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**FERROELECTRIC AND PIEZOELECTRIC PROPERTIES OF A QUENCHED
POLY(VINYLDENE FLUORIDE-TRIFLUOROETHYLENE) COPOLYMER**

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Ferroelectric and Piezoelectric Properties of a Quenched Poly(vinylidene Fluoride-Trifluoroethylene) Copolymer

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Synopsis

The ferroelectric and piezoelectric properties of melt-quenched unoriented poly(vinylidene fluoride-trifluoroethylene) (73:27) copolymer films as a function of the number of poling cycles have been studied. The investigation revealed that quenched films exhibit a decrease in D - E hysteresis behavior as the number of poling cycles increases when the samples are poled at room temperature. Corresponding decreases in remanent polarization, P_r , as well as small increases in the coercive field, E_c , were observed as the material was subjected to successive poling cycles. The piezoelectric coefficients, d_{31} and e_{31} , also decreased as the number of poling cycles increased. In addition, a clear reduction in the 'apparent' Curie transition temperature between unpoled and poled material was observed. Preliminary evidence indicates that films quenched below T_c do not form a stable ferroelectric crystal phase as previously believed.

Keywords: copolymer • quenching • ferroelectric, • Curie transition

INTRODUCTION

Uniaxially oriented poly(vinylidene fluoride) is well known to exhibit appreciable ferroelectric, piezoelectric, and pyroelectric behavior.^{[1][2][3]} In addition, copolymers of vinylidene fluoride with other fluorolefin polymers also show significant electroactive response.^{[4][5]}

One class of these copolymers, the poly(vinylidene fluoride-trifluoroethylene) random copolymer, P(VDF-TrFE), has been shown to be ferroelectric and piezoelectric within the composition range of ~55% to ~85 mole % vinylidene fluoride content.^[6] These copolymers also show increases in the Curie transition temperature as the vinylidene fluoride content increases.^[7] In addition, they generally crystallize from the melt into a crystal form analogous to the polar α phase I or β -phase of PVDF, characterized by an all-trans conformation of the polymer chains, pseudohexagonal chain packing and a polar unit cell, and therefore these

polymers do not require mechanical drawing before poling.^[8] The electroprocessing history represents another determinant in the electroactive response obtained, i.e., different thermal, mechanical, and electrical poling histories can result in clear differences in the observed piezoelectric and ferroelectric behavior.^[9]

The effects of thermal history on the microstructure and subsequent ferroelectric and piezoelectric response of electroactive polymers have been studied by many researchers. Oka *et al.*^[10] and Yang *et al.*^[11] have shown that although PVDF samples prepared by crystallization from the melt generally result in formation of the non-polar *phase II*, which must then be mechanically oriented in order to produce the polar *phase I*, thin films (<30 μ m) prepared by rapid quenching from the melt to about 30 °C and below results in the formation of a disorganized *phase I*. X-Ray and FTIR studies show that subsequent annealing of these samples at 120°C for 50 hours results in a complete transformation to *phase I*. When the material was quenched to higher temperatures (>40 °C), the result was predominantly *phase II* with a trace amount of *phase I*. Nevertheless, annealing of these materials at 120 °C for 50 hours also resulted in the formation of almost all *phase I* material. A mixture of *phase I* and *II* was reported to form in quenched films which were on the order of 200 μ m thick. A small amount of *phase I* was produced close to the surface, while a large amount of *phase II* was reported to form in the interior. This was attributed to a skin-core morphology when the thick films were quenched. Quenching results in low temperature nucleation and growth. This regime favors the formation of the *phase I* crystal form in PVDF. As-crystallized *phase I* can also be produced by epitaxial growth techniques or pressure quenching.^{[12][13]}

In the case of poly(trifluoroethylene) PTrFE, fast quenched samples show some pyroelectricity when poled at elevated temperature. Its slow cooled counterpart does not exhibit this characteristic, but shows ferroelectric response comparable to that seen in low VDF (<<50 mol %) copolymers.^[10]

For the copolymers of VDF and TrFE, the structure and electrical response strongly depend on electroprocessing history as well as chemical composition. High VDF content copolymers have higher electroactive response than low VDF content materials. High temperature annealing of quenched as well as slow cooled films produces very high crystallinity, enhanced crystal size and perfection and high ferroelectric and piezoelectric response.^{[14][15][16]} In their study, Oka *et al.*^[10] concluded from the results of their DTA and x-ray diffraction experiments that an

ordered ferroelectric phase is formed when high VDF content copolymer films are prepared by quenching, however, no electrical measurements were performed to substantiate the claim of ferroelectricity in these copolymer films.

X-Ray diffraction and electromechanical coupling constant measurements performed by Ohigashi and Koga^[17] showed that annealing high VDF content copolymers (70-80 mol%) produces material having large electromechanical coupling constant, ($k_t \sim 0.3$) compared to the homopolymer PVDF ($k_t \sim 0.05$), when annealed at temperatures above the Curie transition temperature, T_c , prior to poling.

Tanaka and co-workers^[18] suggested that the structure of the ferroelectric phase in P(VDF-TrFE) strongly depends on the crystallization temperature, especially on whether the copolymer is crystallized above or below T_c . They concluded that two ferroelectric phases are produced; a less ordered ferroelectric phase designated F_A , and a well ordered phase, F_B , having a higher Curie transition temperature. These phases are produced when the material is crystallized above and below the Curie point respectively. Further, it was proposed that the ordered ferroelectric phase F_B can only be produced when crystallization occurs below T_c , and that T_c decreases as the crystallization temperature increases.^[18] In their study, no electrical measurements were performed to support the conclusion that both the F_A and F_B phases are ferroelectric.

In a more recent paper^[19], it was proposed that the works of Ohigashi et al.^[17] and Tanaka et al.^[18], were not contradictory. The well ordered ferroelectric phase, F_B , is formed in high VDF copolymers when the crystallization temperature, T_{crys} , is lower than the Curie transition temperature, T_c , because defects become frozen-in when crystallization occurs in the paraelectric region, $T > T_c$. These defects make transformation to the complete ferroelectric phase more difficult on cooling through T_c .

In order to gain a better understanding of the ferroelectric nature of samples crystallized below T_c , we produced a set of quenched copolymer films that were crystallized below T_c . This study will focus on the ferroelectric and piezoelectric behavior of these as-quenched P(VDF-TrFE) (73/27) copolymer films.

EXPERIMENTAL

The samples used in this study were prepared by melt-pressing P(VDF-TrFE) (73/27) powder, supplied by Atochem Sensors Inc., between aluminum foils at

210 °C. The samples were then quenched in an ice-water bath, after which the films were removed from the aluminum foil. The average film thickness ranged between 25-35 microns.

Rectangular gold electrodes with offset tabs were deposited by vacuum evaporation on opposing sides of the films, creating an effective electrode area of approximately 25mm². Much care was taken in order to avoid annealing of the quenched films during the process of evaporation of electrodes onto the surface of the films.

Samples were poled in a silicone oil bath at room temperature by applying a triangular electric field waveform. The period of the applied waveform was 1000 seconds and the maximum amplitude was 150 MV/m. Measurements of current density versus electric field (J - E) were made, and equipment control, data collection and processing were carried out using an IBM microcomputer. The characteristic D - E hysteresis loops, from which the coercive field, E_c , and the remanent polarization, P_r , were obtained, were also generated as previously described.^[20]

After poling the sample for one full cycle, the film was removed from the bath. The silicone oil was removed and d_{31} and e_{31} , the piezoelectric strain and stress coefficients respectively, were measured simultaneously. Measurements were carried out at room temperature at a frequency of 104 Hertz, using a Toyoseiki (Japan) Rheograph Solid[®]. The ferroelectric switching and piezoelectric measurement procedures were repeated until no further change in the ferroelectric and piezoelectric response occurred. In addition, aging studies were conducted in order to determine the stability of the polarization after each poling cycle. Poled samples were stored at ~28 °C and repoled 1, 2, 3 and 14 days later and their switching behavior was compared with that of the as-poled material.

