

High-Temperature Characteristics of Nylon-11 and Nylon-7 Piezoelectrics

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Received March 12, 1991

ABSTRACT: The piezoelectric strain constant, d_{31} , stress constant, e_{31} , and electromechanical coupling coefficient, k_{31} , of Nylon-11 and Nylon-7 films were measured up to a temperature close to their melting points. They were found to exhibit their highest values and, in addition, excellent thermal stability at temperatures between 100 and 200 °C. Maximum stable values were $d_{31} = 14$ pC/N and $e_{31} = 21$ mC/m² for Nylon-11, and $d_{31} = 17$ pC/N and $e_{31} = 27$ mC/m² for Nylon-7. Corresponding values of k_{31} were 0.049 and 0.054. Poled and then annealed Nylon samples exhibited little decay of these values even after annealing at 185 and 200 °C for Nylon-11 and Nylon-7, respectively, while poly(vinylidene fluoride) samples showed a large decay in response, decreasing to $d_{31} = 4.9$ pC/N, $e_{31} = 11$ mC/m², and $k_{31} = 0.019$ after annealing at 175 °C. The extraordinary stability of the piezoelectric activity of these Nylon samples was considered to be related to ferroelectric reorientation of the amide group dipoles followed by closer packing of the hydrogen-bonded sheet structure in the crystalline regions after the annealing treatment.

Introduction

Compared with the large number of studies of Nylons in terms of their molecular structure and elastic characteristics, studies of the piezoelectric characteristics of Nylons have been confined to restricted groups of researchers.¹⁻⁹ The first significant piezoelectric response (piezoelectric strain constant $d_{31} \approx 3.0$ pC/N) of a poled Nylon-11 film was reported by Newman et al. in 1980.² Recently, our laboratory has been studying the piezoelectric and ferroelectric characteristics of odd Nylons. Scheinbeim³ reported that the piezoelectric response of poled, melt-quenched, Nylon-11 films continued to increase rapidly with increasing temperature to a value of ~ 12 pC/N at the maximum measurement temperature of 107 °C. Mathur et al.⁵ reported that the piezoelectric stress and strain constants (e_{31} and d_{31}) showed hysteresis-like loops when uniaxially oriented Nylon-11 films were polarized under a series of positive and negative poling fields. In addition, studies of Nylon-11 films crystallized from solution under high electric fields showed d_{31} values of 7.1 pC/N at room temperature.⁶ Wu et al.⁷ studied the piezoelectric response of poled Nylon-9 and Nylon-11 films. More recently, we discovered that melt-quenched and cold-drawn Nylon-11 films with three-dimensional order exhibit clear ferroelectric behavior in electric displacement versus electric field (D - E) hysteresis studies.^{8,9}

As far as the ferroelectric behavior and remanent polarization are concerned, Nylon-11 and Nylon-7 show properties comparable with those of poly(vinylidene fluoride) (PVF₂). The question arises as to why the piezoelectric constants of these odd Nylons are small compared with those of PVF₂. To answer this question, it is important to note the large difference in their glass transition temperatures, T_g . The values of T_g were reported to be 68¹⁰ and ~ 50 °C^{11,12} for Nylon-11 and PVF₂, respectively. If we compare piezoelectric constants at room temperature, we find that this is ~ 50 °C below and 70 °C above T_g for Nylon-11 and PVF₂, respectively. It should be noted that d_{31} for PVF₂ at a temperature of -100 °C (that is ~ 45 °C below the glass transition temperature) is only ~ 1.7 pC/N, so that the values of d_{31} for Nylon-11 and Nylon-7 at comparable temperatures with respect to the glass transition temperature are actually quite high. It is therefore necessary to obtain the

piezoelectric constant data above T_g for the odd Nylons in order to compare them to PVF₂. We note that the piezoelectric constants, d_{31} and e_{31} , and dielectric constant rapidly increase with increasing temperature above T_g .^{3,7} It is also well-known that the dielectric constant steeply increases above T_g at higher temperatures due to ionic conduction. In fact, above the glass transition temperature, the ionic conduction in the Nylons becomes so large that the automatic measurement system used stopped due to charge amplifier saturation caused by the large dc offset current. In manual operation, the measurement also became impossible for the same reason. We tried several methods for performing the measurements above the glass transition temperature of the odd Nylons. Finally, we employed three simple and adequate methods: field sweeping of the mobile ionic species, use of a dc blocking capacitor to the input of the charge amplifier, and use of higher frequency measurements. We were then able to measure the piezoelectric constants of Nylon-11 and Nylon-7 up to a temperature close to their melting points ($T_m \approx 195$ °C for Nylon-11 and $T_m \approx 235$ °C for Nylon-7).

The present study demonstrates the excellent high-temperature characteristics of the piezoelectric responses (d_{31} and e_{31}) of Nylon-11 and Nylon-7 film samples compared with those of PVF₂, which were also measured up to the melting point. In addition to the piezoelectric characteristics, the temperature dependences of the modulus and dielectric constant were also measured.

Experimental Section

The Nylon films used in this study were prepared by melting the Nylon powder between aluminum foils in a hot press at 210 and 240 °C for Nylon-11 and Nylon-7, respectively. Then, the molten films were quenched by placing them into an ice bath. The quenched films were then uniaxially stretched to a draw ratio of 3:1 at room temperature. The final film thickness of the sample was 10–30 μ m.

Gold electrodes (area of 12–24 mm²) were evaporated on opposing surfaces of the film after stretching. The evaporation process was carried out carefully in order to avoid heating (annealing) the samples.

Poling of samples was carried out at room temperature by applying a triangular-shaped electric field pulse, with a maximum amplitude of 200 MV/m, to the samples, so as to determine their D versus E characteristics. The samples were placed in a silicone oil bath for these measurements and the period of the triangular

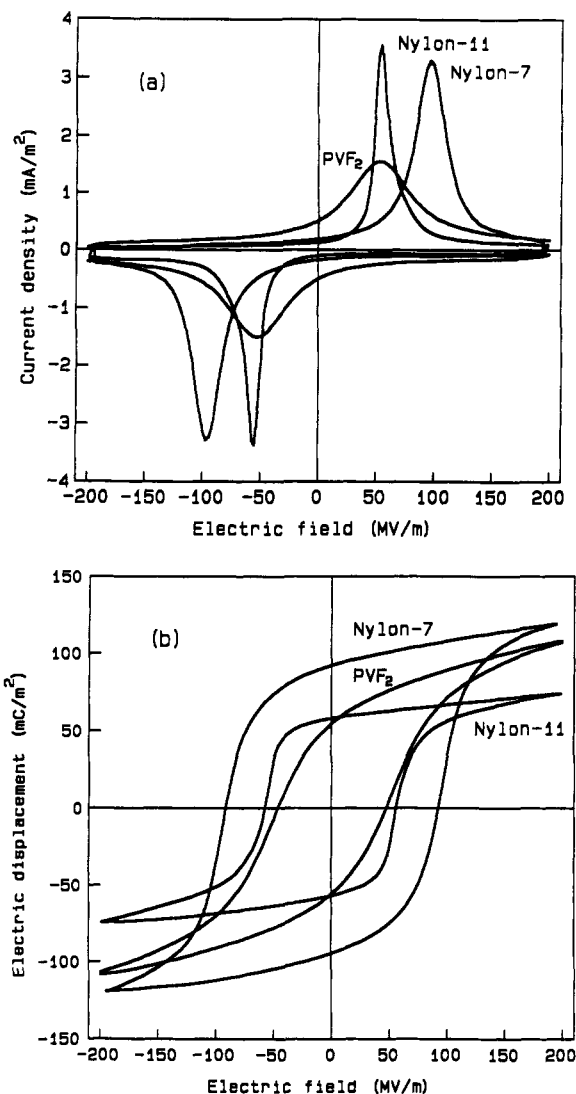


Figure 1. (a) Current density versus electric field and (b) electric displacement versus electric field for three kinds of samples: Nylon-11, Nylon-7, and PVF₂ films. These characteristics were measured at room temperature.

voltage wave form was 1000 s. Before the poling procedure, the samples were pretreated by applying a static electric field of 150–180 MV/m for a few hours for the purpose of field sweeping out most of the mobile ionic species.

