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A New Class of Ferroelectric Polymers, the Odd-Numbered Nylons

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## A NEW CLASS OF FERROELECTRIC POLYMERS, THE ODD-NUMBERED NYLONS

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**Abstract** The thermal stability of the piezoelectric response of a new class of ferroelectric polymer, the odd-numbered nylons has been studied and the behavior compared with the thermal stability of piezoelectricity in poly(vinylidene fluoride). FTIR absorbance spectroscopy and an x-ray diffraction study show that under high applied electric fields a 90° dipole switching mechanism orients amide dipoles in the field direction, prior to 180° switching under repeated reversals of field.

### INTRODUCTION

A general understanding of the piezoelectric, pyroelectric and ferroelectric behavior of polyvinylidene fluoride (PVF<sub>2</sub>) has been attained (1,2), and it is clear that these properties originate from the aggregate properties of polar crystallites with preferred dipole orientation.

Many other polymers, following appropriate poling treatment, have been shown to be piezoelectric, but until recently no studies to observe the phenomenon of ferroelectricity in these materials have been made. Over the past several years, a series of studies of the odd-numbered nylons, such as Nylon 11 or Nylon 7, has been carried out in this laboratory (3-6). It has been shown that these polymers are piezoelectric, with fairly large piezoelectric coefficients  $d_{31}$  and  $e_{31}$ , in magnitude second among the piezoelectric polymers only to PVF<sub>2</sub> and its copolymers at room temperature. The amide group has a large dipole moment and the all-trans conformation, reported for most nylon crystal structures, would give a large net chain dipole moment perpendicular to the chain axis for the odd numbered nylons, with a dipole density magnitude proportional to the number of amide groups per unit length along the chain. Thus, the net dipole moment will be larger for odd-numbered nylons with a smaller number of carbon atoms in the repeat mer.

Studies of the piezoelectric properties of these polymers are important not only in their own right, but because they provide a way to test the generality of concepts advanced to explain the properties of PVF<sub>2</sub>. One significant difference between the odd-numbered Nylons and PVF<sub>2</sub> is the glass transition temperature (T<sub>g</sub>), which for PVF<sub>2</sub> is below room temperature (~ -50°C), while for most of the odd-numbered nylons is above room temperature (in the range 45°C to 60°C). Another difference is the nature of the dipole, which for the polyamides is associated with a hydrogen bond, which has been reported to be stable even at quite high temperatures.

Recently, very clear D-E hysteresis characteristics in Nylon 11 and Nylon 7 were observed (7,8), together with polarization switching

transients, and the remanent polarization measured was found to be  $\sim 50$  mC/m<sup>2</sup> for Nylon 11 (comparable to PVF<sub>2</sub>) and 86 mC/m<sup>2</sup> for Nylon 7, this higher value being anticipated on the grounds of the higher chain dipole density. Polarization switching was found to be accomplished within  $\sim 20$  ms.

To determine directly the effect of electric field and subsequent annealing on dipole direction in the odd-numbered nylons, an FTIR absorbance study combined with an x-ray diffraction investigation was carried out.

### EXPERIMENTAL

The nylon films used were prepared by quenching from temperatures above the melting point (210°C for Nylon 11 and 240°C for Nylon 7) into an ice bath. These quenched films were uniaxially stretched to a draw ratio of 3:1 at room temperature to a final film thickness between 10 to 30  $\mu$ m. Gold electrodes were evaporated onto the film.

The films were poled at room temperature in a silicon oil bath using a series of triangular shaped electric field pulses with a period of 1000 seconds and a maximum field of 200 MV/m. Before poling, the films were subject to a static electric field of 150 MV/m for several hours to field sweep mobile ions and reduce conductivity. Annealed films were prepared by annealing at 185°C for Nylon 11 films and 200°C for Nylon 7 films for two hours.

For purposes of comparison, polarized films of PVF<sub>2</sub> were also prepared using the same polarization techniques. The dielectric constant  $\epsilon$ , piezoelectric strain and stress coefficients,  $d_{31}$  and  $e_{31}$ , and elastic modulus of polarized Nylon 11, Nylon 7 and PVF<sub>2</sub> films were measured at 104 Hz at temperatures from room temperature up to the melting point, using a Rheograph Solid® (Toyo Seiki, Japan). Infrared spectra were obtained using a Perkin Elmer FTIR spectrometer (model 1720-X), these film samples being sufficiently thin to ensure the Beer-Lambert law applied. Flat film x-ray diffraction photographs were also taken using nickel-filtered CuK $\alpha$  radiation.

### RESULTS AND DISCUSSION

The piezoelectric strain coefficients  $d_{31}$  were measured for unannealed and annealed films of Nylon 11, Nylon 7 and PVF<sub>2</sub>, at temperatures from room temperature to temperatures close to the melting point. These results are shown in Figures 1 and 2.