The thermal behavior of different samples was obtained by using a Perkin-Elmer DSC-4 Differential Scanning Calorimeter. Three types of samples were studied, unpoled samples, samples which were poled for one cycle, and samples which were poled through at least six cycles, i.e., when the response stabilized. The samples were heated from -60°C to 190 °C at a rate of 5 degrees per minute.

X-ray diffraction patterns of all three types of samples were obtained using a flat plate Statton camera and an American Instruments[®] 3100 x-ray generator with CuK_α radiation filtered using a nickel foil. X-ray diffraction patterns were taken

in the transmission mode, (x-ray beam perpendicular to the copolymer film surface), and the edge mode, (x-ray beam parallel to the copolymer film surface) for each type of sample. Diffraction studies were also carried out using a vertical wide angle x-ray diffractometer which employs a Phillips® XRG 3100 x-ray generator. X-ray diffraction scans for both reflection and transmission modes were examined and the results analyzed for relative crystallinity, crystal orientation and crystal phases.

RESULTS AND DISCUSSION

Ferroelectric Response and Poling Behavior

Figure 1a. shows the measured current density corrected for conduction, J (mA/m^2) versus the applied electric field as the sample is poled. The current switching peaks observed in each half-cycle indicates a reversal of the polarization.

Most noteworthy is the following phenomenon. As the sample is poled, there is a gradual reduction in the magnitude of the switching peak, which essentially disappears after approximately five full cycles, where one cycle represents a ramping of the electric field from $E=0$ to maximum positive through to maximum negative, and then back to $E=0$ (MV/m). This suggests that although a large number of dipoles switched on the first cycle, fewer dipoles in the material switched on each successive poling cycle, and the number switching reached a minimum after five or six full cycles.

The electric displacement versus electric field D - E hysteresis data shown in figure 1b. were generated by integration of the J - E data over time. The series of curves show a large D - E hysteresis loop resulting from the first poling cycle. This hysteresis, also observed in well poled films of PVDF and blend composites with P(VDF-TrFE) copolymer, the odd numbered Nylons and laminate composites of PVDF and Nylon-11 films is characteristic of ferroelectric materials.^{[21][22][23][24]} For all of these materials, an increase in the magnitude of the switching peaks is observed with successive cycles. However, for the quenched P(VDF-TrFE) films examined here, as the sample is poled through successive cycles, a decay in the ferroelectric D - E hysteresis toward the more linear paraelectric behavior was observed. The corresponding remanent polarization, P_r , also decreased while the coercive field, E_c , shifted to slightly higher electric fields before stabilizing after about the sixth cycle, as shown in figures 2a and 2b. The remanent polarization measured from the first cycle of poling was considerably larger ($\sim 100 \text{ mC/m}^2$) that

that seen in copolymer films prepared by slow cooling from the melt, after six cycles ($\sim 75 \text{ mC/m}^2$ see figure 3b). The results show that for the quenched films, a gradual loss in the remanent polarization occurs as the samples undergo successive poling cycles. The loss in polarization results from changes in the crystal properties of the material which results in dipoles becoming more and more difficult to switch. These changes may occur as a result of an electric field induced crystal structure transformation to a non-polar phase. There is also a small increase in the switching energy barrier observed as a slight increase in the coercive field, E_c . This process is soon exhausted, and after several cycles, the previously switchable dipoles lose their switching ability within the crystals and are therefore unable to respond to the electric field.

For other samples the successive switching cycles were interrupted by storing for different periods of time. Samples which were poled for one through six cycles and which showed the characteristic decrease in ferroelectric properties were stored for 1, 2, 3 and 14 days. These samples, when poled with the next switching cycle after storing for the specified time period, exhibited ferroelectric responses that were identical in magnitude to samples for which the successive switching cycles had not been interrupted by storing for prolonged periods. This suggests that the depolarization phenomenon arises primarily from the interaction of the material and the electric field and that the structure obtained is stable.

The results obtained in this study are in disagreement with the work of Tanaka *et al.*^[18] and others.^{[10][11]} These authors concluded that an ordered ferroelectric phase is formed when the copolymer is crystallized with large undercooling, below T_c . The response of ordered ferroelectric copolymer films subjected to electric field poling cycles is well known. Figures 3a and 3b show the ferroelectric response after at least six cycles of poling of the same material, PVDF-TrFE, prepared by melt-quenching-and-cold-drawing, and by slow-cooling. The current density, J , and the remanent polarization, P_r , increase up to a maximum as the material is taken through the switching cycles. In addition the coercive field, E_c , is distinct, and does not increase as the number of poling cycles increase. Although the remanent polarization, P_r , after the first cycle of poling for quenched copolymer films is roughly comparable to that obtained in slow cooled material, the polarization for quenched films decreases with increasing number of poling cycles, while for the melt-quenched and drawn films and the slow cooled films, the polarization goes to a stable maximum after many cycles. The latter is characteristic of ferroelectric materials.

Piezoelectric and Dielectric Measurements

After each cycle of poling, the piezoelectric strain coefficient, d_{31} , the piezoelectric stress coefficient, e_{31} , and the dielectric constant ϵ , were measured. Figures 4a. and 4b. show the piezoelectric strain and stress coefficients, d_{31} and e_{31} of the material as a function of the number of poling cycles. Both d_{31} and e_{31} exhibit decay characteristics consistent with a decreasing Pr as the sample is subjected to successive poling cycles. The results appear to be in direct qualitative agreement with the ferroelectric switching behavior discussed earlier. Data showing the room temperature dielectric constant, ϵ , as a function of the number of poling cycles, indicates that there was no significant change in the value of ϵ as the samples were poled, implying no large change in crystallinity. Since the dielectric constant of the material above the glass transition temperature, T_g , is derived mostly from the amorphous regions in a polar semicrystalline polymer system, an increase in crystalline content would give rise to a decrease in ϵ . The constant value of ϵ with the number of switching cycles indicates that little field induced crystallization occurs.

DSC Measurements

The possibility of crystal structure or other microstructure changes occurring in the quenched material as a result of poling was examined by thermal analysis. Three types of samples were studied; unpoled, poled for one cycle (highest ferroelectric and piezoelectric response) and poled for many cycles (lowest ferroelectric and piezoelectric response). Figure 5. shows the results of the DSC experiments. All three samples were found to have similar melt transition temperatures ($T_m=145.5\text{ }^\circ\text{C} \pm 5^\circ\text{C}$); however, a significant change in T_c occurred, with the Curie transition temperatures being $T_c=117.6\text{ }^\circ\text{C}$, $110\text{ }^\circ\text{C}$, and $109.6\text{ }^\circ\text{C}$ respectively. These results show a $\sim 7\text{ }^\circ\text{C}$ decrease in the Curie temperature between the unpoled sample and both of the poled samples and indicate that a significant change occurs in these materials during the first cycle of poling.