The dielectric constant, ϵ , piezoelectric strain constant, d_{31} , piezoelectric stress constant, e_{31} , elastic modulus, c , were measured at 104 Hz using a Rheograph Solid (Toyoseiki). At higher frequencies, the dielectric constant was measured using an impedance analyzer (HP 4192A) at 1, 10, and 100 kHz.

Operation of various functions in the system was consigned to a microcomputer.

Results and Discussion

1. D-E Hysteresis Characteristics. Parts a and b of Figure 1 show the current density, J , and electric displacement, D , as a function of electric field, respectively, for three kinds of samples: Nylon-11, Nylon-7, and PVF₂. These measurements were performed at room temperature. The Nylon samples exhibit a much higher current density peak at the coercive field than PVF₂. The remanent polarizations, P_r , of the present samples were 58, 93, and 55 mC/m², and the coercive fields, E_c , were 56, 92, and 46 MV/m for Nylon-11, Nylon-7, and PVF₂ samples, respectively.

From the unit cell parameters^{13–15} and the value^{1,16} of the dipole moment of the amide group ($\sim 1.24 \times 10^{-29}$

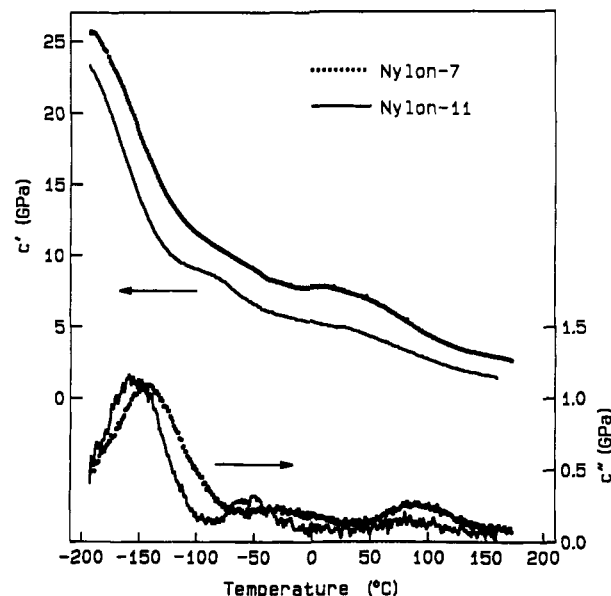


Figure 2. Temperature dependence of the modulus (real part c' and imaginary part c'') for samples of Nylon-11 and Nylon-7 measured at 104 Hz.

C·m) and the CF₂CH₂ unit (7×10^{-30} C·m), we estimated the spontaneous polarization of Nylon-11, Nylon-7, and PVF₂ crystals to be 48, 73, and 132 mC/m², respectively. The measured values of P_r for the Nylon samples were larger than these values. This is considered to be related to the nature of semicrystalline polymers. The measured bulk remanent polarization may be estimated as $P_r = fLP_s$,¹⁷ where f is the portion of reorientable dipoles and L is given as $3\epsilon/(2\epsilon + \epsilon_c)$, which is applicable to a two-phase model consisting of spherical crystals with dielectric constant ϵ_c , distributed in an amorphous matrix with dielectric constant ϵ . The present Nylon samples usually showed significant high-field dc conduction at room temperature. The D-E hysteresis measurements were carried out at a very low frequency, 1 mHz. Therefore, the value of ϵ is much larger than ϵ_c , resulting in $L \approx 1.5$. In this case, the measured remanent polarization is expected to be 72 mC/m² for Nylon-11 and 110 mC/m² for Nylon-7. The PVF₂ used with a capacitor-grade film and showed no obvious dc conduction at room temperature. For PVF₂, we obtain the value $L = 1.34$ by using $\epsilon = 14$ and $\epsilon_c = 3.3$. We can estimate, approximately, that 81%, 85%, and 31% of the dipoles are reoriented by the external electric field for Nylon-11, Nylon-7, and PVF₂, respectively. It is obvious from this analysis that the Nylon samples give rise to much larger degrees of dipole orientation than PVF₂ samples when poled at room temperature.

2. Modulus and Dielectric Constants. Since piezoelectricity is a property resulting from a combination of the electrical and mechanical characteristics of a material, it is important to measure both mechanical modulus and dielectric constant. Figure 2 shows the temperature dependence of the modulus (real part c' and imaginary part c'') for samples of Nylon-11 and Nylon-7. The measurement frequency was 104 Hz. The Nylon samples exhibit three noticeable relaxation processes. The high-temperature relaxation appears at 80–100 °C and is commonly designated the α relaxation. As the temperature decreases, the β relaxation appears at -55 °C for Nylon-11 and at -33 °C for Nylon-7, and, finally, the γ relaxation appears at -156 °C for Nylon-11 and -143 °C for Nylon-7.

Figure 3 shows a logarithmic plot of the dielectric constant, ϵ , as a function of temperature for Nylon-11

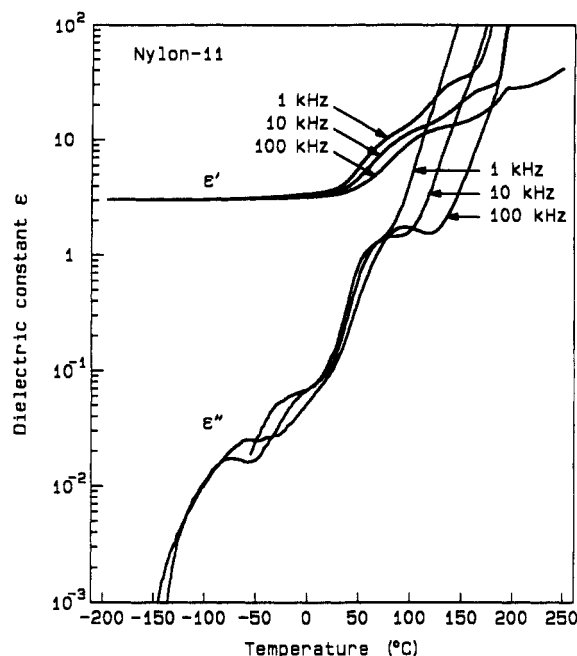


Figure 3. Logarithmic plot of dielectric constant as a function of temperature for Nylon-11 measured at frequencies of 1, 10, and 100 kHz.

