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ELECTRIC FIELD-INDUCED CHANGES IN ODD-NUMBERED NYLONS

by J.I. Scheinbeim and B.A. Newman

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in
Trends in Polymer Science

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ELECTRIC FIELD-INDUCED CHANGES IN ODD-NUMBERED NYLONS

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Summary

Most studies of ferroelectricity and piezoelectricity in polymers have been directed towards poly(vinylidene fluoride) and its copolymers. A long series of investigations in our laboratory of the odd-numbered nylons has culminated in the discovery that these polymers are also ferroelectric and piezoelectric. These studies are important not only to test the generality of the phenomena discovered in poly(vinylidene fluoride), but to examine the effect of hydrogen bonding on ferroelectricity and piezoelectricity in polymers. One important result of this work was the discovery of a mechanism to stabilize the piezoelectric activity of these hydrogen bonded polymers to the melting point.

Introduction

Since the initial discovery by Kawai¹ in 1969 of what would become the first class of electroactive (ferroelectric) polymers--polyvinylidene fluoride (PVF₂) and its copolymers²--more than twenty years have passed. During this time, a great deal of effort has been devoted to the search for other such polymers. This has, however achieved limited success. The only real success was the discovery in 1980 by Miyata et al³ that a copolymer of vinylidene cyanide-vinyl acetate, an electret, could be given a significant polarization resulting in a useful piezoelectric material. This polymer is amorphous, and

electric polarization is achieved by application of high static electric fields at or above the glass transition temperature. On cooling below the glass transition temperature, dipole orientation is frozen in, and thus, the material is an electret, and exhibits piezoelectric and pyroelectric response, similar to the behavior of poly(vinyl chloride)⁴.

The α -phase crystal structure of nylon 11 suggested by Slichter⁵ is polar. The molecular conformation of the proposed structure was all-trans, and for an odd-numbered nylon, this entails a net dipole moment per chain. Since the α -structure proposed contained one chain in the asymmetric unit, this means that the unit cell must be polar, with one amide-group per unit cell volume. The amide group is a very polar group ~ 3.7 Debyes, and so the theoretical dipole density can be estimated to be $1.34D$ per 100\AA^3 , a value which is about one third of the corresponding value for the β -phase of polyvinylidene fluoride (the most polar crystal form). For this reason, nylon 11 was examined by Kawai and Heiji⁶ in 1970 and by Litt et al⁷ in 1977, to determine whether this polymer could be polarized to exhibit pyroelectricity or piezoelectricity. These studies were an attempt to determine whether the crystal polarization (electric dipoles in the crystalline regions) could be switched under an applied electric field into the field direction; that is, whether the crystals were ferroelectric. The piezoelectric response of poled nylon 11 measured by these researchers was negligible (much less than that of poled polyvinylidene fluoride). On the basis of pyroelectric measurements, Litt et al⁶ stated that electric dipoles in the crystalline regions were oriented (implying ferroelectricity), but since the measured piezoelectric response was so small, and since the interpretation of the pyroelectric measurements posed considerable difficulties, these results lacked conviction.

However, we noticed that nylon 11, as is the case for PVF_2 , is polymorphic and, in fact, may exhibit both non-polar and polar crystal structures. PVF_2 has at least four polymorphic crystal forms, three of which are polar, phase I (β -phase), phase III (γ -phase) and phase IV (δ -phase, or polar α -phase), and one which is non-polar, phase II (α -phase).

We had shown^{8,9} that for PVF₂, electric field induced phase transitions from less polar to more polar and non-polar to polar forms could occur under appropriately high electric fields, depending on the crystal orientation with respect to the applied field. These results encouraged us to re-examine the odd-numbered nylons, such as nylon 11, to determine whether or not we could find a set of appropriate electroprocessing conditions that would facilitate the formation of a polarized polymer film. This decision was based on the belief that there was a possibility that the electric polarization residing in the crystalline regions might be switchable under reversed electric fields if the polymer films were prepared with the appropriate microstructure, i.e., that the odd-numbered nylons might be ferroelectric. Figure 1 shows a schematic representation of the triclinic crystal structure for nylon 11, based on the description of Slichter⁵. The unit cell parameters for this structure are: $a = 4.9\text{\AA}$, $b = 5.4\text{\AA}$, $c = 14.9\text{\AA}$, $\alpha = 49^\circ$, $\beta = 77^\circ$, $\gamma = 63^\circ$. It is important to notice that for an odd-numbered nylon chain with the all-trans conformation, all the amide groups on one chain will be parallel. For an all-trans even-numbered nylon, successive amide groups would point in opposite directions, and the net dipole moment of the chain would be zero. Thus, for a structure such as that proposed by Slichter, an all-trans conformation with one chain per unit cell, there must be a net dipole moment associated with each unit cell. In contrast, even-numbered nylons with an all-trans conformation are required to be non-polar since in this case, subsequent amide groups going along a chain will be in opposed directions and the net dipole moment per unit cell must be zero.

Piezoelectric Properties of Odd-Numbered Nylons

In our first studies¹⁰ of nylon 11 in 1980, we decided to compare the properties of poorly crystallized nylon 11 films (obtained by the rapid cooling of melt-pressed films) with well crystallized films (obtained by annealing the quenched films at 120°C for four hours). Silver electrodes were placed on opposing film surfaces using a thick silver paste.

High static electric fields (poling fields, E_p) were applied across the film thickness for a fixed time (poling time, t_p) at various temperatures (poling temperature, T_p). The piezoelectric activities (at 3 Hz) of these poled films were then determined by measurements of the piezoelectric strain coefficient, d_{31} , and piezoelectric stress coefficient, e_{31} , using a commercial instrument. In this instrument, the poled films were subjected to a sinusoidally varying applied stress, while measurements of the film strain and surface charge density were simultaneously made.

The convention with respect to indices for the piezoelectric coefficients is as follows: the 1 direction is the direction of mechanical orientation (draw), the 2 direction is perpendicular to the draw direction and in the plane of the film, and the 3 direction is perpendicular to the plane of the film and is the direction of the applied electric field. The piezoelectric strain coefficient, d_{ij} , is defined as the change of film polarization in the i -direction with respect to the change in stress in the j -direction. The piezoelectric stress coefficient, e_{ij} , is defined as the change in field polarization in the i -direction with respect to change in strain in the j -direction¹¹.

Some of the results obtained are shown in Figure 2, where the piezoelectric strain coefficient, d_{31} , (measured at 3 Hz) as a function of poling temperature is shown for both the quenched films and the annealed films, using a poling field of 33 MV/m. The initial results obtained were encouraging in that the highest value of d_{31} obtained (about 3 pc/N for the quenched films) corresponded to the largest piezoelectric activity of any polymer measured at that time with the exception of PVF₂ and this value was orders of magnitude greater than values previously obtained for nylon 11^{6,7}. The surprising result was that the piezoelectric response of the poled nylon 11 films was greatest for the quenched films. The effect of annealing prior to poling decreased the resultant piezoelectric activity and this did not conform to expectations that were based on the fact that annealing quenched films significantly enhances crystallinity which should increase bulk polarization and,

therefore, piezoelectric response, assuming that the polarization resides in the crystalline regions¹¹.

This gave rise to questions concerning the origin of the piezoelectric response in the nylon films. One suggestion was that if the bulk polarization in the odd-numbered nylons arises from the field-oriented crystalline regions, thus giving rise to the piezoelectric response, it might disappear at the Brill transition ($\sim 95^\circ\text{C}$ for nylon 11) because of the onset of large scale librational molecular motions at this transition temperature causing a randomization of hydrogen bonds. This would then imply that the Brill transition temperature would be equivalent to the Curie temperature (temperature at which crystal polarization vanishes). Later, infrared studies by Itoh¹² and X-ray diffraction studies¹³ in our laboratory revealed that the hydrogen bonding network in the crystalline regions did not randomize at the Brill transition and, in fact, did not randomize until the temperature exceeded the melting point. Taken alone, these facts might be thought to suggest that the origin of the piezoelectric response might be the orientation of the hydrogen bonds in the amorphous regions of the polymer. However, comparable studies of quenched even-numbered nylon films showed that the piezoelectric response of these films, prepared in the same way, was zero. Further, if the bulk polarization responsible for the piezoelectric activity resided in the amorphous regions, then it would be anticipated that heating the films to temperatures above the glass transition temperature (T_g) ($\sim 50^\circ\text{C}$ for nylon 11) would lead to depolarization and a corresponding decrease in piezoelectric activity. This was reported, for example, in poled films of amorphous poly(vinyl chloride)¹⁴. This was not observed for odd-numbered nylons and, in fact, the piezoelectric coefficient, d_{31} , was found to increase dramatically above T_g from $d_{31} \sim 3$ pc/N to $d_{31} \sim 12$ pc/N¹⁵. A similar sharp increase in the piezoelectric coefficient above T_g is also observed for PVF₂¹⁶ ($T_g \sim -55^\circ\text{C}$).