In Figure 1, a rapid increase in  $d_{31}$  from values  $\sim 2$  pc/N to values exceeding 15 pc/N is observed for Nylon 11 films (both annealed and unannealed) as the temperature rises above the glass transition temperature. This compares with a similar rapid increase in the piezoelectric coefficients of PVF<sub>2</sub> known to occur at the glass transition temperature ( $T_g \sim -55^\circ\text{C}$ ). The values for  $d_{31}$  for Nylon 11 obtained (15 pc/N to 20 pc/N) at temperatures above  $\sim 140^\circ\text{C}$  are comparable to those values obtained for PVF<sub>2</sub> at temperatures more than 80°C above the glass transition temperature.

Further, we notice that for films annealed for two hours at 5°C below the melting point, the piezoelectric response is decreased from  $\sim 20$  pc/N to stable values of  $\sim 15$  pc/N at temperatures above 140°C. At room temperature the response is not decreased at all from the initial values of the unannealed samples. This confirms the hypothesis proposed

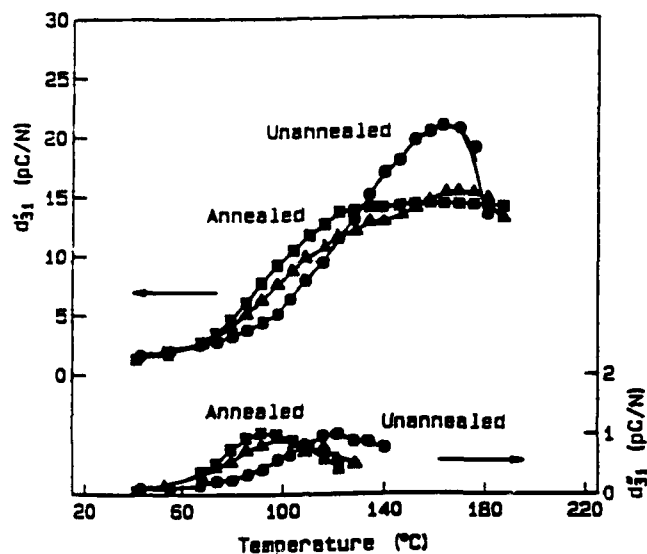


FIGURE 1 Annealing effects after poling on the  $d_{31}$  versus  $T$  characteristics of Nylon-11.

that the dipole orientations associated with hydrogen bonded sheet structures is extremely stable, even at very high temperatures, and so the piezoelectric activity associated with these materials is very thermally stable. Similar behavior was observed for Nylon 7.

Poled films of  $PVF_2$ , with measured piezoelectric strain coefficients  $d_{31}$  exceeding 20 pc/N, were annealed at 175°C for two hours and cooled to room temperature, to compare with the nylon films. In Figure 2 the

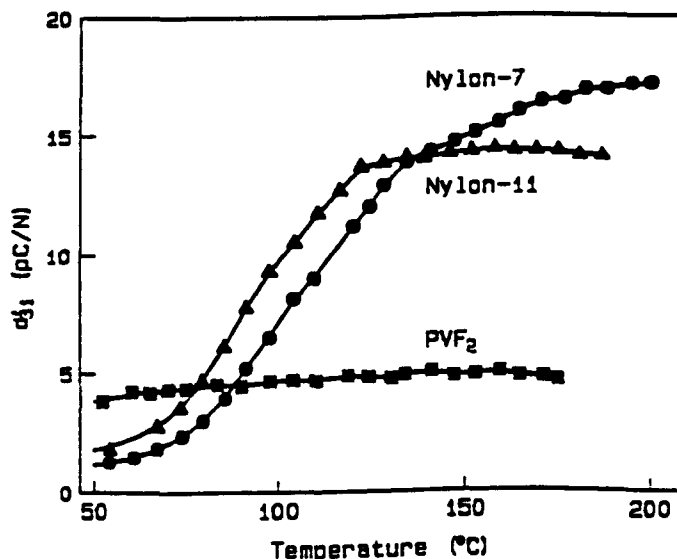


FIGURE 2 Piezoelectric strain constant ( $d_{31}$ ) versus  $T$  characteristics of Nylon-11, Nylon 7, and  $PVF_2$  films.

measured  $d_{31}$  values of annealed films of Nylon 11, Nylon 7 and  $PVF_2$  are compared. The striking difference in thermal stability between Nylon 11 and Nylon 7 with their hydrogen-bonded sheet structures and  $PVF_2$  with  $CF_2$  dipoles which readily randomize at elevated temperatures to give much smaller piezoelectric coefficients, is evident.