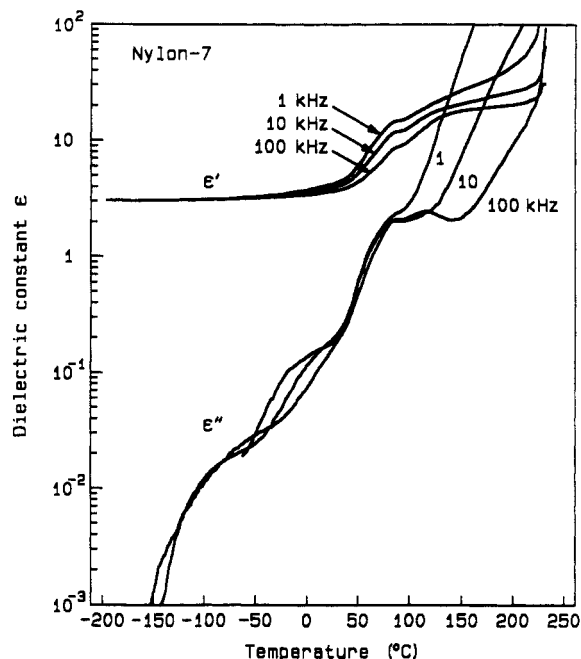


Figure 4. Logarithmic plot of dielectric constant as a function of temperature for Nylon-7 measured at frequencies of 1, 10, and 100 kHz.

measured at frequencies of 1, 10, and 100 kHz. A similar plot for Nylon-7 is shown in Figure 4. The dielectric constant also exhibits three relaxation processes: α , β , and γ relaxations. However, there is a significant difference in the relaxation behavior when the modulus and the dielectric constant are compared. The modulus exhibits two strong relaxations, the α and the γ relaxations. The γ relaxation is much stronger than the α relaxation, while the dielectric constant exhibits a stronger α relaxation and a weaker γ relaxation. Although the α relaxation in Nylons has normally been designated as the glass transition temperature, T_g , some questions¹⁰ were posed about this designation due to the very strong γ relaxation. The modulus and dielectric constant data obtained provide convincing evidence for the mechanisms involved. As the

temperature gradually increases, the micro-Brownian motion of hydrocarbon sections of the Nylons is excited in the noncrystalline regions, while the amide groups stay as unexcited states, probably due to hydrogen bonding. The hydrocarbon sections of Nylon-11 and Nylon-7 are much longer than the amide group and only the amide group has a strong dipole moment. As a result, the strong and glass-transition-like γ relaxation appears only in the modulus data. In fact, the γ relaxation in Nylons also obeys the WLF relation.¹⁰ As the temperature increases further, some hydrogen bonds will break and longer chain segments, including both amide groups and hydrocarbon sections, begin micro-Brownian motion in the noncrystalline regions. The α relaxation also obeys the WLF relation¹⁰ and can be designated as the glass transition process.

On the other hand, it is well-known that PVF₂ films with form-I crystals do not show a noticeable α relaxation but exhibit a strong β relaxation around -40 °C followed by a γ relaxation. Only the β relaxation is very strong and appears in both the elastic modulus and dielectric constant data, and this relaxation is commonly designated as the glass transition temperature of PVF₂. PVF₂ has a dipole moment in the small CF₂CH₂ monomer unit, and as a result, segmental chain motion cannot occur without dipole motion. This structural difference gives a qualitative difference to the elastic modulus characteristics for Nylons and PVF₂; Nylons exhibit two steps related to the onset of micro-Brownian motions in molecular chains, while PVF₂ exhibits only one step. On the other hand, the behavior of the dielectric constant is essentially the same for Nylon and PVF₂. From this understanding of the response of the dipoles in Nylon and PVF₂, we expect that if the response of the dipoles to an electrical excitation is essentially the same in both Nylon and PVF₂, the response to the mechanical excitation (piezoelectric effect) may also be the same. It is also important to remember that the Nylons studied have much higher T_g 's than that of PVF₂ (a ~120 °C difference), and that the Nylons do not show a dielectric anomaly, which would indicate a Curie transition, until they melt. These two features of Nylons may be important in terms of high-temperature piezoelectric applications.

3. Piezoelectric Constants. Once we observed the superior D - E hysteresis characteristics of the Nylon samples and also, essentially, the same type of dielectric response of Nylons as that of PVF₂, we expected reasonably high piezoelectric activities for the Nylon samples above T_g . In Figure 5, we show the piezoelectric strain constant, d'_{31} , and in Figure 6 the piezoelectric stress constant, e'_{31} , versus temperature for Nylon-11, Nylon-7, and PVF₂ measured at 104 Hz from 50 °C to temperatures close to their melting points. The stable values of the piezoelectric constants presented here occur after the poled samples are annealed at 185 °C for Nylon-11 and at 200 °C for Nylon-7 for 2 h and after measurements to 175 °C for PVF₂. The signs of d'_{31} and e'_{31} of the Nylon samples were the same as those of PVF₂, positive. Both the d'_{31} versus T and e'_{31} versus T curves of the Nylons exhibit large increases around the glass transition temperature. Both curves show a shoulder between 120 and 140 °C and exhibit a tendency to saturate. The maximum values of d'_{31} for Nylon-11 and Nylon-7 are 14 and 17 pC/N, respectively, and the maximum values of e'_{31} for Nylon-11 and Nylon-7 are 21 and 27 mC/m², respectively. On the other hand, the PVF₂ sample exhibits an almost constant d'_{31} and an almost linearly decreasing curve for e'_{31} with increasing temperature. The values of d'_{31} and e'_{31} for

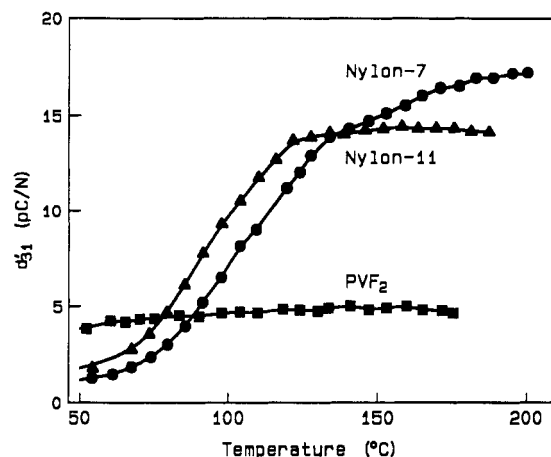


Figure 5. Piezoelectric strain constant, d'_{31} , for Nylon-11, Nylon-7, and PVF₂ samples measured at 104 Hz from 50 °C to temperatures close to their melting points. Stable values are shown after annealing the poled samples at 185 °C for Nylon-11 and at 200 °C for Nylon-7 for 2 h, and after measurement up to 175 °C for PVF₂.

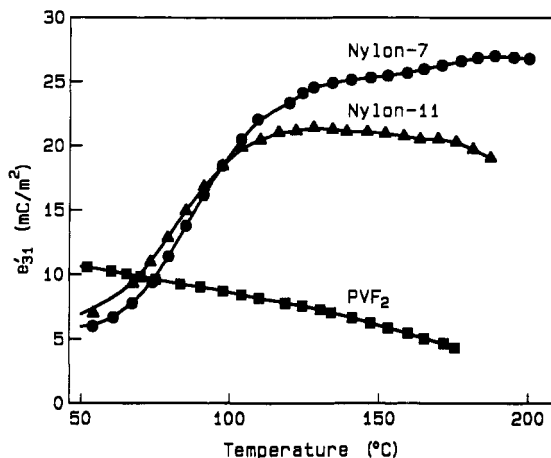


Figure 6. Piezoelectric stress constant, e'_{31} , for samples of Nylon-11, Nylon-7, and PVF₂ measured at 104 Hz. Stable values are shown similar to those of Figure 5.