X-ray Diffraction

X-ray diffraction patterns of quenched mechanically unoriented copolymer samples which were unpoled, poled for one cycle, and poled for many cycles were obtained. There was no significant difference observed among the diffraction patterns, (see Figure 6). The results of the wide angle diffraction scans are shown in Figure 7. We observed that the crystallinity for both poled and unpoled samples

was ~60% . We also observed greater amorphous scattering on the lower 2θ side of the (200) reflection in the unpoled samples versus samples which were poled, which might suggest a possible improvement in the crystal perfection in the material induced by the poling procedure. Since no significant change in the halfwidths of the (001) and (110) reflections between the poled and the unpoled material is evident, it appears that poling did not result in any significant increase in the size or perfection of the crystal lamellae . However, the (001) reflection occurred at a slightly higher 2θ angle for poled samples versus unpoled samples, indicating a decrease in the d-spacing as a result of poling. If we assume that the unit cell angles remain fixed at 90° , this decrease in (001) spacing implies a move away from an all-trans chain conformation thereby shortening the chain repeat length.

CONCLUSIONS

Our study of the ferroelectric and piezoelectric properties of melt quenched P(VDF-TrFE) (73/27) copolymer films showed a decrease in the remanent polarization, P_r , and a collapse of the D - E hysteresis behavior from characteristic ferroelectric hysteresis toward a linear paraelectric curve , as the number of poling cycles increased. In addition , the coercive field, E_c , increased slightly for each successive poling cycle, indicating a gradual increase in the energy barrier for switching.

The piezoelectric strain and stress coefficients, d_{31} , and, e_{31} , correspondingly decreased as the number of poling cycles increased. DSC analysis revealed a decrease in the apparent Curie transition temperature by about 7°C between the unpoled and the poled material. These results suggest the possible formation of an unstable ferroelectric phase upon quenching which tends to transform to a stable non-ferroelectric phase as the material is poled through successive switching cycles. The transitions observed in our DSC studies are not Curie transitions by definition, because the films are shown to be non-ferroelectric, hence the use of the term, "apparent" Curie transition temperature.

While the mechanisms of ferroelectric polarization switching in polymers are not completely understood, the 60 degree incremental step rotation based on pseudo-hexagonal packing gives the best explanation for the previously observed experimental results.^[25] This polarization mechanism, also predicted by a kink propagation theory, assumes that a small distortion in the unit cell (~1%) would permit 60 degree step rotation without disruption of the polymer morphology.^[26] Except for entropy effects due to high temperature and some time dependent

dipole relaxation, the mechanisms for depolarization in ferroelectric polymers, particularly P(VDF-TrFE) systems are relatively unknown. Our experiments with the P(VDF-TrFE) (73/27) system indicates that when crystallized by quenching from the melt, the material undergoes an apparent polarization-depolarization process when subjected to successive cycles of electric field poling. An additional x-ray diffraction and FTIR study is under way to determine the structural changes which occur as the crystals change from the ferroelectric to the paraelectric phase. The temperature dependence of this phenomena is also being investigated.

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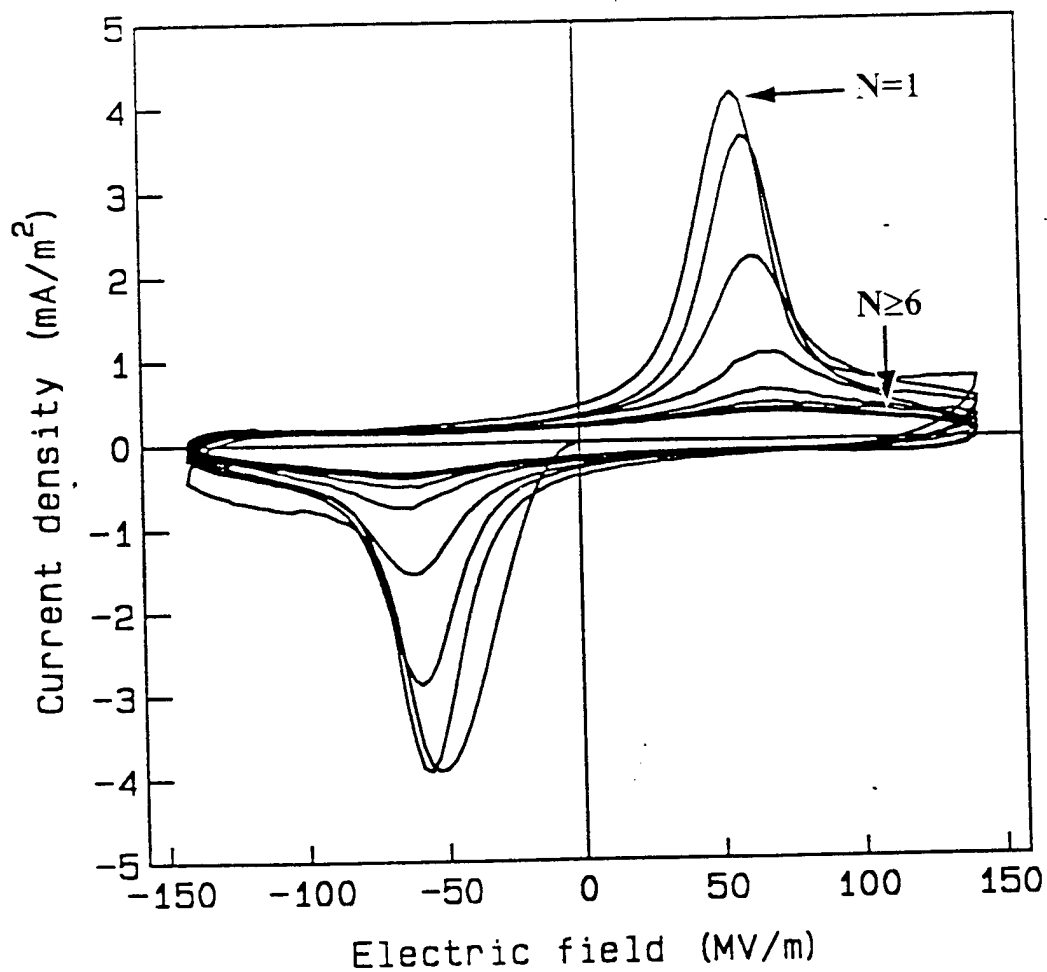


Figure 1a.

Current density, J , versus Electric Field, E , for **quenched P(VDF-TrFE) 73:27 copolymer films**, showing a systematic decrease in the current density as the sample is poled.