Finally, even though several X-ray diffraction studies of nylon 11 had been made by various investigators^{5,13,17-19}, no definitive X-ray crystal structure determination had

been carried out for any of the various polymorphic forms reported. Comparative X-ray diffraction studies of poled and unpoled, initially unoriented nylon 11 films, did not reveal any significant or unambiguous differences in the x-ray diffraction patterns that were expected if indeed the dipoles (hydrogen bonds) were re-oriented in the direction of the applied electric field to give rise to a bulk polarization. For this latter reason, it was decided to study the doubly oriented odd-numbered nylon films that were known to be formed on drawing quenched nylon films at temperatures below T_g ²⁰. It was hoped that the more detailed X-ray diffraction data available from these doubly oriented films would provide insight into the electroprocessing of nylon 11, that is, into the relationship between poling conditions, piezoelectric response and crystal structure and orientation for the odd-numbered nylons.

Ferroelectric Behavior of Odd-Numbered Nylons

Nylon 11 and nylon 7 films were prepared by quenching melt-pressed films into ice water. These films were then uniaxially stretched (cold drawn) at room temperature to a draw ratio of 2.8:1. After the drawing process, silver paint electrodes were coated onto opposing film surfaces prior to poling. The poling procedure utilized a periodic triangular-shaped applied voltage with a period of 640 secs, applying an electric field which increased linearly to give a maximum field of 250 MV/m in one direction and then linearly decreased to give the same magnitude field in the opposite direction. A schematic representation of this apparatus and the applied electric field is shown in Figure 3(a).

In Figure 3(b) is shown the current density (J) (corrected by subtraction of the D.C. current) as a function of applied field (E) at a series of temperatures from -60°C to room temperature for nylon 11. These results are similar to those typically obtained for PVF₂ and, in fact, are typical behavior for a ferroelectric material. In Figure 3(c) is shown the analogous J vs E data obtained for a film of PVF₂, except that the low

temperature range is extended down to -140°C , since the T_g for PVF₂ is $\sim -55^{\circ}\text{C}$. At constant temperature, as the electric field is increased in the positive direction, the current density J increases and, at high enough fields, J increases sharply for nylon 11 giving a maximum value of J . At the very highest fields (above 150 MV/m at room temperature), the value of J is again quite small. Then, as the electric field is reduced to zero, J monotonically decreases. As the field becomes negative, the behavior is repeated with the peak in J occurring in the reverse direction. The current density peak corresponds to dipole switching and the value of the electric field corresponding to the maximum in J is termed the coercive field E_c . That is, the orientation of the bulk polarization switched to the opposite direction at a critical electric field value. This, of course, corresponds to a reorientation of electric dipoles in the crystalline regions of ferroelectric materials such as PVF₂. We notice also that at temperatures below T_g , the coercive field is higher as the temperature decreases, both for PVF₂ and nylon 11.

Further, integrating these current density data to give electric displacement D , and graphing this data as a function of the applied field E at different temperatures, showed the hysteresis behavior, presented in Figure 3(d) for nylon 11. This hysteresis behavior is typical for ferroelectric materials. The value of the electric displacement D when the electric field E returns to zero, corresponds to the remanent polarization, P_r , which remains in the film. This arises from electric dipoles (hydrogen bonds in the crystalline regions) with a preferred field-induced orientation with respect to the plane of the film. The value obtained for this remanent polarization for nylon 11, ($P_r \sim 55 \mu\text{C}/\text{m}^2$), is the same as that obtained for PVF₂. A larger remanent polarization was measured for nylon 7, $P_r \sim 90 \mu\text{C}/\text{m}^2$, and is comparable to that obtained for a PVF₂/PVF₃ copolymer¹¹. Both nylon 11 and PVF₂ films showed dipole switching at comparable coercive electric fields on poling at room temperature, and showed similar remanent polarizations. The higher value of P_r obtained for nylon 7 was consistent with the fact that the hydrogen bond density (and thus dipole density) was higher. Values of the piezoelectric

coefficient, d_{31} , at temperatures below the glass transition temperature (-55°C for PVF_2) were comparable (~ 2 to 3 pc/N) and these values increased greatly at temperatures above the glass transition temperature (50° for nylon 11).

These results²¹ were the first to show classic displacement versus electric field (D v E) ferroelectric hysteresis characteristics for the odd-numbered nylons and clearly demonstrated that nylon 11 and nylon 7 are ferroelectric materials.

Annealing and Thermal Stability Studies

These results showed that the behavior of the odd-numbered nylons is in fact very similar to that of PVF_2 with regard to ferroelectric properties. An additional study²² was carried out to examine the effects of annealing prior to poling on the ferroelectric behavior of nylon 11 and nylon 7 films, by examining the D-E hysteresis behavior. These results are shown in Figure 4(a) and 4(b). As the annealing temperature increased, the hysteresis loops became smaller and P_r decreases until, for annealing temperatures $\sim 180^{\circ}\text{C}$, a straight line D-E behavior, typical of a paraelectric material, was obtained both for nylon 11 and nylon 7. Figure 5(a) shows the decrease in remanent polarization, P_r , for nylon 11 and nylon 7 with increased annealing temperature. Figure 5(b) shows the variation in coercive field E_c for nylon 11 and nylon 7 films annealed at various temperatures. These results provide a clue to the understanding of the effect of annealing on the polarization of the odd-numbered nylon films. It was apparent that E_c increased with annealing temperature, until at some value E_c exceeded the dielectric strength (breakdown strength) of the polymer and the film could not be polarized. In other words, the effect of annealing was to "lock-in" the molecular dipoles (hydrogen bonds) in a particular direction so that they could not be re-oriented by applied electric fields of intensity less than the dielectric strength of the polymer.

This discovery led us to consider whether it would be possible to thermally stabilize the bulk polarization, P_r , by an annealing treatment of the odd-numbered nylon

films after poling. Poled films of nylon 11 and nylon 7 were prepared and then annealed for two hours at 180°C. If such an annealing treatment had been carried out for PVF₂, the depolarization that would have occurred as the poled films were heated above 120°C would have led to a dramatic decrease or disappearance of the piezoelectric activity of such annealed films. Figure 6 shows the temperature dependence of the piezoelectric strain coefficients of poled nylon 11 and nylon 7 films annealed after poling at 180°C. It is interesting to note that the value of d_{31} increased markedly for temperatures above T_g , a response similar to that of PVF₂, where T_g is -55°C. Furthermore, this piezoelectric response is stable at any temperature up to the melting point²³. Depolarization of poled films, that is, the randomization of dipole directions, appears not to occur for any temperature less than the melting temperature of the polymer. This represents an important advantage with respect to applications, in that depolarization with resulting loss of piezoelectric activity occurs at temperatures greater than 120°C for PVF₂, whereas depolarization does not occur at temperatures below the melting point for the odd-numbered nylons (for example, 185°C for nylon 11, 210°C for nylon 7, and 260°C for nylon 5).

