage to the inner electrodes in electrical
contact while keeping the outer electrodes electrically grounded. Diffraction-angle scans at selected set temperatures were programmed so as to collect diffraction data after a 15 min thermal stabilization time following every programmed change of temperature.

Polarization: Relative polarization measurements were made using the thermal pulse method described elsewhere [6]. A nonzero thickness-averaged polarization shows up as a nonzero (homogeneous pyroelectric) response at long times compared to the thermal transit time. The shape of the response gives an indication of the polarization distribution.

Results

Neutron Scattering: The Bragg scattering peaks for the nonirradiated air-quenched copolymers appear in Fig. 1 for temperatures from below the glass transition to well into the paraelectric state. The curves for temperatures below 65 °C are for the ferroelectric material. They show two peaks, in agreement with earlier X-ray findings [3]. As previously suggested, these peaks probably come from crystallites that are a mixture of a crystalline phase with the 3/1-helix conformation (at 14.56°) and another crystalline phase with the trans conformation (at 14.96°) identified with the polar phase of PVDF. Both phases have hexagonal symmetry [3]. The composition used here thus shows the two previously observed crystalline forms [2,3]. Figure 1 shows that, as the Curie temperature is approached, the intensity of the trans conformation decreases while that of the helical conformation becomes more pronounced. For temperatures greater than 65°C, a single diffraction peak is observed that must come from the 3/1-helical paraelectric phase. This peak indicates quite good order for this phase.

Figure 2 shows neutron Bragg peaks at several temperatures from an air-quenched copolymer film irradiated at 75 °C to a dose of 70 Mrads. Only a single peak is seen and it shows a typical temperature dependence, namely a shift to smaller angles with increasing temperature. As the angle where this peak is seen is greater than the angle where the trans peak was seen in Fig. 1, and the peak shifts continuously with increasing temperature until it overlaps the paraelectric peak, we identify it with the paraelectric or a paraelectric-like phase for all temperatures shown. This behavior is in sharp contrast to the thermal behavior of the nonirradiated sample that shows a marked change in the Curie transition region.

Figure 3 shows a similar set of diffraction peaks for another copolymer sample, this one irradiated at 35 °C to a dose of 100 Mrads. Again, the appearance of a single peak suggests that only the higher temperature 3/1-helix phase occurs in the entire range of temperatures shown. The film subjected to the greater irradiation of 100 Mrads exhibits a larger intermolecular lattice d-spacing. In order to arrive at a more conceptual view of the changes in the lattice dimensions, each diffraction curve was fit with one or two gaussians. The best-fitting peak positions gave the lattice spacings in Figs 4, 5, and 6 to a standard uncertainty of ±0.1 Å (the size of the symbols). Figure 4 shows the lattice spacings vs temperature. The nonirradiated sample displays two d-spacings corresponding to the 3/1 helix (4.67 Å) and trans lattice (4.53 Å). The spacings show similar thermal expansion below the Curie temperature and go into a single spacing (corresponding to the paraelectric phase) above it. In contrast, a single paraelectric-like d spacing is observed in the whole temperature range for both irradiated samples. Figure 4 also shows that
both crystalline phases of the nonirradiated film have a thermal expansion coefficient above the glass transition that increases with increasing temperature. This effect becomes more pronounced as the Curie temperature is approached suggesting that precursors of the transition appear in the thermal expansion below the Curie temperature.

The irradiated samples exhibit a larger d-spacing than the nonirradiated film, with the higher dosed sample having the larger spacing. The thermal expansion from the glass transition temperature to room temperature is seen to be very similar for the irradiated and nonirradiated samples. However there is no indication of a Curie transition in either of the irradiated samples. We note that above 70 °C the lattice spacings of the irradiated films are greater than those of the nonirradiated film. This could also indicate that irradiation produces a thermodynamically nonequilibrium distribution of conformations, that may result in an expansion of the lattice dimensions. We also note that upon cooling of the 35 Mrad sample (the inverted triangles in Fig.4), the d-spacings obtained are slightly smaller than those obtained upon heating. Note that DSC measurements show a partial recovery of the ferroelectric phase upon cooling from the melt. This is consistent with the relaxation of gauche conformations or annealing to trans conformations in the irradiated samples during heating which would contract the lattice.

Figure 5 compares d-spacings for a nonpoled sample and for a sample poled at room temperature with a poling field of 120 V/μm. The poled sample shows two lattice d spacings correspond to mixed phases of the 3/1- helical and the trans crystalline forms. For samples that are highly poled, it has been shown with x-ray diffraction[3] that both the helical and trans crystalline forms are transformed into a more tightly packed trans form. However, in our case the d-spacings of the poled sample are slightly greater than those for the nonpoled one. This is in spite of the high poling field. The most marked difference in thermal expansion occurs at about 290 K where both the 3/1- helical and trans crystalline phases of the poled sample show a constant or continuous thermal expansion in contrast to the sharp increase in expansion noted for the unpoled sample. Interestingly, the poled sample shows a jump in lattice spacing for both of the crystalline phases whereupon the paraelectric phase is obtained. Thus the application of the poling electric field, while not converting the 3/1 helical phase to a trans phase, appears to have electrically annealed or altered the helical phase to show a more uniform thermal expansion extending into the transition region. This is in contrast to the slower and broader change occurring at lower pre transition temperatures for the unpoled sample. This trend is expected for the trans crystal of the poled sample and has been reported only for the trans phase in previous work [3].

The lattice spacings also were measured for a pair of irradiated films with an applied field of 63.6 V/μm while heating over the temperature range from 200 K (-73 °C) to 375 K (102 °C). This pair was irradiated at 95 °C to 70 Mrads and shows a larger lattice spacing than those samples presented above. The observed trends are very similar to those seen for irradiated samples that where not held under field. During the cooling cycle the field was switched off. We notice a small decrease in lattice spacing very similar to that which occurred in the previous samples (Fig. 4) As described previously, this effect may be due to supercooling of the sample or to annealing effects that may convert a fraction of the gauche conformations to trans and reduce the lattice d spacing. It would appear that, if a large electrostriction were present in a sample

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under a constant applied voltage, a decrease in average d spacing should be observed. Also, no change in intensity or shape of the diffraction curve was observable. As this study is preliminary, we make the following cautionary comments. Our film samples were air quenched and not slowly cooled in order to maximize crystallinity. This was done in order to produce films of good mechanical integrity. Irradiated films of these thermal histories have been shown to have an electrostrictive strain of 1% or greater for the field used of 63.6 V/µm and a value of 2% strain at 120 V/µm, about half those reported for the slowly crystallized films [7]. For such macroscopic strains, we expected measurable field-induced neutron-scattering changes related to a decrease in average crystalline lattice d-spacing.

Thermal analysis: The Curie and melting temperatures, as expected, were found to be depressed by the electron irradiation. We mention only that the downward shifts in those temperatures were observed in all three thermal cycles even though the temperature limit of 200°C (90°C above the depressed melting temperature) was reached in the first cycle. This indicates that permanent changes occurred in the molecular chain.

Polarization: Thermal pulse measurements in nonirradiated samples after the application of a field comparable to the coercive field show a large step response indicative of nominally uniform ferroelectric polarization. Similar measurements on irradiated samples, in contrast, showed weaker response by two orders of magnitude indicative of only a small and nonuniformly distributed field-induced polarization. These results are consistent with irradiation destroying the ferroelectricity at room temperature.

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References

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