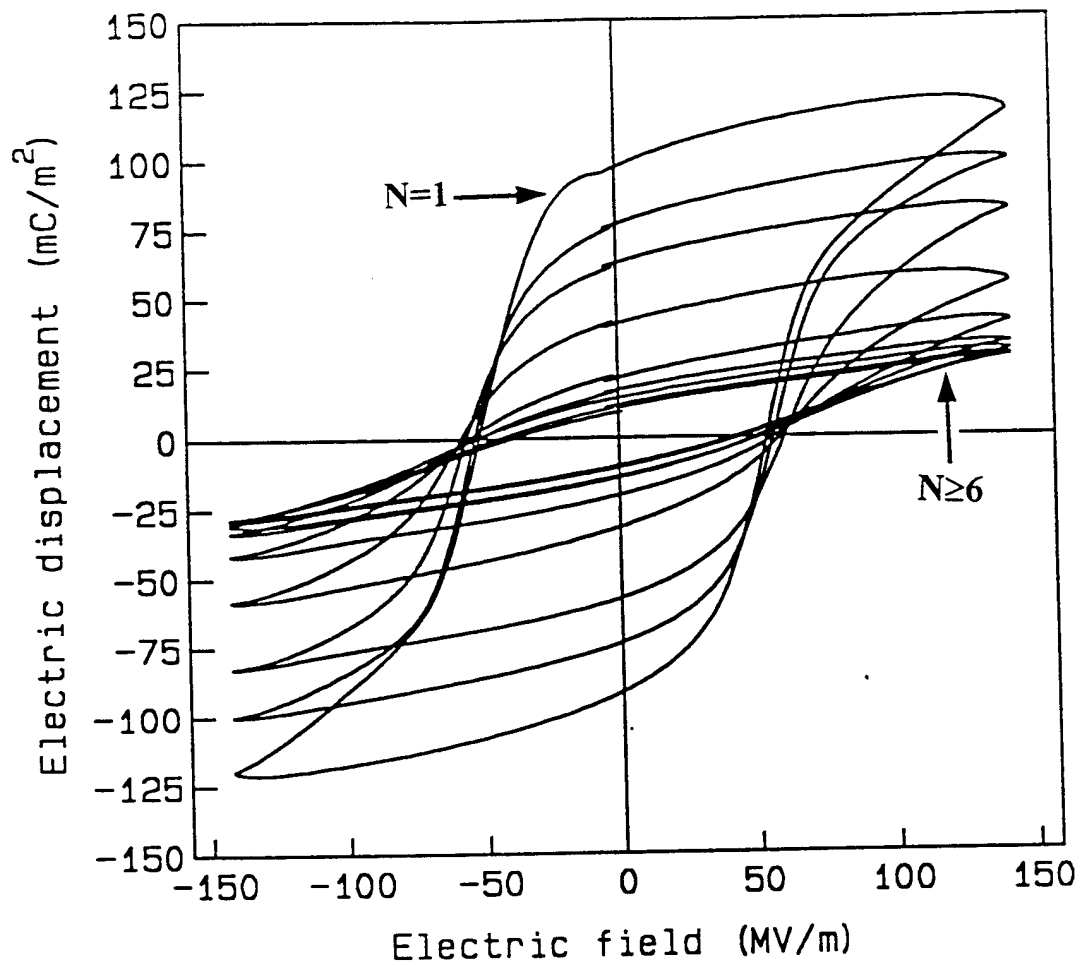


Figure 1b.

Electric displacement, D , versus Electric field, E , for **quenched P(VDF-TrFE) 73:27**, showing the decay of the ferroelectric hysteresis loop as the polarization of the sample is reversed.

Quenched P(VDF-TrFE) 73:27
Remanent Polarization vs. N, The Number of Poling Cycles

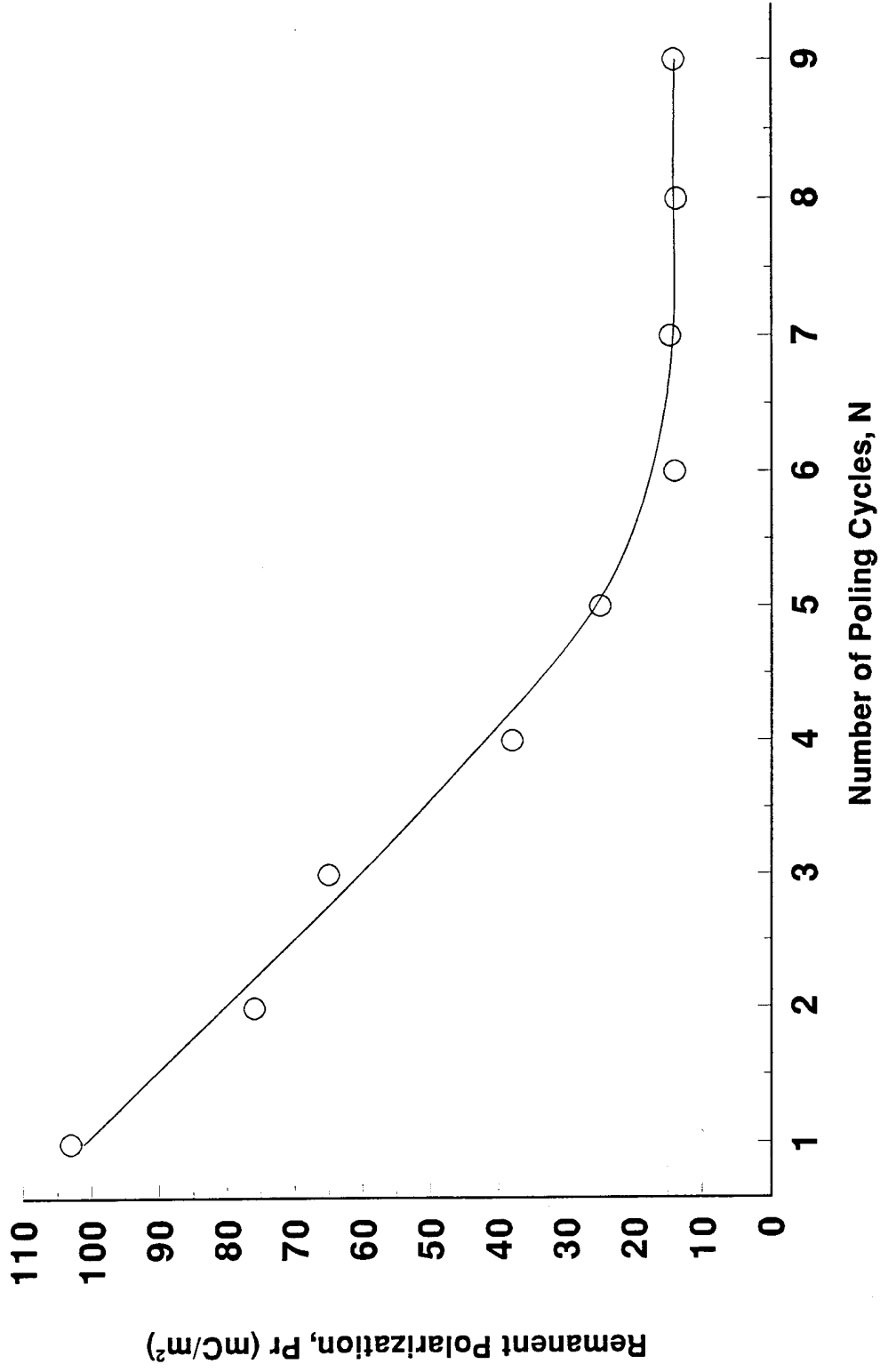


Figure 2a.