PVF₂ at high temperatures, for example at 100 °C, are 5 pC/N and 7 mC/m², respectively. PVF₂ of course never reaches the highest temperatures, since it melts around 175 °C. It is obvious that the high-temperature piezoelectric characteristics of these Nylons are better than those of PVF₂. To our knowledge, no other polymeric material exhibits useful values of d'_{31} and e'_{31} at these high temperatures.

To understand the present data, it is necessary to remember that we added a dc blocking capacitor to the input of the charge amplifier to prevent saturation while obtaining the high-temperature data. The maximum value of the real and imaginary parts of the dielectric constant of the Nylon-11 sample were $\epsilon' = 1014$ and $\epsilon'' = 1894$ at 187 °C, and of the Nylon-7 sample were $\epsilon' = 401$ and $\epsilon'' = 1566$ at 200 °C. At these temperatures, the impedance becomes 51.9 and 118 k Ω for the Nylon-11 and Nylon-7 samples, respectively. We used a capacitance of 2.2 μ F, whose impedance is much smaller (696 Ω at 104 Hz) than the sample impedance. We found, however, that this large capacitance also passed dc drift noise, which is randomly distributed over some very low frequency region and sometimes large enough in amplitude to cause the charge amplifier to saturate. We selected the capacitance to be between 0.15 and 2.2 μ F, depending on the sample impedance. The major side effect of the dc blocking

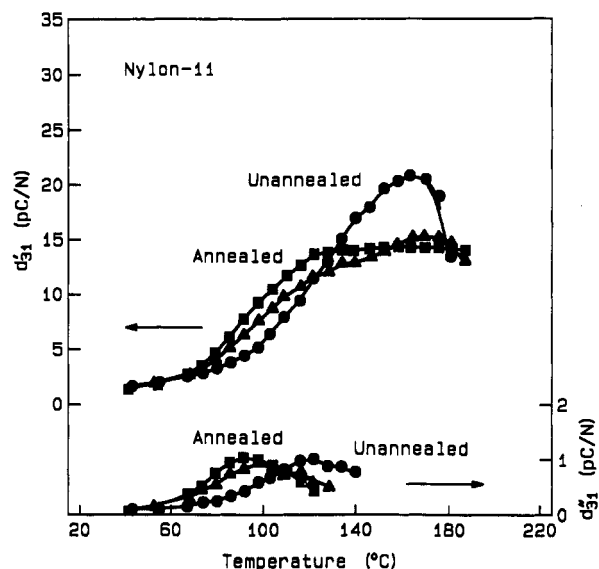


Figure 7. Annealing effect (after poling) on the d_{31} versus T characteristics of Nylon-11. The measurement frequency was 104 Hz, and the annealing temperature and time were 185 °C and 2 h, respectively.

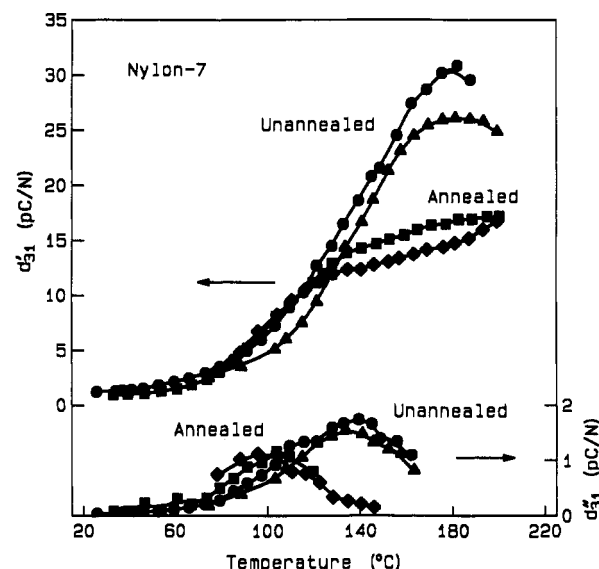


Figure 8. Annealing effect (after poling) on the d_{31} versus T characteristics of Nylon-7. The measurement frequency was 104 Hz, and the annealing temperature and time were 200 °C and 2 h, respectively.

capacitor was a significant change in the value of the imaginary part of the piezoelectric constants above ~ 160 or ~ 180 °C for Nylon-11 and Nylon-7, respectively. These data were considered unreliable and are not presented.

4. Annealing Effects on the Piezoelectric Properties. In a previous study⁹ we reported the effect of annealing on the ferroelectric behavior of Nylon-11 and Nylon-7. We pointed out that quenched and then cold-drawn and annealed Nylon-11 and Nylon-7 films show clear ferroelectric behavior at annealing temperatures below ~ 70 °C for Nylon-11 and below ~ 115 °C for Nylon-7. When the Nylon samples were exposed to a temperature above the glass transition, the ferroelectric behavior significantly decreased.

Figures 7–9 show the effect of annealing after poling on the d_{31} versus T characteristics of Nylon-11, Nylon-7, and PVF₂ samples, respectively. The measurement frequency was 104 Hz. The curves labeled “unannealed” indicate characteristics of the first measurement after poling. The

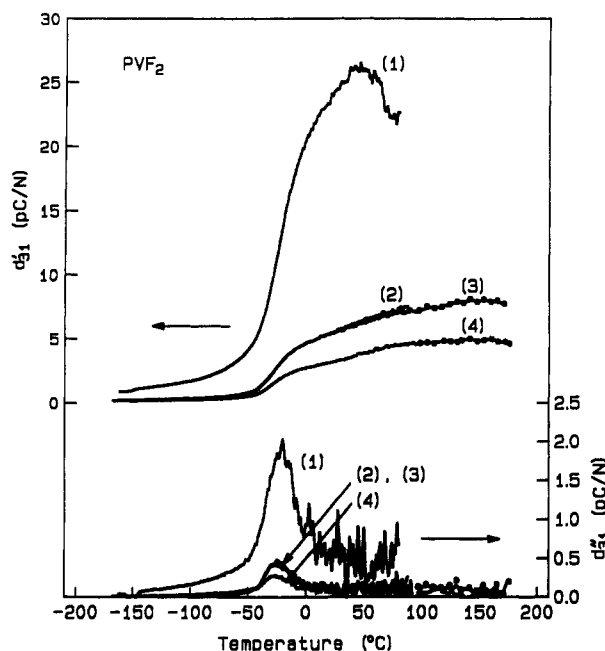


Figure 9. Annealing effect (after poling) on the d_{31} versus T characteristics of PVF_2 . Curve 1 represents the first run of an unannealed sample, curve 2 the second run after the first measurement, curve 3 the third run after annealing at 120 °C for 17 h, and curve 4 the fourth run after the measurement up to 175 °C. The measurement frequency was 104 Hz.