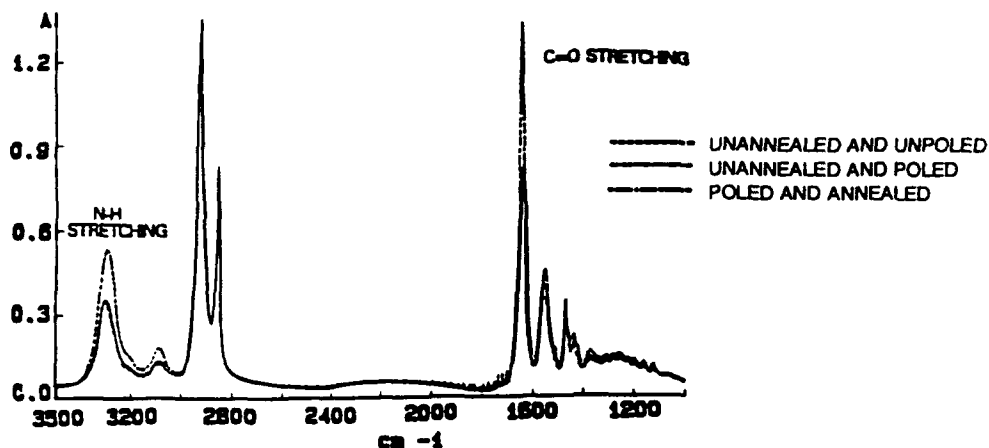


FIGURE 3 Infrared spectra of unannealed and unpoled, unannealed and poled, and poled and annealed Nylon 11 films.

In Figure 3, the results of the polarized FTIR absorbance spectroscopy study are shown for three samples; unannealed and unpoled, unannealed and poled, and poled and annealed. The incident beam is perpendicular to the plane of the film and is polarized in a direction perpendicular to the draw direction of the samples. The largest differences observed is for the C=O stretching modes at  $1650\text{ cm}^{-1}$  and the N-H stretching modes at  $3300\text{ cm}^{-1}$ . The peak heights associated with these modes are much less for the poled films, both unannealed and annealed, than for the unpoled films, which is the result expected if these amide dipoles are initially predominantly oriented in the plane of the film perpendicular to the draw direction and after poling are predominantly oriented perpendicular to the plane of the film and also perpendicular to the draw direction. Further, we observe very little difference in the absorbance spectra and, in particular, in the peaks corresponding to the NH and C=O stretching modes for unannealed and annealed samples. Thus, this result further confirms the hypothesis that the amide dipoles are not easily reoriented, even after annealing at  $5^{\circ}\text{C}$  below the melting point for two hours. A number of x-ray diffraction photographs were taken both for unpoled annealed and poled annealed films of Nylon 1. All x-ray reflections could be indexed using the unit cell proposed by Hasegawa (9).

Figures 4 and 5 show x-ray diffraction flat film photographs, together with schematic representations, for Nylon 11 samples, unpoled and annealed, and poled and annealed. To obtain Figure 4, Nylon 11 films unpoled but annealed were oriented with the incident x-ray beam parallel to the plane of the film and perpendicular to the draw direction. The meridian corresponds to the direction of draw and the equatorial line corresponds to a direction normal to the plane of the film. The strong equatorial reflection with a measured d-spacing of  $3.89\text{Å}$ , corresponds to the spacing between hydrogen bonded sheets, and can be indexed as the (020) reflection. The meridional reflections are  $00l$ . This diffraction pattern shows that a three-dimensional crystallite texture is obtained for Nylon 11 films, quenched, drawn and annealed, with a hydrogen bonded sheet structure oriented in the plane of the film, as well as the usual c-axis orientation. This observation was first made by Norbert.

To obtain Figure 5, poled annealed films of Nylon 11 were oriented with the incident x-ray beam perpendicular to the plane of the film and perpendicular to the draw direction. The meridian corresponds to the

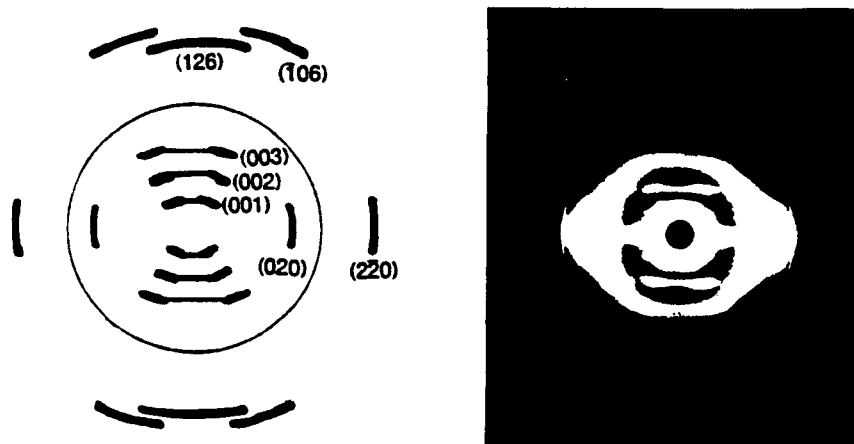


FIGURE 4 The wide angle x-ray diffraction pattern of unpoled but annealed Nylon 11 film, incident x-ray beam parallel to plane of film.