X-Ray Diffraction and FTIR Studies

Comparative x-ray diffraction studies of unpoled, annealed nylon 11 films with respect to films poled and then annealed confirmed our interpretation of the switching of hydrogen bond dipoles in the crystalline regions, and illustrates the importance of using the doubly oriented nylon films²⁴. Figures 7(a) and 7(b) show the x-ray diffraction photographs obtained from quenched, drawn (3:1) nylon 11 films which had been annealed at 180°C for two hours but not poled. In Figure 7(a), the incident x-ray beam is perpendicular to the plane of the nylon film, while in Figure 7(b), the incident x-ray beam is in the plane of the film and perpendicular to the draw direction. These patterns reveal that the films are doubly oriented in that the molecular chains are in the direction of draw

as expected (meridian of figure) and the hydrogen-bonded sheet structure (typical of most nylon crystal structures) is in the plane of the film. For unpoled films, the dipoles are in the plane of the film. In Figure 8(a) and 8(b) is shown the x-ray diffraction patterns taken for the nylon 11 films which had been quenched and drawn as before, but poled before being annealed at 180°C for two hours. In this case, the direction of the incident x-ray beam with respect to the film geometry is the same as before, but we notice that the resulting X-ray diffraction patterns appear to have switched, i.e., Figure 8(a) is similar to Figure 7(b) and Figure 8(b) is similar to 7(a). This reveals very clearly that the crystal orientation of these doubly oriented nylon 11 films which have been poled before annealing, is rotated by 90° about the chain axis. The hydrogen-bonds (electric dipoles) on the poled films are perpendicular to the plane of the film. In other words, the effect of applying the high electric field perpendicular to the plane of the nylon film has been to rotate dipoles (hydrogen-bonds) by 90° from the plane of the film to the direction of the applied field creating a new set of hydrogen bonded sheets.. Presumably, this reorientation of dipoles by 90° occurred on the first application of the electric field, and gave rise to the first switching peak observed. Repeated field reversals to give subsequent switching peaks would arise from a 180° switching of direction of the electric dipoles, which would give rise to no further change in the X-ray diffraction patterns.

A series of more detailed X-ray diffraction studies utilizing Weissenberg methods, together with an analysis using Polarized Fourier Transform Infrared further confirmed this interpretation²⁴. Studies of nylon 5, nylon 7, and nylon 9 have also been carried out. Figure 9 shows the values obtained for the remanent polarization P_r of these polymers plotted as a function of dipole density. The linear variation obtained confirms the general understanding of the phenomenon discussed here, and indicates that we have indeed discovered that the odd-numbered nylons constitute the second-known class of ferroelectric polymers.

Concluding Remarks

Over the past several years, we have completed a long series of investigations of the odd-numbered nylons beginning with nylon 11. Our early work demonstrated that, contrary to other reports, significant piezoelectric activity could be imparted to nylon 11 films. The origin of this piezoelectric response was initially unclear because no consistent set of x-ray diffraction data existed which showed dipole re-orientation in crystalline regions, i.e., ferroelectricity. This situation also existed for many years for poly(vinylidene fluoride), the piezoelectric activity being attributed at first to charge injection, or space charge effects. For this reason, it seemed to us probable that a similar situation would exist for the odd-numbered nylons. The key to finally understanding the piezoelectric properties of these materials resulted from our study of doubly oriented films, with hydrogen-bonded sheets (dipoles) in the plane of the film, so that any bulk polarization due to electric-field induced dipole re-orientation in the crystalline regions must then result in a change of orientation of the hydrogen bonded sheets. X-ray diffraction studies directly revealed an electric field induced 90° re-orientation of hydrogen-bonded sheets in the crystalline regions. This observation, coupled with the electric displacement versus electric field hysteresis measurements confirmed that the odd-numbered nylons are ferroelectric. Further, annealing studies of these films explained why polarization of well-crystallized annealed films gave a smaller piezoelectric activity than poled quenched films. In addition, this suggested a mechanism for stabilizing piezoelectric activity to the melting point.

These studies have led naturally to the consideration of other polymer hydrogen bonded structures such as the polyureas²⁵ with regard to ferroelectric and piezoelectric properties. The existence of two distinct classes of ferroelectric polymers (poly(vinylidene fluoride) and odd-numbered nylons) has given rise to the possibility of creating new types of ferroelectric polymer composite structures. We have already begun to explore the ferroelectric and piezoelectric properties of a layered composite structure of

these two polymers (a bilaminate) as well as physical blends. Initial studies in our laboratory have indicated large increases in remanent polarization and piezoelectric response for these composite structures. Future work should address the origin of this enhancement, along with studies of other polymers with polar crystal structures. We hope that our work has rekindled interest in the general area of ferroelectric polymers.

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FIGURE CAPTIONS

- Figure 1: A schematic representation of the unit cell and molecular structure suggested by Slichter⁵ for nylon 11.
- Figure 2: The piezoelectric strain coefficient, d_{31} , at 3Hz as a function of poling temperature for quenched and annealed films of nylon 11 poled at 33MV/m.
- Figure 3(a): Schematic representation of poling apparatus.
- Figure 3(b): Current density J versus applied electric field E for nylon 11.
- Figure 3(c): Current density J versus applied electric field E for PVF₂.
- Figure 3(d): Electric displacement D versus applied electric field E showing D-E hysteresis behavior of nylon 11.
- Figure 4(a): Annealing temperature dependence of the electric displacement D as a function of the applied electric fields E for nylon 11 films. Samples are subjected to electric fields up to $E_{\max}=150\text{MV/m}$.
- Figure 4(b): Annealing temperature dependence of the electric displacement D as a function of the applied electric fields E for nylon 7 films. Samples are subjected to electric fields up to $E_{\max}=150\text{MV/m}$.
- Figure 5(a): Remanent polarization P_r for nylon 11 and nylon 7 films as a function of annealing temperature for samples annealed prior to poling.
- Figure 5(b): Coercive field E_c for nylon 11 and nylon 7 films as a function of annealing temperature for samples annealed prior to poling.
- Figure 6: Temperature dependence of piezoelectric strain coefficients d_{31} of poled nylon 11 and nylon 7 films annealed after poling at 180°C for two hours.

Figure 7: X-ray diffraction photographs of quenched cold-drawn nylon 11 films, annealed for two hours at 180°C but not poled.

- (a) Incident X-ray beam perpendicular to plane of nylon 11 film.
- (b) Incident X-ray beam in the plane of the film and perpendicular to the draw direction.

Figure 8: X-ray diffraction photographs of quenched cold-drawn nylon films, annealed for two hours at 180°C poled before annealing.

- (a) Incident X-ray beam perpendicular to plane of nylon 11 film.
- (b) Incident X-ray beam in the plane of the film and perpendicular to the draw direction.

Figure 9: Remanent polarization P_r of nylon 11, nylon 9, nylon 7, and nylon 5 as a function of their dipole density.