**Quenched P(VDF-TrFE) 73:27
Coercive Field Vs. N, The Number of Poling Cycles**

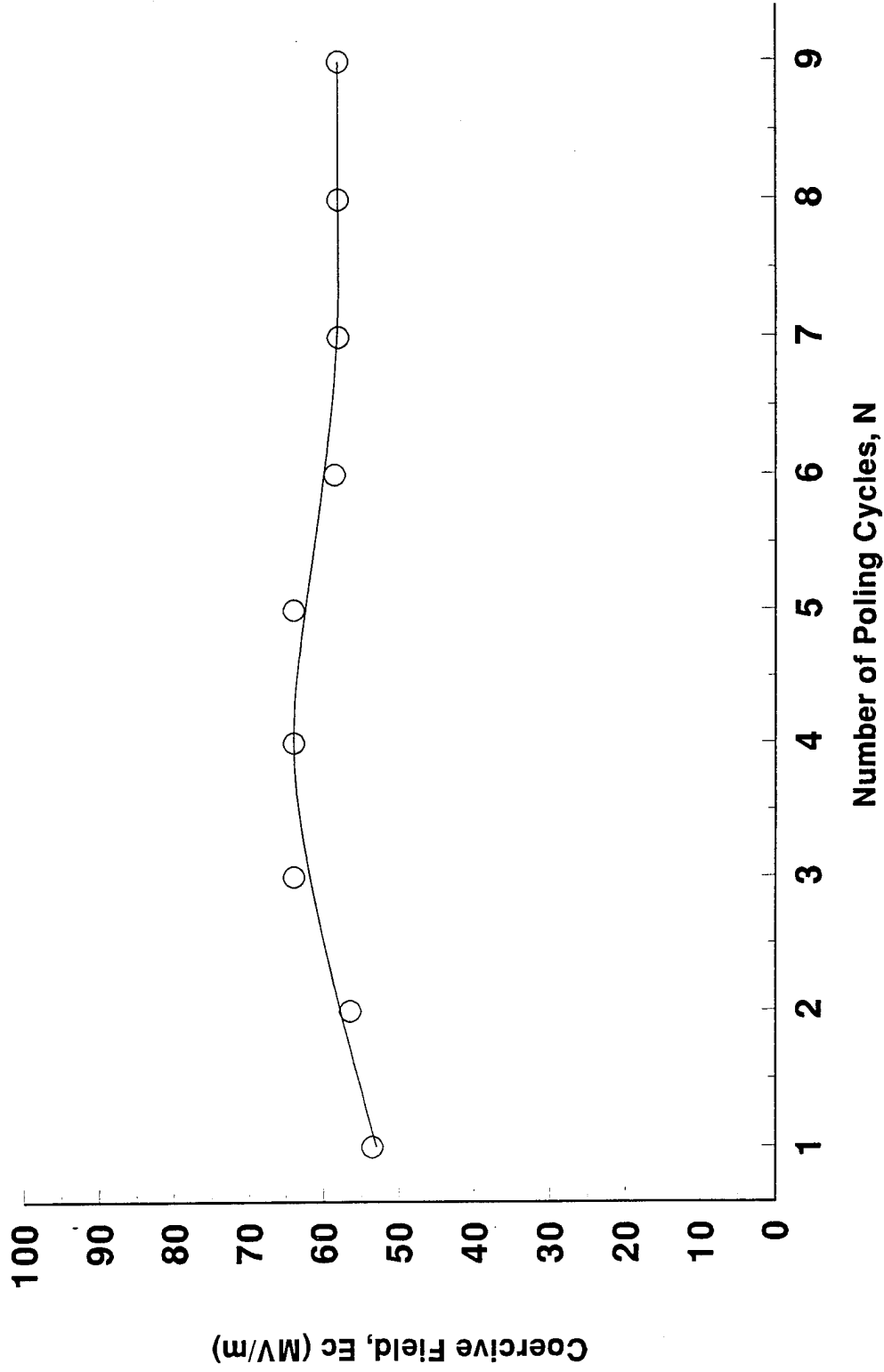


Figure 2b.

J-E, for Quenched & Drawn, and Slow Cooled 73:27

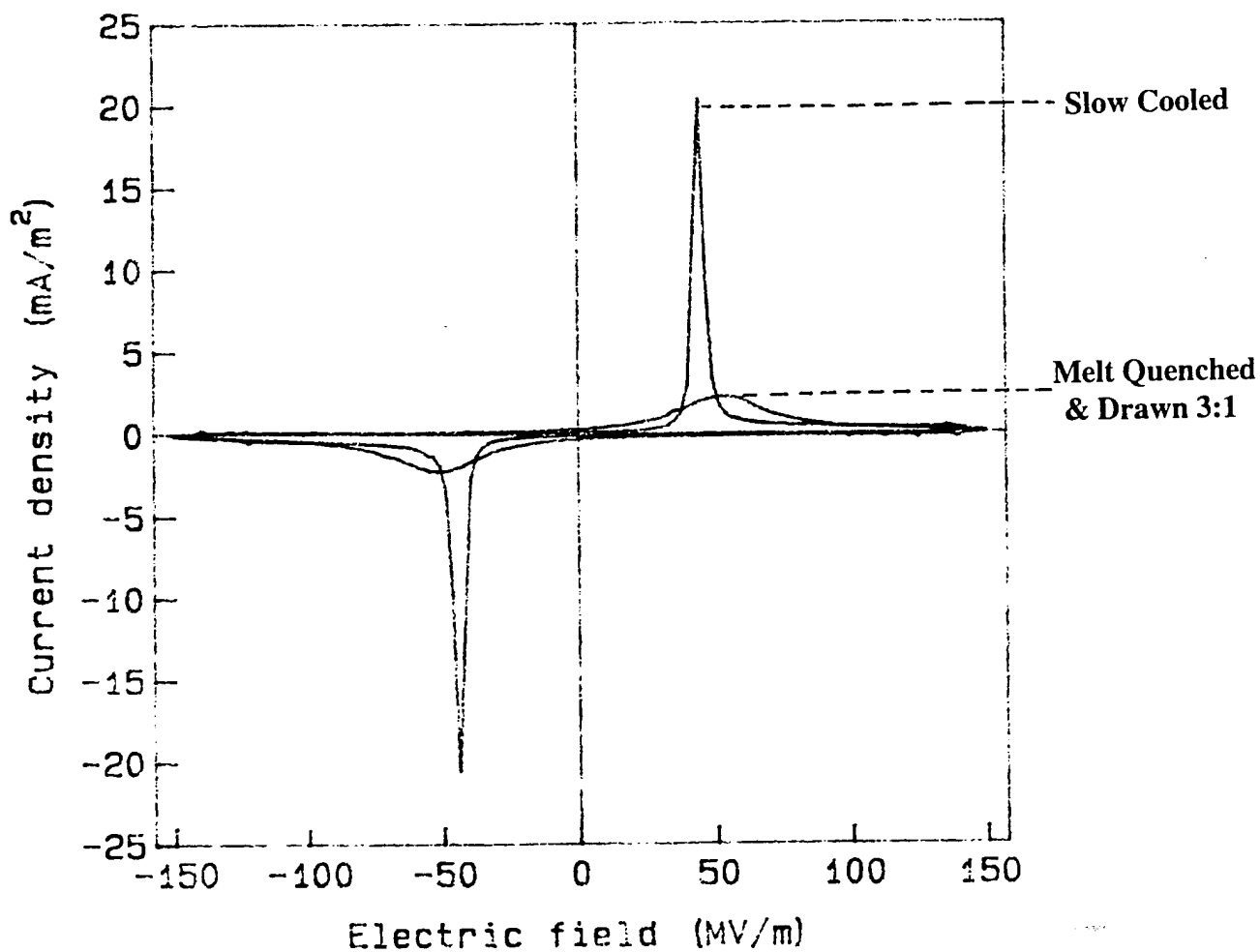


Figure 3a.

Current density, J , versus Electric field, E , for *melt quenched and drawn* and *slow cooled* P(VF₂-VF₃) 73:27.