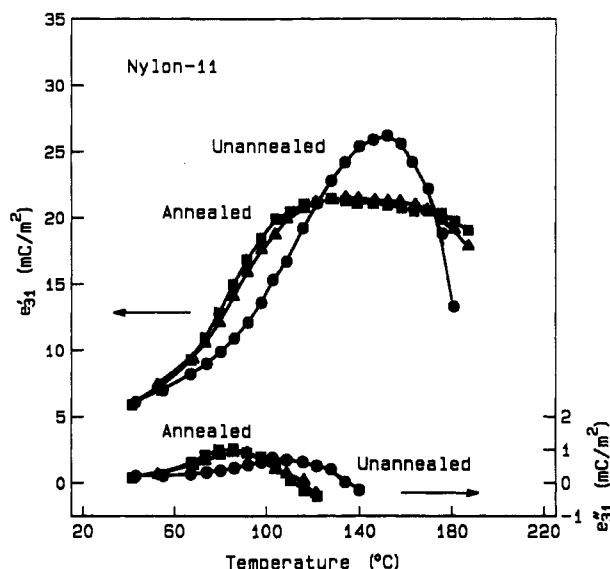


Figure 10. Annealing effect (after poling) on the e_{31} versus T characteristics of Nylon-11. The measurement frequency was 104 Hz, and the annealing temperature and time were 185 °C and 2 h, respectively.

curves labeled "annealed" indicate characteristics measured after annealing of the poled samples. The annealing temperatures of the Nylon-11 and Nylon-7 samples were 185 and 200 °C, respectively, and the annealing time was 2 h. For the PVF_2 samples, four characteristics are presented: Curve 1 represents the first run of the unannealed sample, curve 2 the second run after the first measurement, curve 3 the third run after annealing at 120 °C for 17 h, and curve 4 the fourth run after the measurement up to 175 °C.

Figures 10–12 show the annealing effect after poling on the e_{31} versus T characteristics of Nylon-11, Nylon-7, and PVF_2 samples, respectively. The labeling of the curves is similar to those used in Figures 7–9. Even for PVF_2 , piezoelectric measurements at temperatures above ~120

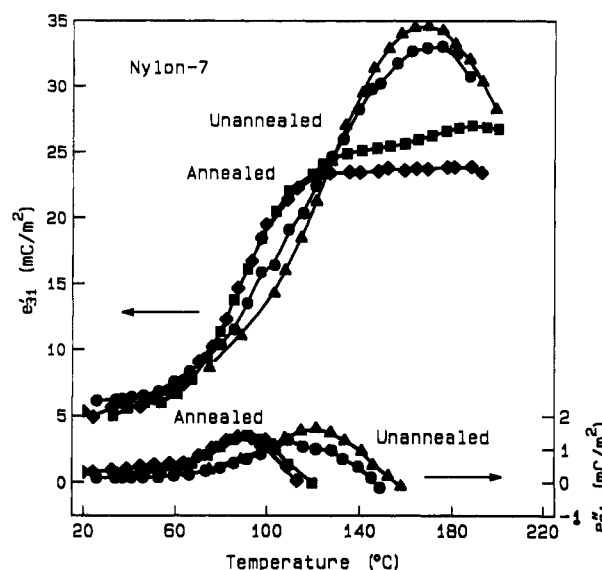


Figure 11. Annealing effect (after poling) on the e_{31} versus T characteristics of Nylon-7. The measurement frequency was 104 Hz, and the annealing temperature and time were 200 °C and 2 h, respectively.

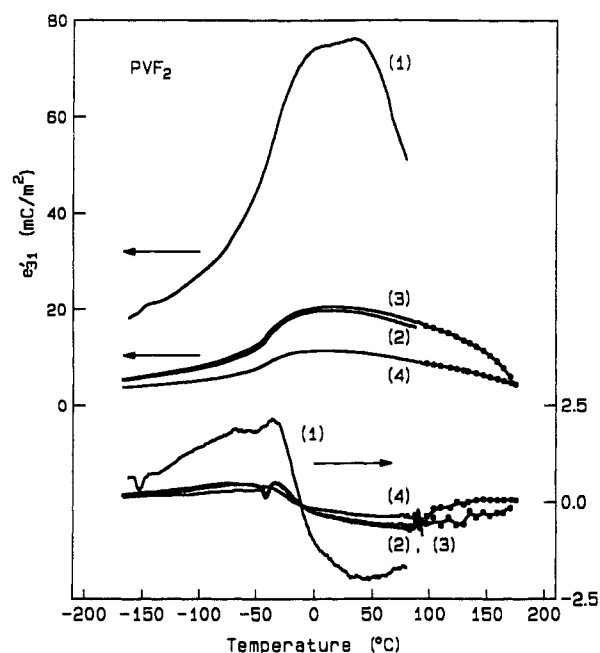


Figure 12. Annealing effect (after poling) on the e_{31} versus T characteristics of PVF_2 . Curve 1 represents the first run of the unannealed sample, curve 2 the second run after the first measurement, curve 3 the third run after annealing at 120 °C for 17 h, and curve 4 the fourth run after the measurement up to 175 °C. The measurement frequency was 104 Hz.

°C are difficult to obtain and no data have been published. We performed the measurements carefully by using a manual (as opposed to automatic) mode of the equipment. The continuous lines represent data obtained using the automatic mode and the explicit data points represent data obtained using the manual mode.

Both the Nylon and PVF_2 samples reveal certain characteristic changes in the curves after annealing. However, we can easily notice that there is a significant difference in the annealing behavior comparing Nylon-11 and Nylon-7 with PVF_2 . Change in the d_{31} versus T and e'_{31} versus T curves of Nylon appears only in the temperature region above the glass transition temperature, while the change in the case of PVF_2 is an irreversible overall decrease in the measured temperature region. This

difference leads us to one important conclusion. Poled and then annealed Nylon films do not suffer from dipolar randomization even at high temperatures close to the melting point.

Each d'_{31} versus T and e'_{31} versus T curve for the unannealed Nylons exhibits a convex shape with a single peak. The maximum values of d'_{31} are 21 pC/N at 163 °C for Nylon-11 and 30 pC/N at 180 °C for Nylon-7, and the maximum values of e'_{31} are 26 mC/m² at 150 °C for Nylon-11 and 34 mC/m² at 168 °C for Nylon-7. After annealing, the curves show a plateau with an almost constant value of $d'_{31} = 14$ pC/N for Nylon-11, $d'_{31} = 17$ pC/N for Nylon-7, $e'_{31} = 21$ mC/m² for Nylon-11, and $e'_{31} = 26$ mC/m² for Nylon-7. After annealing, the values of d'_{31} and e'_{31} decrease to about 65–75% of the initial maximum value. However, both d'_{31} and e'_{31} begin to show less temperature dependence and do not show further decreases even after several exposures at a high temperature close to the melting point.

The PVF₂ sample, on the other hand, exhibits much poorer thermal stability for d'_{31} and e'_{31} . The unannealed sample shows convex-shaped d'_{31} versus T and e'_{31} versus T curves similar to Nylon-11 and Nylon-7. The maximum values are as high as 26 pC/N at 26 °C and 77 mC/m² at 35 °C, respectively. However, this piezoelectric response significantly decreases after annealing. The maximum values of d'_{31} decrease to 8.1 pC/N (31%) after annealing at 120 °C and to 4.9 pC/N (19%) after measurement up to 175 °C. Similarly, the maximum values of e'_{31} decrease to 20 (26%) and to 11 mC/m² (15%) after exposure to temperatures of 120 and 175 °C, respectively. As expected, PVF₂ also exhibits this significant decrease in piezoelectric response even at temperatures lower than T_g . For example, at -100 °C, the initial value of d'_{31} was 1.7 pC/N and of e'_{31} was 27 mC/m². This decreases to 0.35 pC/N (21%) and 8.1 mC/m² (30%) after annealing at 120 °C, and 0.23 pC/N (14%) and 5.1 mC/m² (19%) after the measurement to 175 °C.