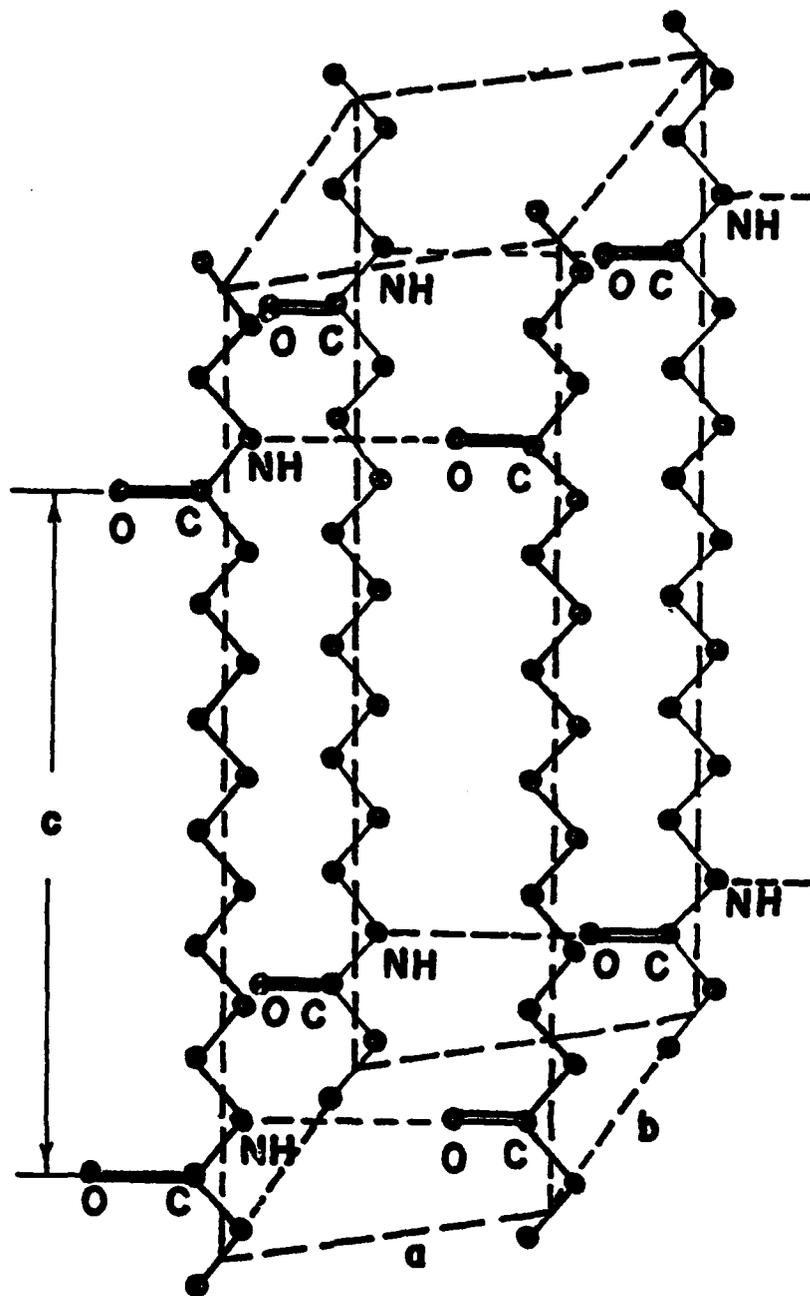
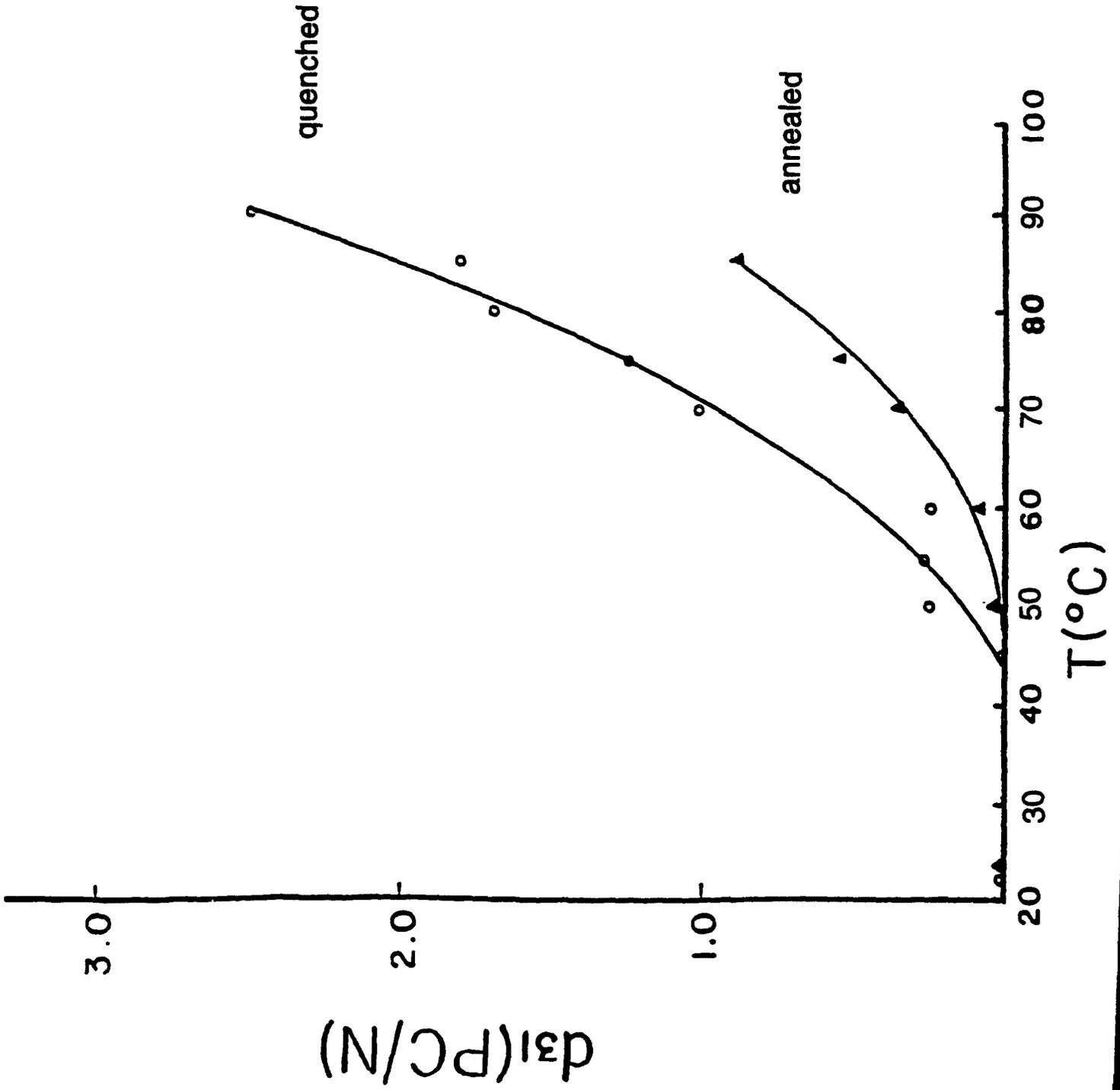


Fig 1

Fig. 2.



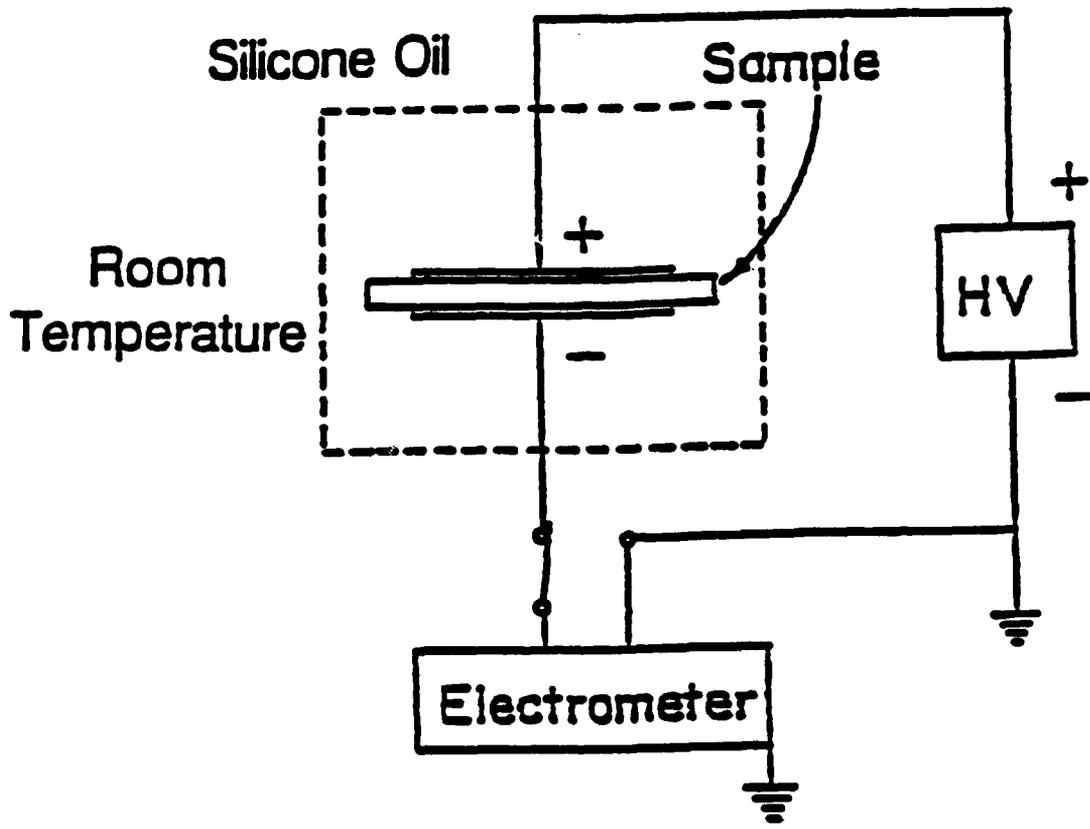


Fig 3(a)