D-E, for Quenched & Drawn, and Slow Cooled 73:27

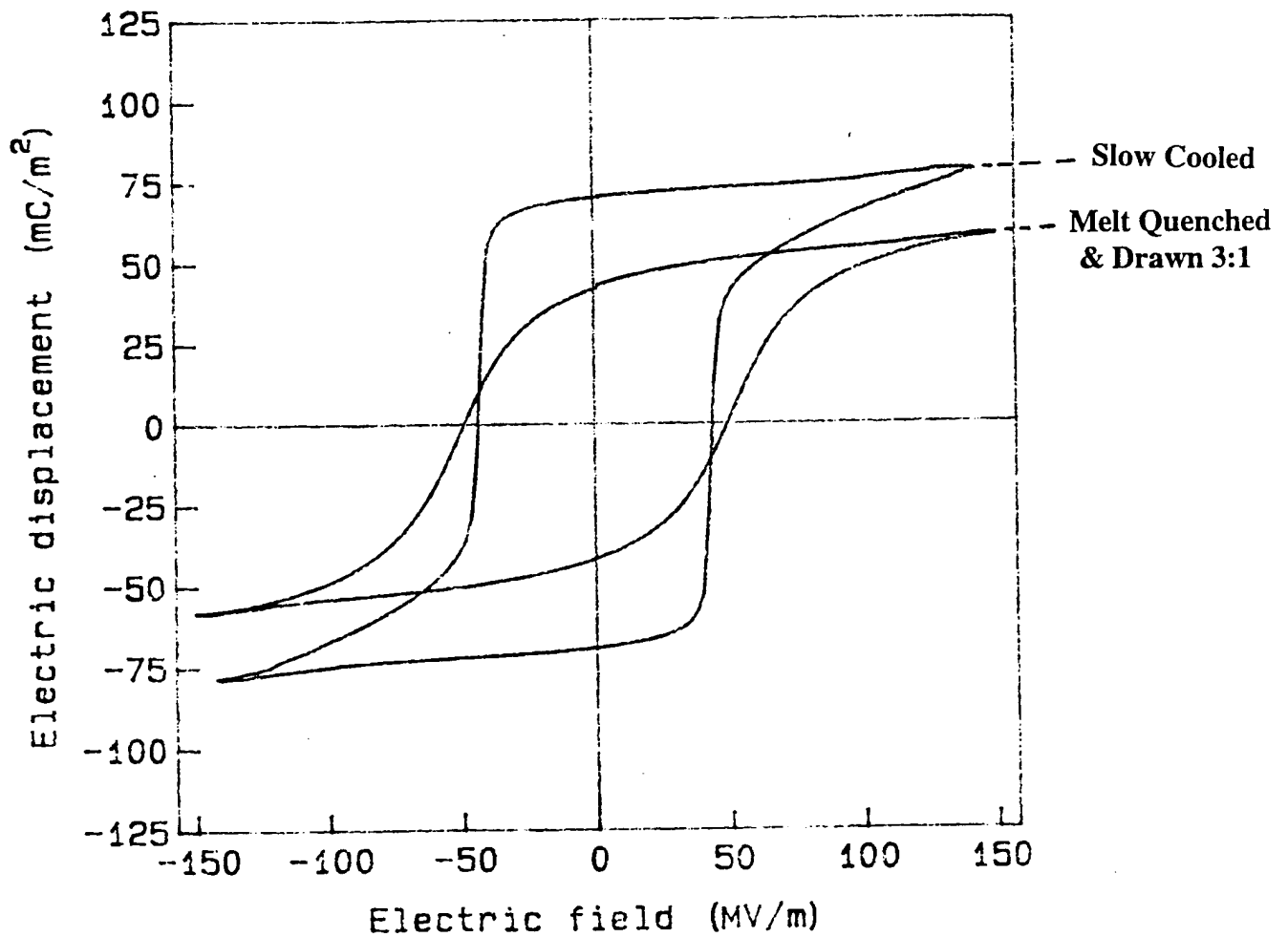


Figure 3b

Electric displacement, D , versus Electric field, E , for *melt quenched and drawn* and *slow cooled* P(VF₂-VF₃) 73:27.

QUENCHED P(VDF-TrFE) 73:27
Piezoelectric Strain Coefficient vs. N, The Number of Poling Cycles

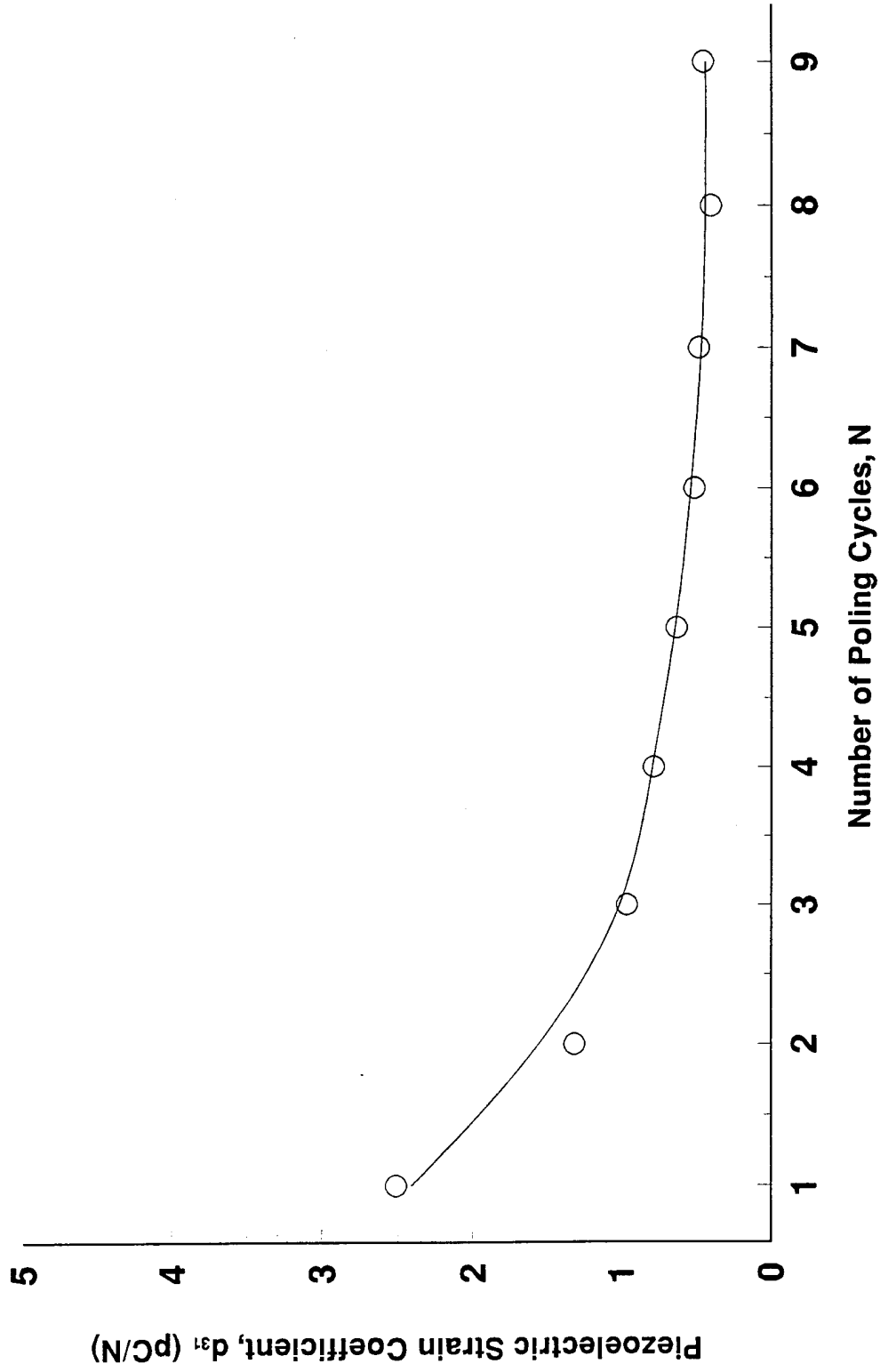


Figure 4a

Quenched P(VDF-TrFE) 73:27
Piezoelectric Stress Coefficient vs. N, The Number of Poling Cycles