The measured piezoelectric constants have been considered to be proportional to the remanent polarization and also to be a function of Poisson's ratio and the electrostriction constant of the sample.¹⁷ The large increases in the piezoelectric constants, d'_{31} and e'_{31} , above the glass transition temperature of highly stretched PVF₂ films have been explained in terms of the change in Poisson's ratio.¹⁸ In temperature regions lower than T_g , the measured piezoelectric constants begin to show a "pure" piezoelectric effect. The present experiments revealed that the piezoelectric constants, d'_{31} and e'_{31} , of Nylon samples exhibit a temperature dependence essentially similar to that of PVF₂. Since the measured piezoelectric constants are proportional to remanent polarization regardless of temperature, it is easy to conclude that the observed large decrease in the piezoelectric constants of PVF₂ is due to significant loss of dipole orientation, which was initially induced by poling. On the other hand, the decrease in the piezoelectric constants of the Nylon samples observed only in the temperature region above T_g may be ascribed to changes in the dimensional effect (Poisson's ratio) caused by crystallographic and morphological changes produced by annealing. The lack of any observed changes in the piezoelectric constants in the temperature region below T_g after high-temperature annealing indicates, essentially, that no loss of dipole orientation occurs as a result of the annealing process.

The large difference observed in the annealing effect between Nylons and PVF₂ originates in the difference in molecular structures between Nylon and PVF₂. In a

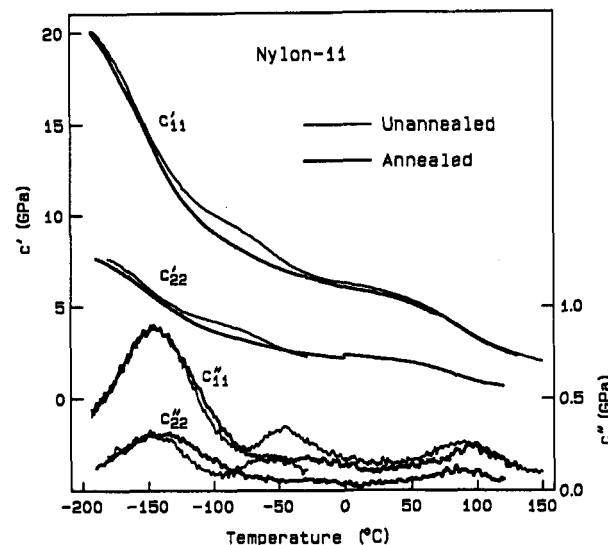


Figure 13. Temperature dependence of the elastic modulus along the draw direction, c_{11} , and perpendicular to the draw direction, c_{22} , of Nylon-11 measured at 10 Hz.

previous X-ray study,¹⁹ it was pointed out that quenched and then cold-drawn Nylon films had three-dimensional molecular order; the hydrogen-bonded sheet structure was parallel to the film surface with the chains in the draw direction. During poling, these hydrogen-bonded sheets rearrange and re-form with the hydrogen-bonded sheets perpendicular to the film surface with the dipoles aligned along the applied electric field direction. Similar to the conclusions of the previous study, the effects of annealing in these Nylons can be interpreted in terms of a rearrangement of the hydrogen-bonded sheet structure, i.e., a significant decrease in spacing between the hydrogen-bonded sheets after annealing, which results in an increased difficulty for the amide groups to reorient with increasing thermal motion. Structural studies of this behavior using X-ray diffraction and IR absorbance measurements will be published separately.

5. Anisotropy of Drawn Nylon Films. The Nylon film samples studied were highly stretched and we expected a certain degree of anisotropy with respect to the modulus and piezoelectric constants. Figure 13 shows the temperature dependence of the elastic modulus along the draw direction, c_{11} , and perpendicular to the draw direction, c_{22} , measured at 10 Hz. The value of c'_{22} is about 35–40% of that of c'_{11} over the temperature region from -196 to 150 °C, exhibiting the high anisotropy of the sample (for example, at -150 °C, $c'_{11} \approx 14.3$ GPa, while $c'_{22} \approx 5.8$ GPa). According to a study of drawing procedures of polymers by Peterlin,²⁰ the transformation from lamellae to microfibrils is complete at a draw ratio between 2 and 3 in Nylon-6 or -66, and between 8 and 10 in linear polyethylene. We can expect, therefore, that our Nylon samples have almost completed the transformation and consist primarily of microfibrils.

Also related to this highly anisotropy, we noticed some interesting properties of the Nylon samples. The films easily break when stress is applied perpendicular to the draw direction. As we see on the c_{22} versus T curve in Figure 13, the curves are not continuous. This is because of fracture of the samples during measurement. In addition, when the stretched films were annealed, they did not shrink in the draw direction but rather showed a small extension. This is quite different from the behavior of drawn PVF₂ (draw ratio of about 5:1), which showed considerable shrinkage in the draw direction during annealing.

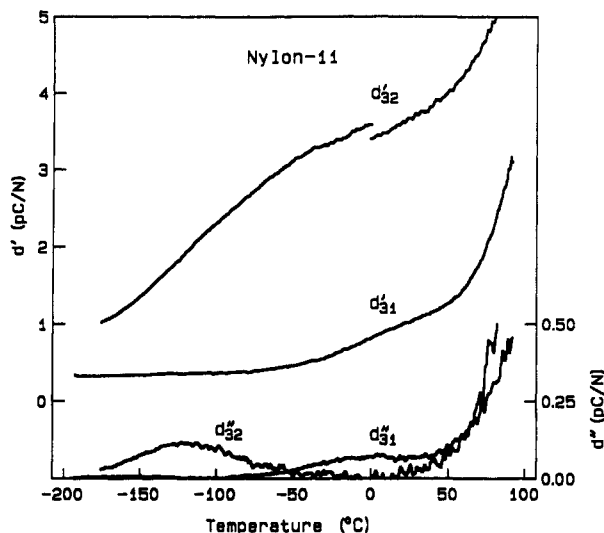


Figure 14. Temperature dependence of the piezoelectric strain constants, d_{31} and d_{32} , of Nylon-11 measured at 10 Hz.

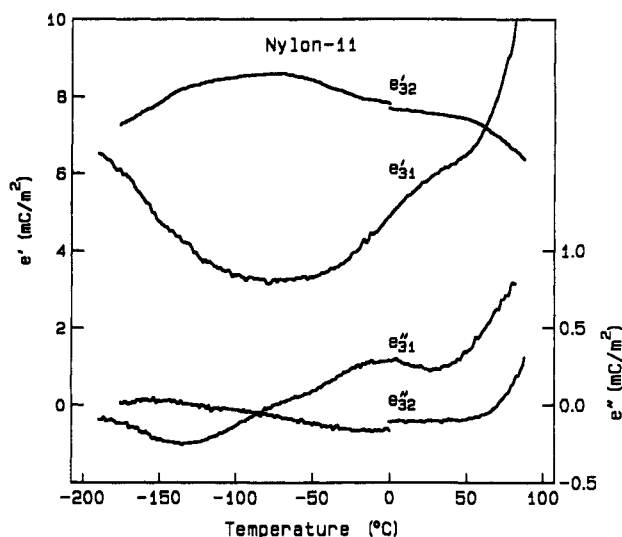


Figure 15. Temperature dependence of the piezoelectric stress constants, e_{31} and e_{32} , of Nylon-11 measured at 10 Hz.

It may also be interesting to observe any anisotropy in the piezoelectric constants of the stretched Nylon films. Figure 14 shows the temperature dependence of the piezoelectric strain constants, d_{31} and d_{32} , of Nylon-11 measured at 10 Hz. The sign of d'_{32} was positive. It is of particular interest that the value of d'_{32} is significantly larger than that of d'_{31} in the temperature region below T_g . For example, at -100°C , $d'_{32} = 2.3 \text{ pC/N}$ while $d'_{31} = 0.36 \text{ pC/N}$. The discontinuity in the curve of d_{32} is due to the fracture of the sample during the measurement.