Fig. 3(b)

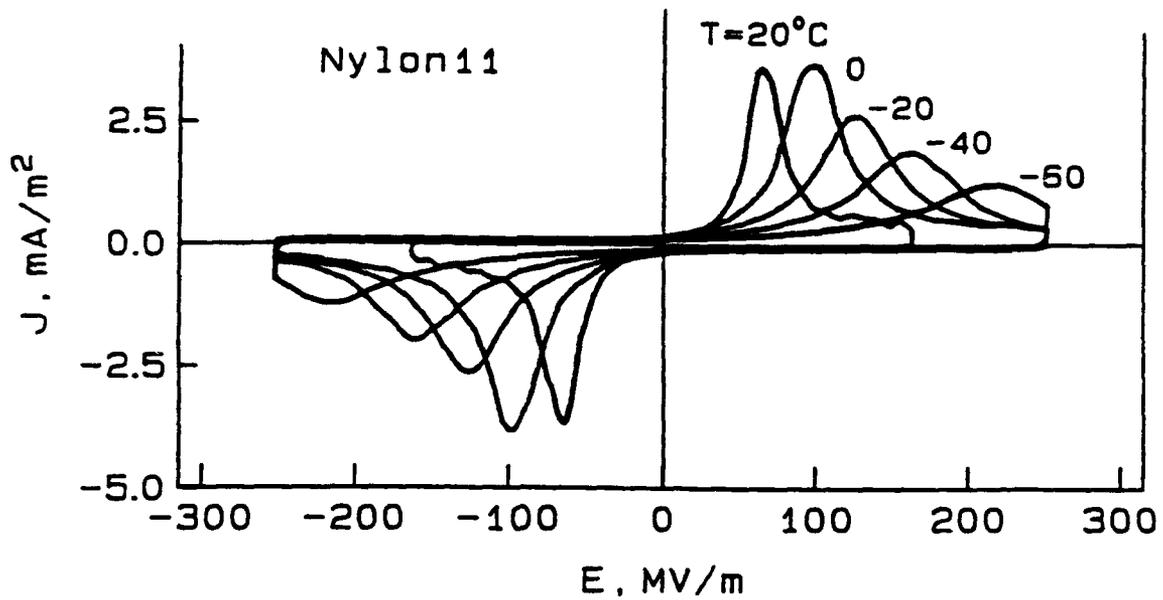


Fig. 3(c)

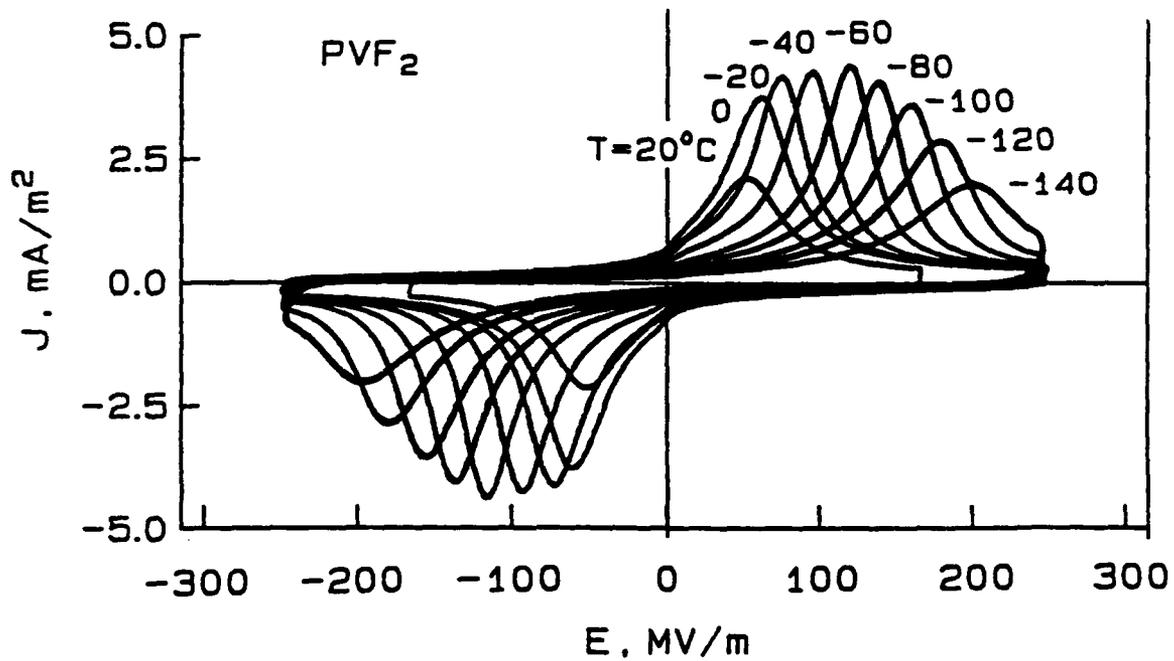
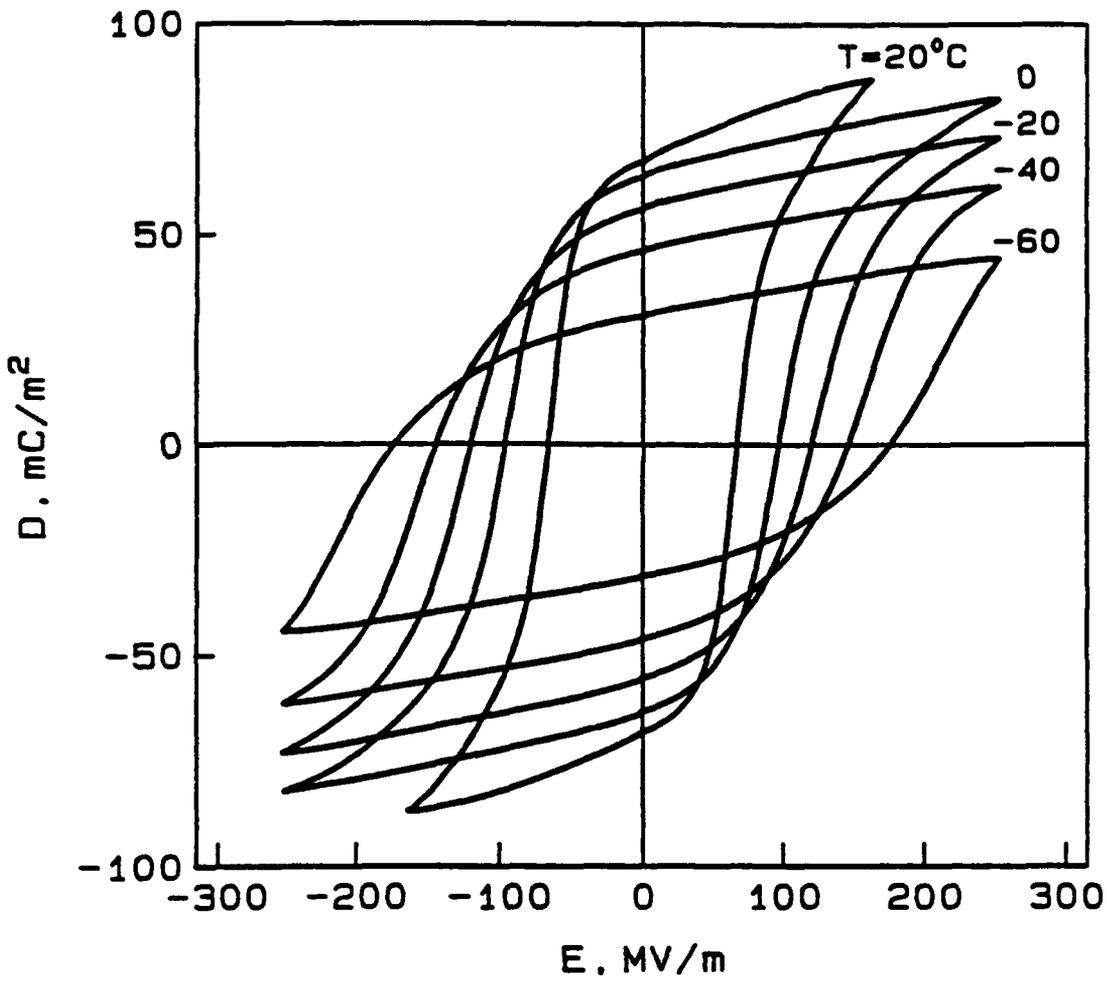