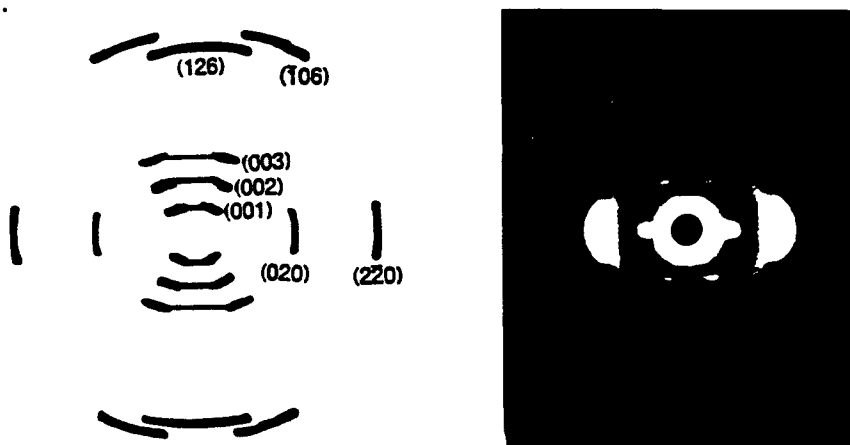


FIGURE 5 The wide angle x-ray diffraction pattern of poled and annealed Nylon 11 film, incident x-ray beam perpendicular to plane of film.

direction of draw and the equatorial line corresponds to a line in the plane of the film perpendicular to the draw direction. The most striking observation made in a comparison of Figure 4 with Figure 5 is that the diffraction patterns are essentially identical, even though the geometry used to obtain these diffraction patterns are related with respect to each other by  $90^\circ$ , and even though a three-dimensional texture is apparent. From the discussion regarding the crystallite preferred orientation observed in Figure 4, it is clear that the same comments apply to Figure 5. In other words, Figure 5 shows a preferred crystallite orientation, after poling, with the hydrogen bonded sheets normal to the plane of the film.

Since the FTIR absorbance study showed that the orientation of N-H and C=O bonds was unaffected by the annealing process, and this is confirmed by the fact that no substantial depolarization is observed after annealing, it can be concluded that the effect of application of the high electric field during the poling process results in a  $90^\circ$  rotation of amide dipoles away from the plane of the film towards the field direction, that is, perpendicular to the plane of the film. The hysteresis loops of electric displacement versus field for Nylon 11 and Nylon 7 reported in a previous publication, and demonstrating for the

first time ferroelectricity in these materials, correspond to repeated 180° reversals of electric field, to give 180° reversals of bulk polarization. This could be achieved by 180° rotations of amide dipoles under reversals of electric field, once the hydrogen-bonded sheet structure perpendicular to the plane of the film and parallel to the applied electric fields has been attained.

### CONCLUSIONS

A new class of ferroelectric material, the odd-numbered nylons, has been studied from the perspective of the thermal stability of remanent polarization and the piezoelectric response at elevated temperatures. Films poled and then annealed at temperatures close to the melting point show an unchanged piezoelectric response on cooling to room temperature. Repeated measurements of piezoelectric response at elevated temperatures up to the melting point for poled and annealed Nylon 11 and Nylon 7 films show an unchanged response. This behavior is different from that observed either for PVF<sub>2</sub> or copolymers of PVF<sub>2</sub>, when either depolarization occurs at elevated temperatures below the melting point or a Curie transition temperature is observed. In either case, the piezoelectric response is drastically reduced following exposure to elevated temperatures. Further, a sharp increase in piezoelectric response for poled annealed Nylon 7 and Nylon 11 films is observed at the glass transition temperature (~60°C), a similar behavior to that observed for PVF<sub>2</sub> (at ~ -55°C). An FTIR study combined with an x-ray diffraction study showed that; for the unpoled nylon films the amide dipoles were in the plane of the film; that under a high applied field these dipoles rotated 90° to orient and form hydrogen bonded sheets perpendicular to the plane of the film; and that under repeated reversals of electric field such as were imposed in the hysteresis study, 180° dipole rotations were consistent with the crystal structure.

### ACKNOWLEDGEMENTS

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