Figure 15 shows the temperature dependence of the piezoelectric stress constants, e_{31} and e_{32} , of Nylon-11 measured at 10 Hz. The value of e'_{32} is much larger than the value of e'_{31} below a temperature of $\sim 50^\circ\text{C}$. The sign of e'_{32} was also positive. The e'_{32} values exhibit less of a temperature dependence than the values of e'_{31} and the maximum value is $\sim 8.6 \text{ mC/m}^2$ at $\sim -70^\circ\text{C}$.

It should be noted that the values of d'_{32} and e'_{32} of Nylon-11 in the low-temperature region are much larger than the stable values of d'_{31} and e'_{31} of PVF₂. For example, at -100°C , $d'_{32} = 2.3 \text{ pC/N}$ and $e'_{32} = 8.5 \text{ mC/m}^2$ for Nylon-11 and $d'_{31} = 0.23 \text{ pC/N}$ and $e'_{31} = 5.1 \text{ mC/m}^2$ for PVF₂. The values of d'_{32} and e'_{32} have been reported to be much smaller than d'_{31} and e'_{31} for PVF₂.²¹

6. Electromechanical Coupling Constant. The electromechanical coupling coefficient, k_{31} , of the present

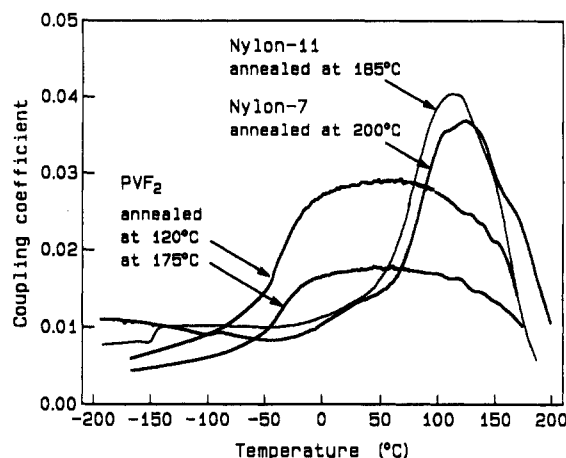


Figure 16. Electromechanical coupling coefficient, k_{31} , as a function of temperature for the annealed samples of Nylon-11, Nylon-7, and PVF₂. The measurement frequency was 104 Hz.

Nylon samples was obtained by using the relation

$$k_{31} = d_{31}(c/\epsilon_0\epsilon)^{1/2} \quad (1)$$

where ϵ_0 is the free space permittivity. Figure 16 shows the coupling coefficient, k_{31} , as a function of temperature for the annealed samples of Nylon-11, Nylon-7, and PVF₂. The value is obtained by using the measured quantities, most of which are shown in Figures 5 and 9. The measurement frequency is 104 Hz. This frequency is low enough to regard the value of k_{31} as the static value except in the high-temperature region for the Nylons.

Annealing effects on the coupling coefficients of Nylons and PVF₂ are very similar to those of the piezoelectric constants discussed in section 4: Change in the coupling coefficient of Nylon appears only in the temperature region above the glass transition temperature, while that for PVF₂ is an overall decrease in the measured temperature region (The maximum value of k_{31} for unannealed PVF₂ is ~ 0.12). It is interesting to note that the values of k_{31} for both Nylon-11 and Nylon-7 become larger than that for PVF₂ in the low-temperature region below $\sim -50^\circ\text{C}$ after the annealing of PVF₂ at 175°C ; for example, $k_{31} = 0.02$ for both Nylons and $k_{31} = 0.008$ for PVF₂. At higher temperatures above the glass transition temperature, the values of k_{31} of Nylons are larger than those of PVF₂. However, they sharply decrease as the temperature increases. This is obviously due to the enormous increase in dielectric constant of the Nylon samples. Since this increase is known to be associated with the response of mobile ionic species, the sharp decrease in k_{31} should not be regarded as an intrinsic phenomenon.

In order to obtain intrinsic values for the coupling coefficient, it is necessary to obtain a dielectric constant which is independent of ionic response. To perform this procedure, we measured the frequency dependence of the dielectric constant at many temperatures and tried a Cole-Cole plot of the data. Figures 17-19 show the frequency dependence of the dielectric constant at the indicated temperatures for the poled and annealed Nylon-11, Nylon-7, and PVF₂ samples, respectively. Above the glass transition temperature, the Nylon samples show characteristic increases in both ϵ' and ϵ'' as the frequency decreases. These increases make it difficult to determine the intrinsic static value of dielectric constant above T_g .

Parts a-c of Figure 20 show the Cole-Cole plots of the dielectric data for Nylon-11, Nylon-7, and PVF₂, respectively. Measured data for the three samples follow the expected Cole-Cole arc except at the very high and the

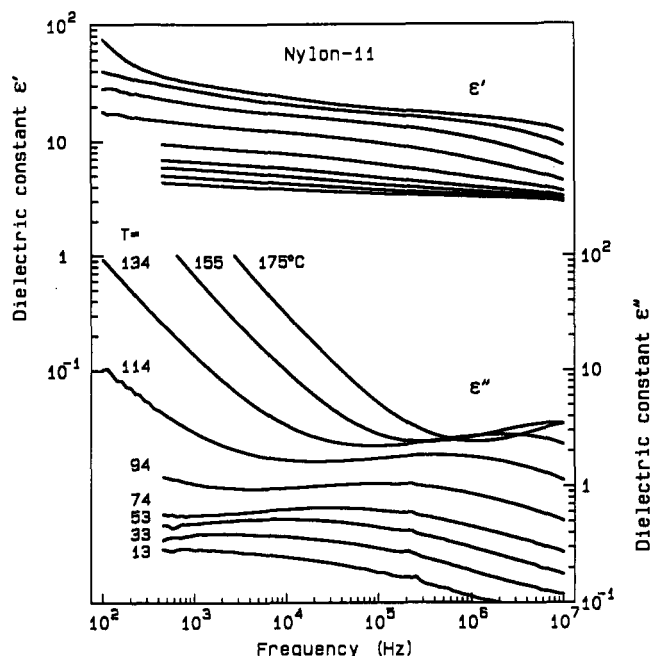


Figure 17. Frequency dependence of the dielectric constant at indicated temperatures for poled and annealed Nylon-11.