Fig
3(d)



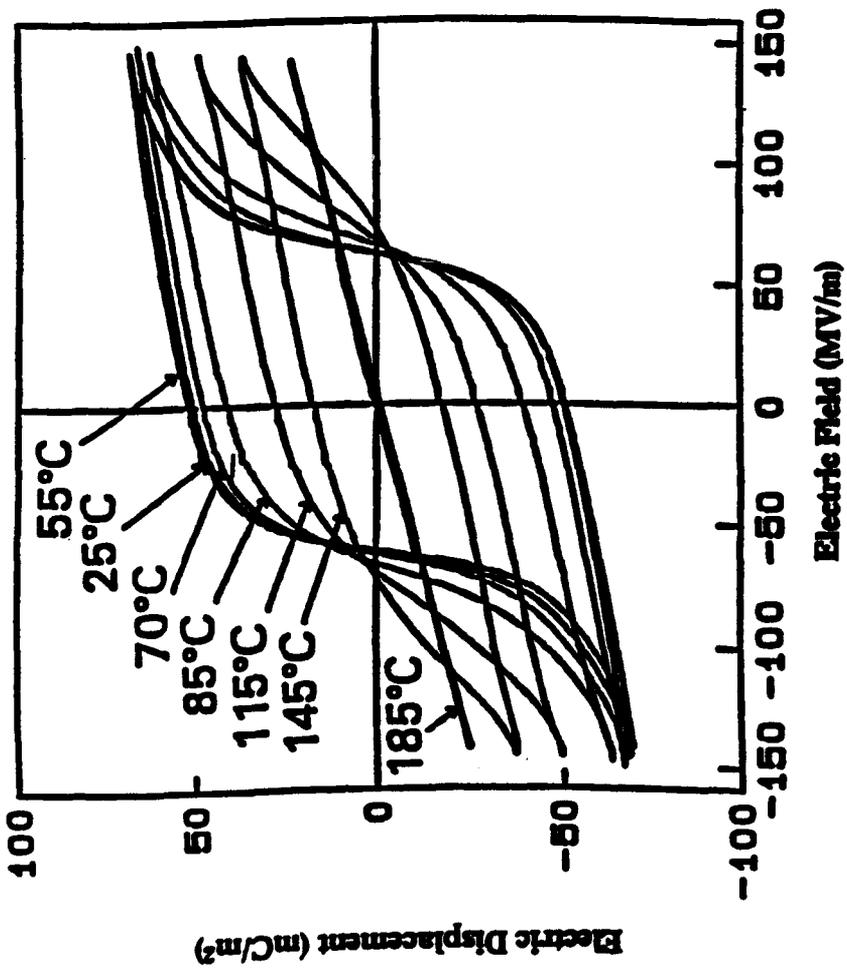


Fig 4(a)

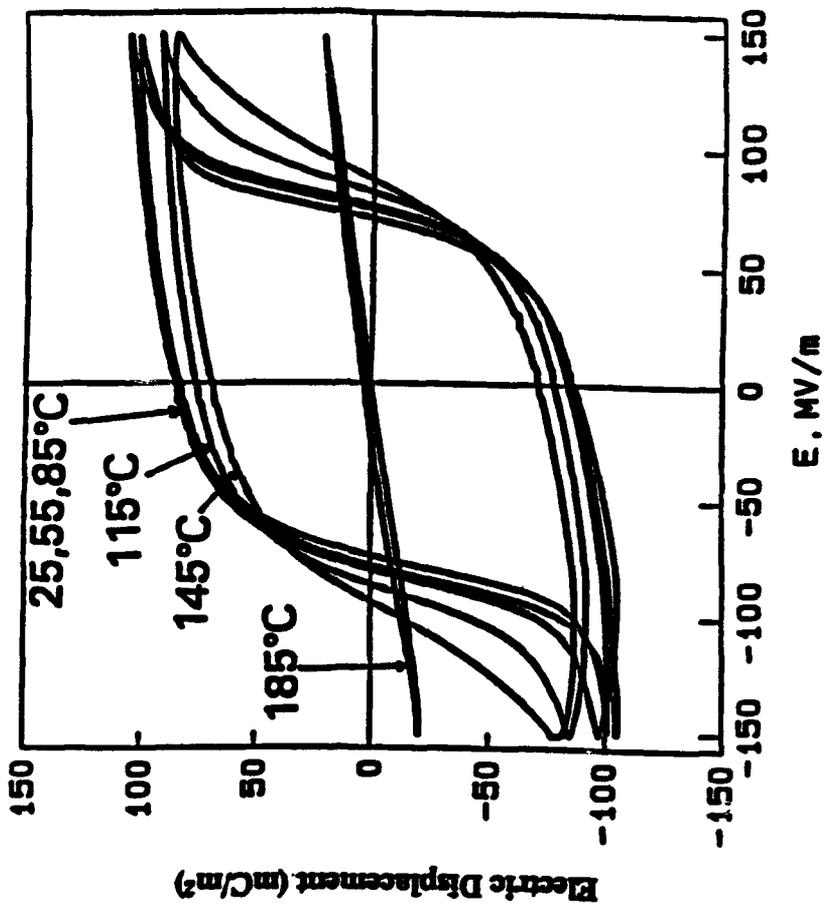


Fig 4(b)