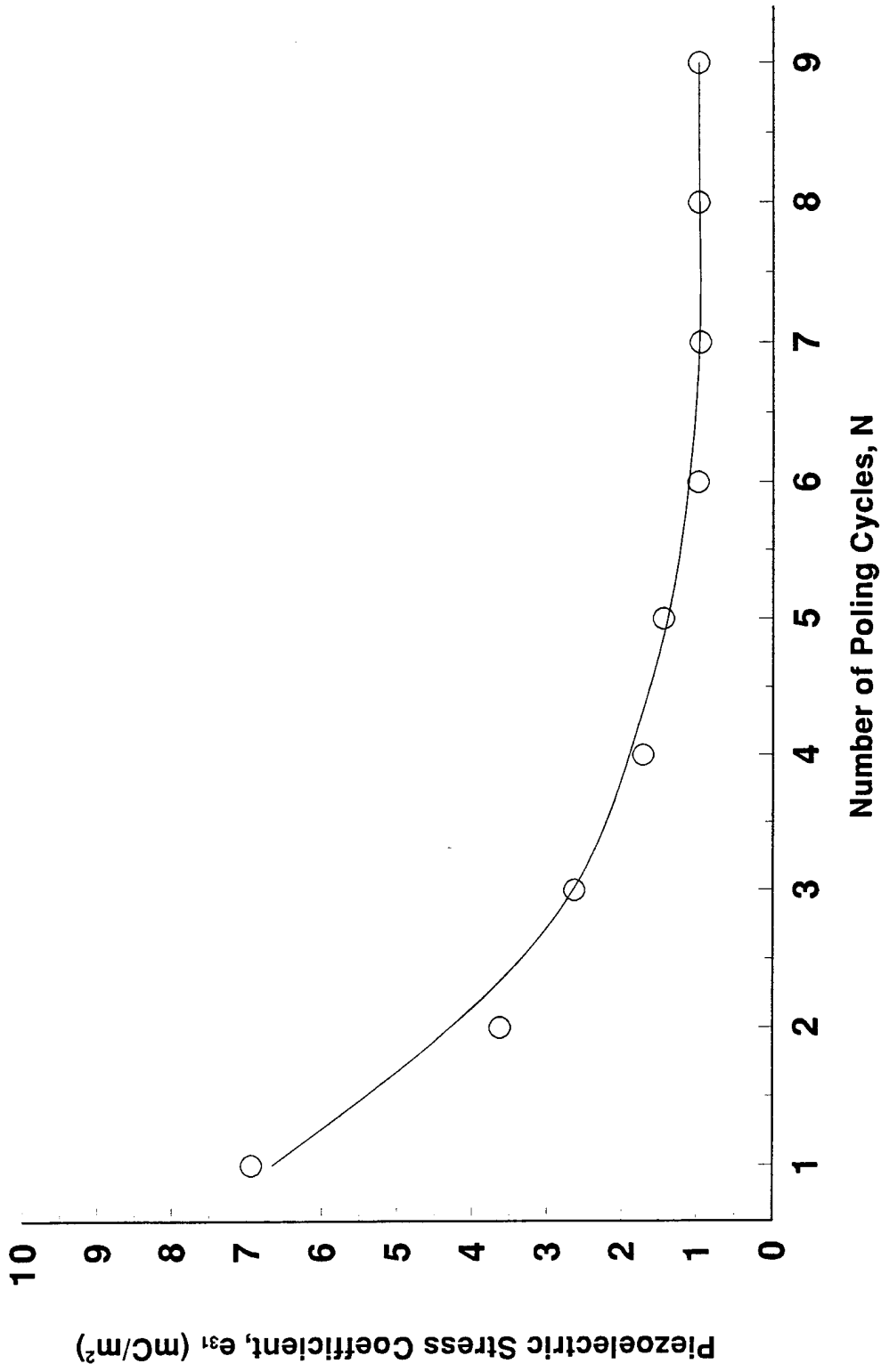


Figure 4b

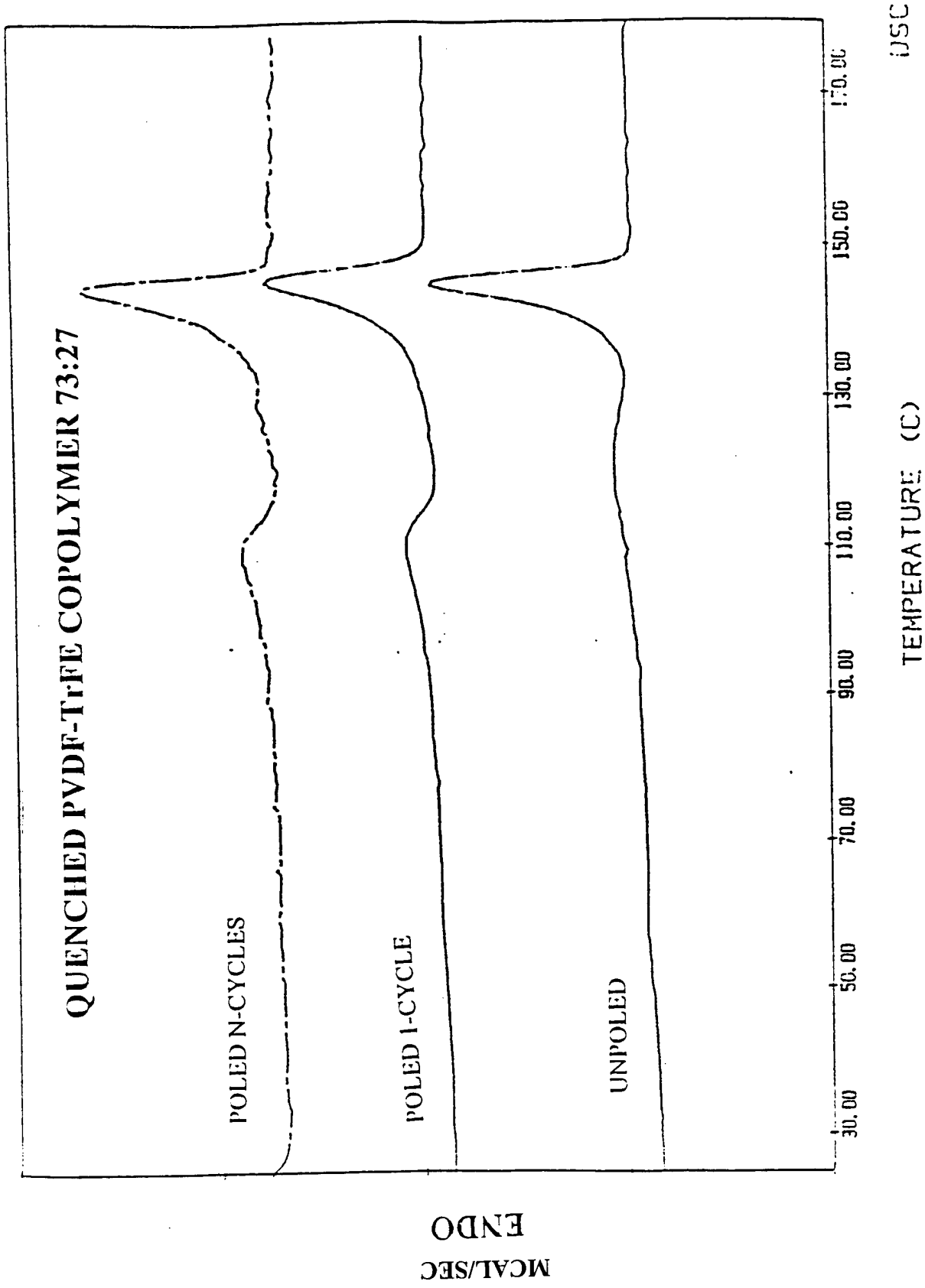
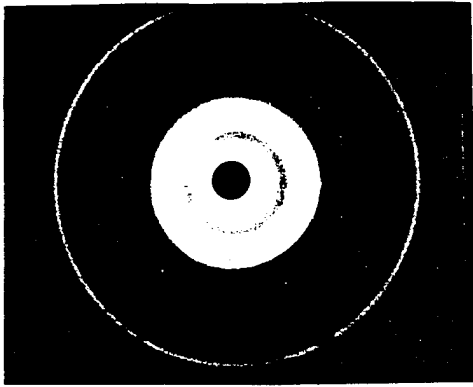


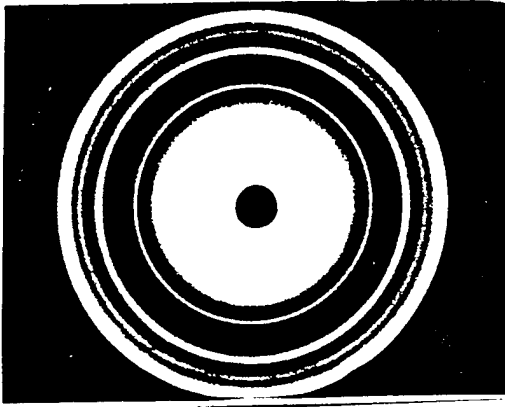
Figure 5.