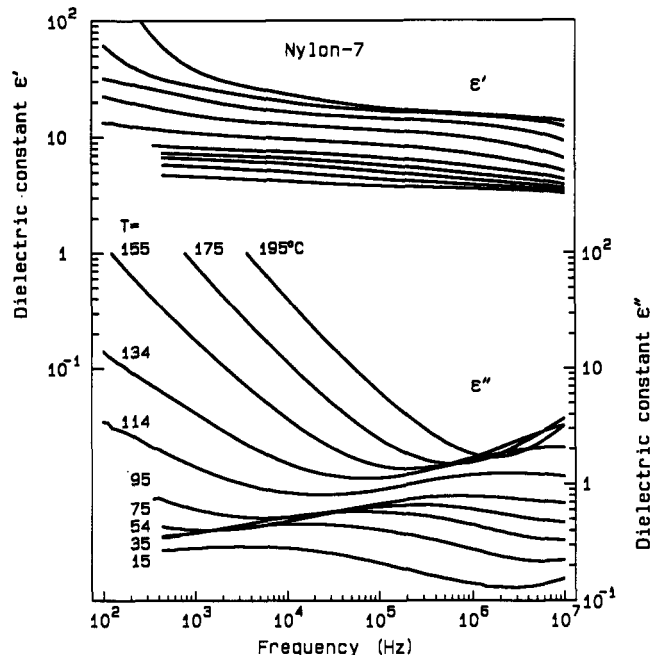


Figure 18. Frequency dependence of the dielectric constant at indicated temperatures for poled and annealed Nylon-7.

very low frequency regions. In the Cole-Cole plot, the shape of the ϵ'' versus ϵ' curve changes to the opposite sign when the ionic contribution dominates. This qualitative change makes it easy to distinguish the intrinsic dielectric constant from the ionic contribution. The extrapolation of the data by using an arc determines both the static value, ϵ'_s , and the instantaneous value, ϵ'_∞ , of the dielectric constant. The values of ϵ'_∞ for Nylon-11, Nylon-7, and PVF₂ are 3.15, 3.35, and 3.25, respectively, almost the same within experimental error. The value of ϵ'_s at the highest temperatures for Nylon-11, Nylon-7, and PVF₂ are about 18, 16, and 15, respectively. It is interesting to note that these values are very similar for Nylon and PVF₂, although the experimental error may be significant for the Nylon samples.

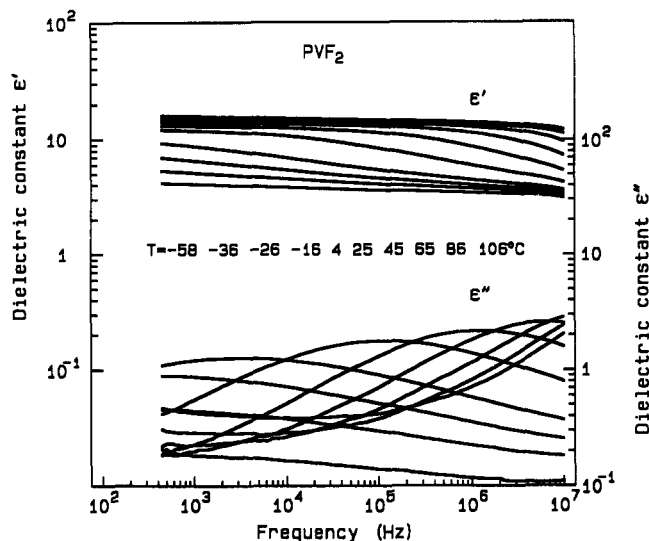


Figure 19. Frequency dependence of the dielectric constant at indicated temperatures for poled and annealed PVF₂.

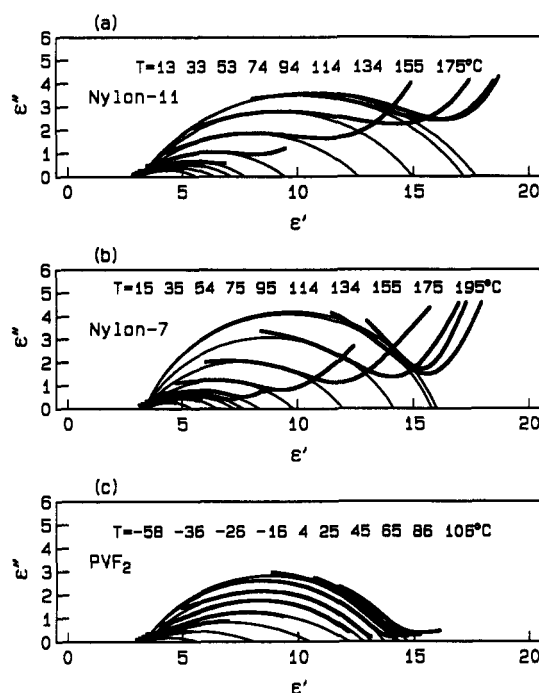


Figure 20. (a-c) Cole-Cole plots of the dielectric data shown in Figures 17-19 for Nylon-11, Nylon-7, and PVF₂ samples, respectively.

Figure 21 shows the intrinsic static values of the coupling coefficients of Nylon-11, Nylon-7, and PVF₂ samples determined by using the static dielectric constants and eq 1. The d_{31} data used are presented in Figure 5. These are the stable values obtained after annealing. Similar to the piezoelectric data shown in Figure 5 and 6, at high temperatures (above $\sim 70^\circ\text{C}$), the intrinsic coupling coefficient values for Nylon-11 and Nylon-7 are higher than values obtained for annealed PVF₂. For example, the maximum values of k_{31} are 0.049, 0.054, and 0.019 for Nylon-11, Nylon-7, and PVF₂ samples, respectively. The Nylon-7 sample shows a flat response with temperature with a k_{31} value of $\sim 52\%$, from ~ 120 to 200°C .

Conclusions

The variation in piezoelectric response of Nylon-11 and Nylon-7 with temperature has been explored and compared with PVF₂, to provide insight into the role of elastic and

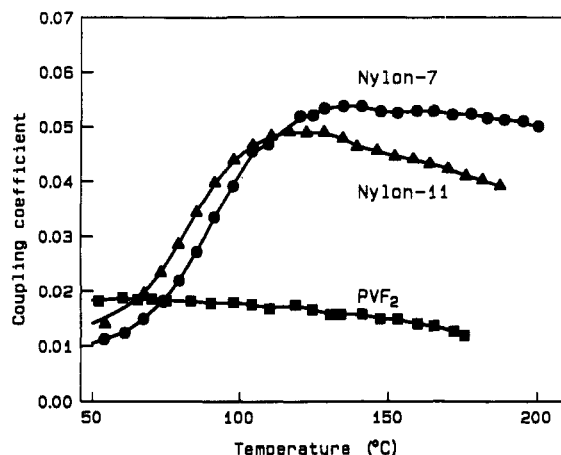


Figure 21. Static values of the electromechanical coupling coefficient, k_{31} , of Nylon-11, Nylon-7, and PVF₂.

dielectric relaxation on piezoelectricity and on the thermal stability of piezoelectricity.

Nylon-11 and Nylon-7 films exhibit the highest values of piezoelectric strain coefficient, d_{31} , stress coefficient, e_{31} , and electromechanical coupling coefficient, k_{31} , together with excellent thermal stability at temperatures between 100 and 200 °C. Maximum stable values obtained were $d_{31} = 14$ pC/N, $e_{31} = 21$ mC/m², and $k_{31} = 0.049$ for Nylon-11 and $d_{31} = 17$ pC/N, $e_{31} = 27$ mC/m², and $k_{31} = 0.054$ for Nylon-7. Poled and then annealed Nylon samples exhibit little decay of these values even after annealing at 185 and 200 °C for Nylon-11 and Nylon-7, respectively, for 2 h. The extraordinary stability of the piezoelectric activity of the Nylon samples is considered to be related to the ferroelectric reorientation of the amide group dipoles followed by closer packing of the hydrogen-bonded sheets in the crystalline regions after the poling and annealing

procedures. In the low-temperature region below ~-50 °C, the Nylons exhibit higher values of d_{32} , e_{32} , and k_{31} than the d_{31} , e_{31} , and k_{31} values of PVF₂.

Acknowledgment. This work was supported by DARPA and the Office of Naval Research.

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Registry No. PVF₂, 24937-79-9; Nylon-7 (homopolymer), 25748-71-4; Nylon-7 (SRU), 25035-01-2; Nylon-11 (homopolymer), 25587-80-8; Nylon-11 (SRU), 25035-04-5.