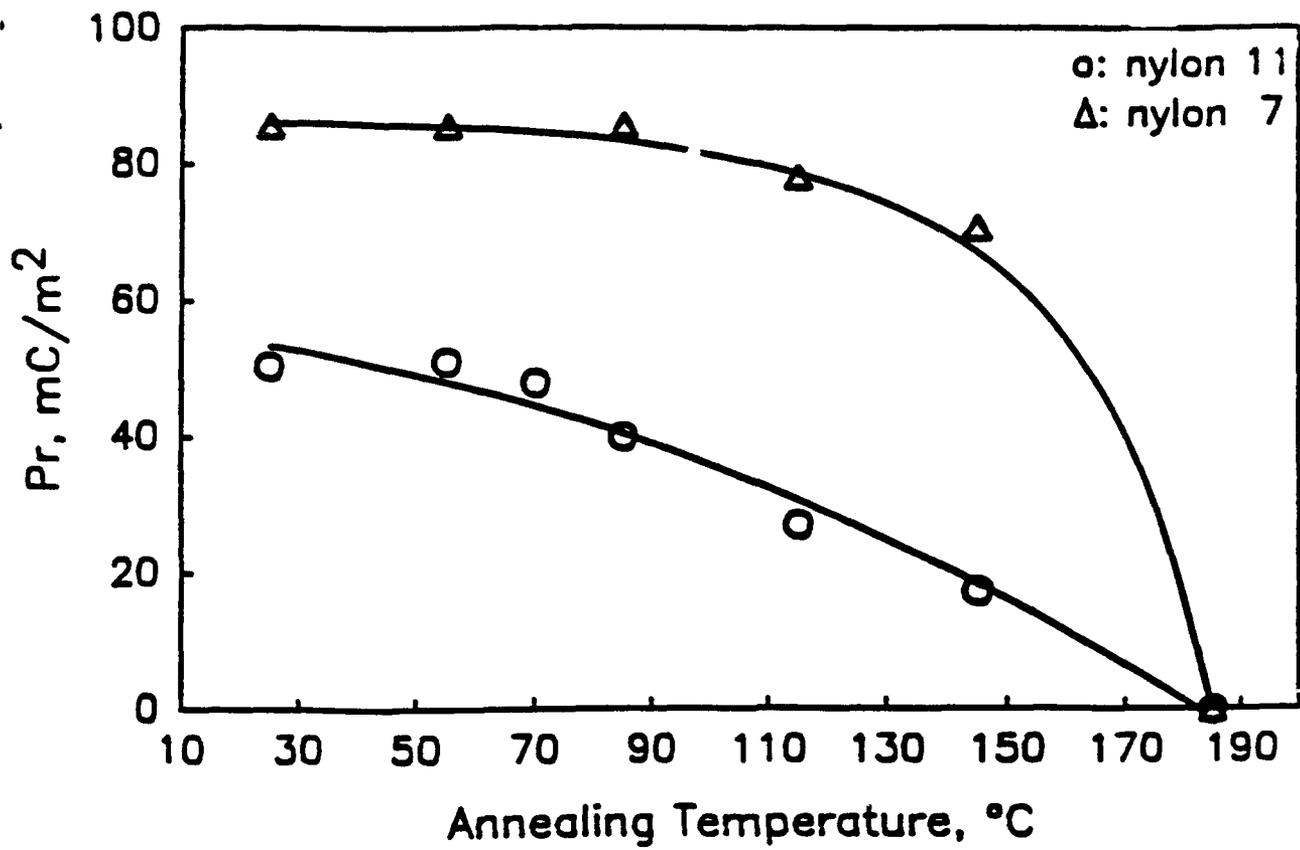


Fig5(a)

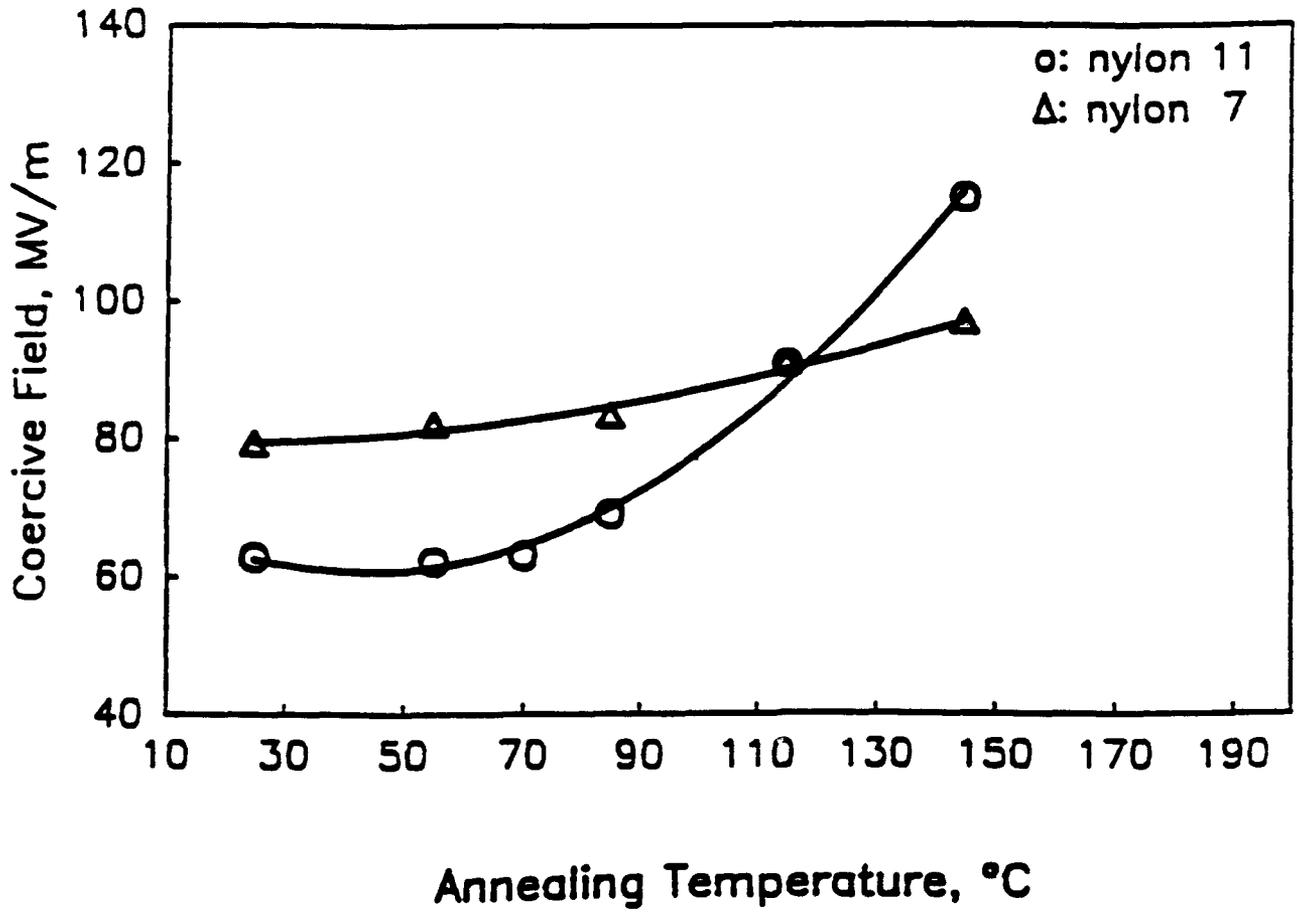


Fig5(b)

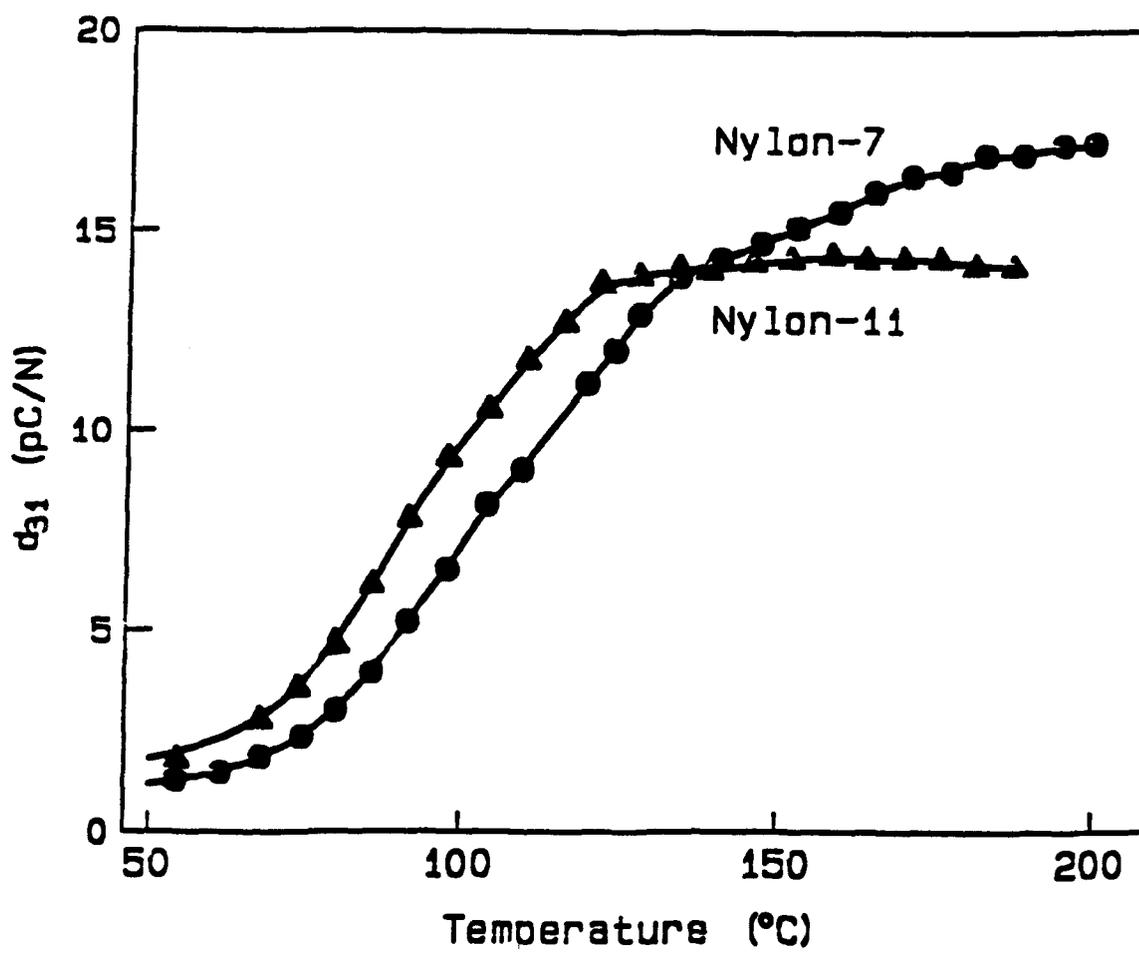
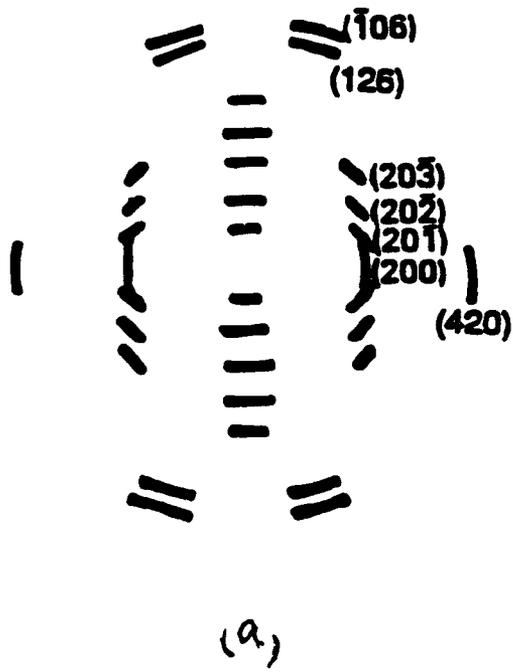
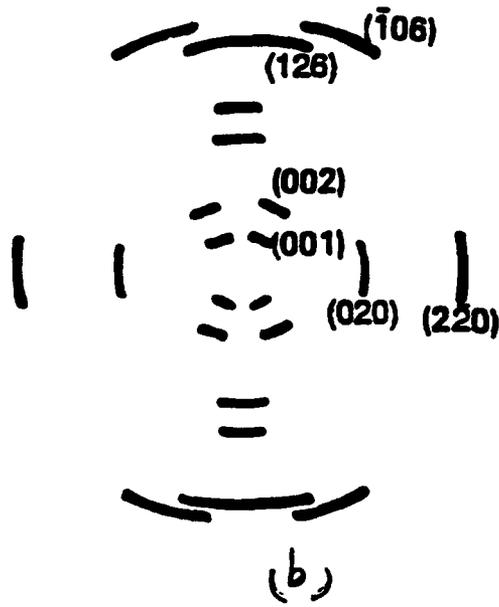