X-ray Diffraction Photographs

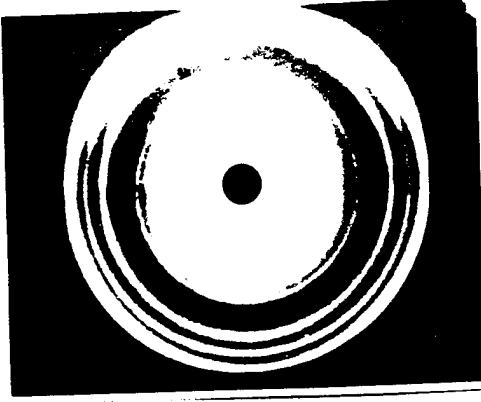
Unpoled



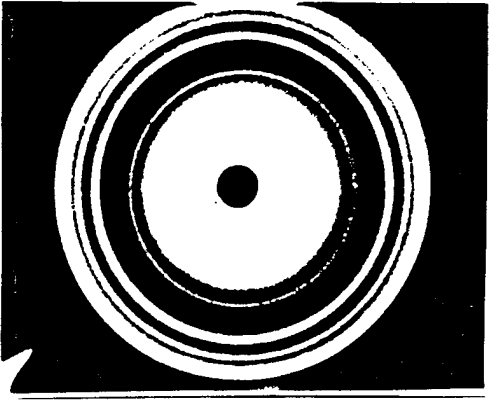
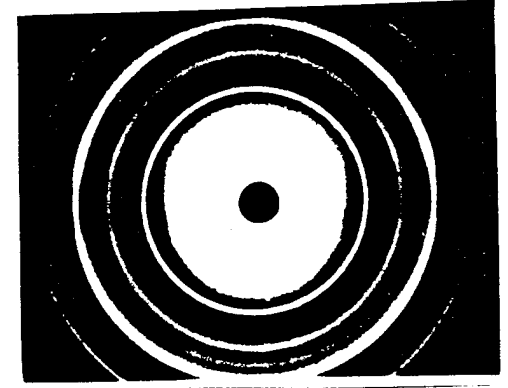
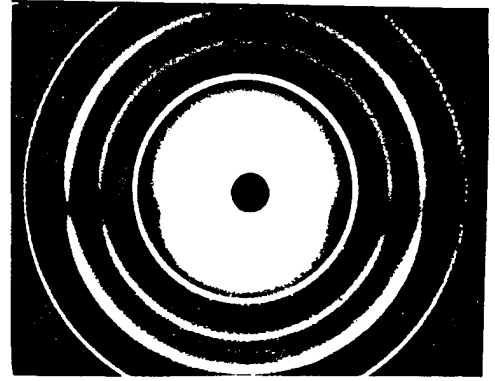
Poled 1-cycle



Poled N-cycles (N≥6)



Transmission



Edge

Figure 6.

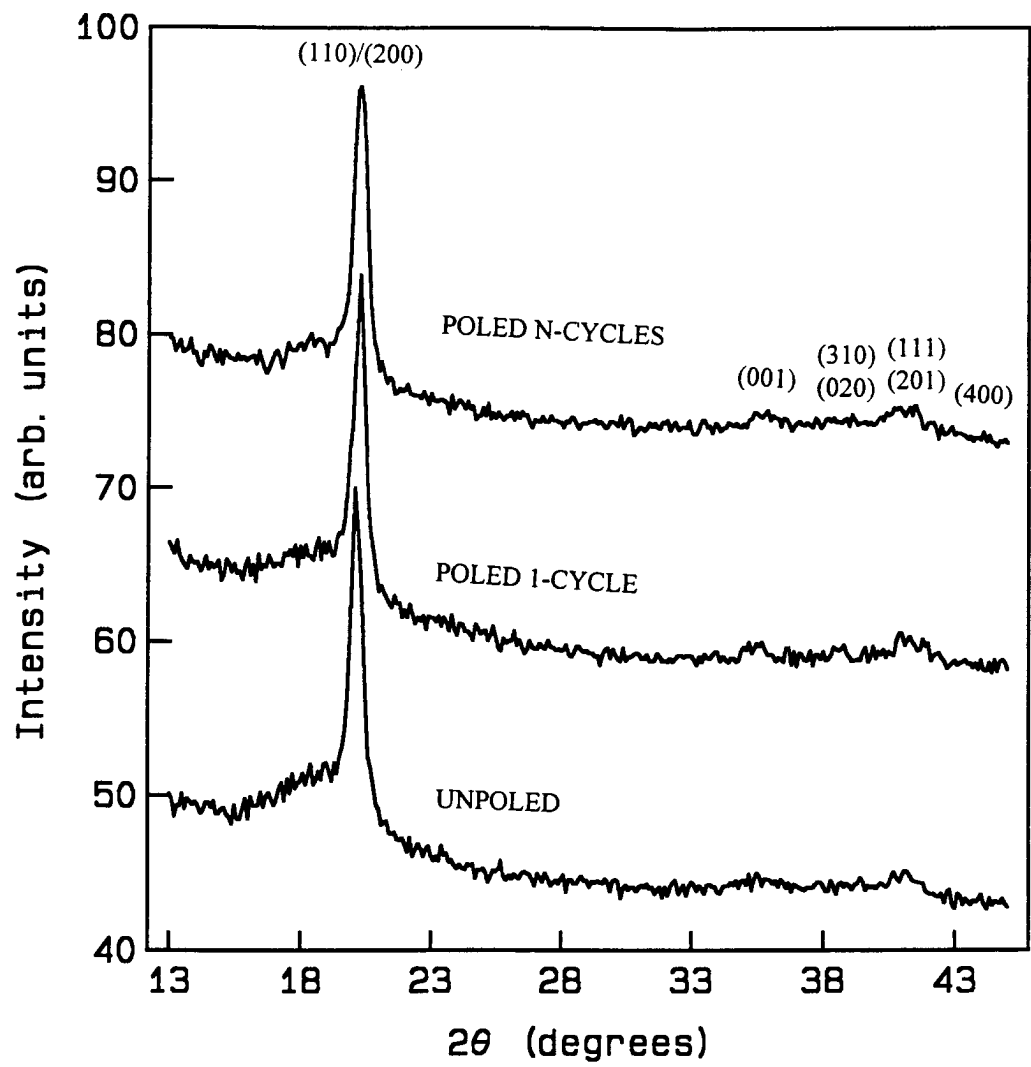


Figure 7. Wide angle x-ray diffraction scans of quenched P(VDF-TrFE) 73:27 copolymer films.