Fig. 6

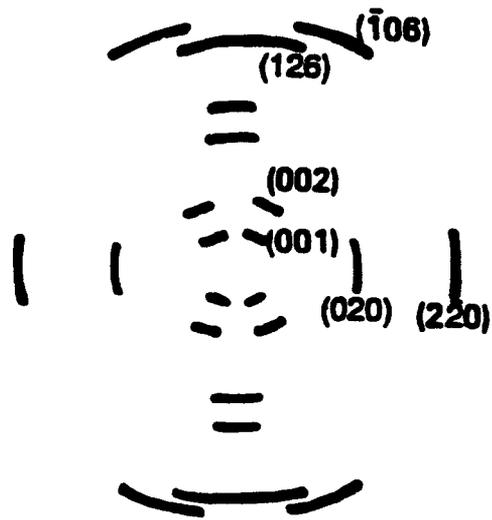


(a)

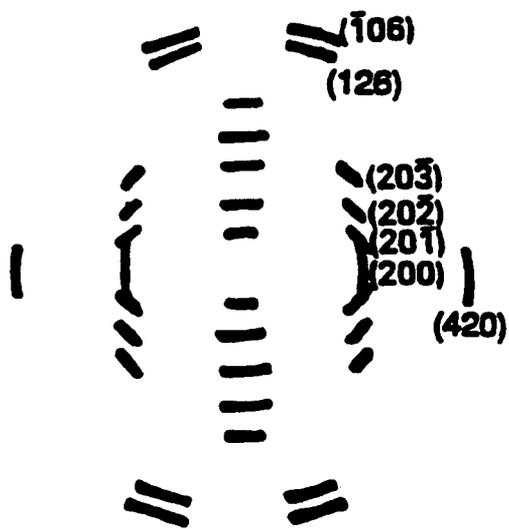


(b)

Figure 7



(a)



(b)

Figure 8

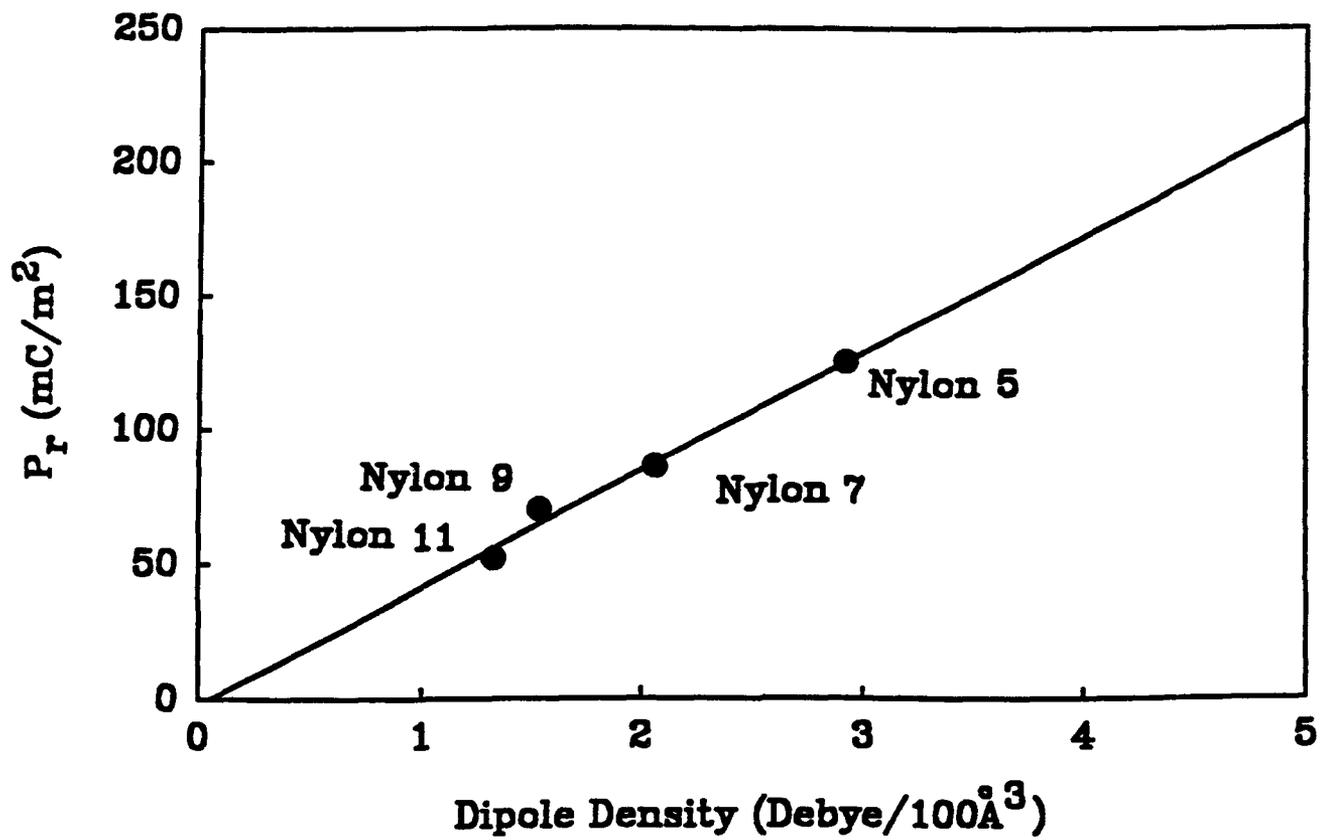


Fig. 9

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