# POLARIZATION AND PIEZOELECTRIC PROPERTIES OF A NITRILE SUBSTITUTED POLYIMIDE

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## ABSTRACT

This research focuses on the synthesis and characterization of a piezoelectric (β-CN)-APB/ODPA polyimide. The remanent polarization and piezoelectric $d_{31}$ and $g_{33}$ coefficients are reported to assess the effect of synthesis variations. Each of the materials exhibits a level of piezoelectricity which increases with temperature. The remanent polarization is retained at temperatures close to the glass transition temperature of the polyimide.

## INTRODUCTION

Fluoropolymers and copolymers such as polyvinylidene fluoride (PVDF) currently represent the state of the art in piezoelectric polymers. The development of other classes of piezoelectric polymers such as polyimides could provide enabling materials technology for a variety of aerospace and commercial applications. Due to their exceptional thermal, mechanical, and dielectric properties, polyimides are already widely utilized as matrix materials in aircraft and as dielectric materials in microelectronic devices. Particularly interesting is the potential use of piezoelectric polyimides in micro electro mechanical systems (MEMS) devices since fluoropolymers do not possess the chemical resistance or thermal stability necessary to withstand conventional MEMS processing.

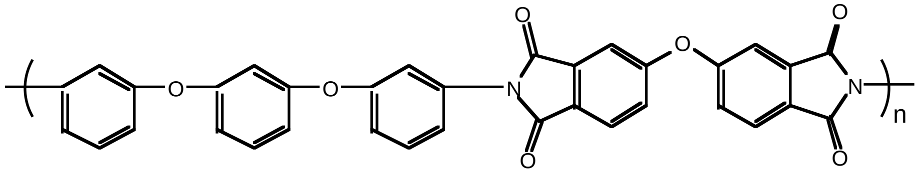
The majority of literature on poled polymers presents semicrystalline systems such as fluoropolymers and nylons [1-3]. In this analysis a high glass transition temperature ($T_g$), amorphous polymer is studied. The piezoelectric phenomena in amorphous polymers differs significantly from semicrystalline polymers and inorganic crystals. In order to induce a piezoelectric response in amorphous systems the polymer is poled by the application of a strong electric field ($E_p$) at an elevated temperature ($T_p$) sufficient to allow mobility of the molecular dipoles in the polymer. The dipoles are polarized with the applied field and will partially retain this polarization when the temperature is lowered below $T_g$ in the presence of $E_p$. The resulting remanent polarization ($P_r$) is key in developing materials with a useful level of piezoelectricity as it is directly proportional to the material's piezoelectric response.

In a previous report [4], computational predictions and experimental measurements of $P_r$ are reported for a nitrile substituted polyimide. In this investigation the piezoelectric coefficients, $g_{33}$ and $d_{31}$, are measured.

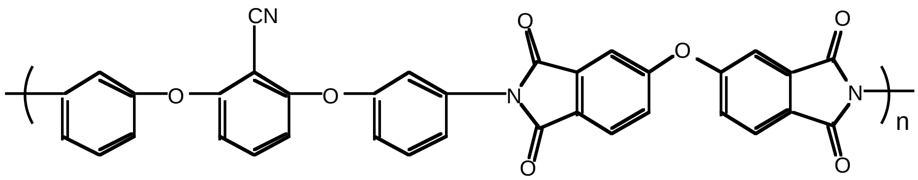
## METHODS

*Synthesis*

Polyimide films are synthesized using two different diamines, (2,6-bis(3-aminophenoxy) benzonitrile ((β-CN)-APB) and 1,3-aminophenoxy benzene (APB), to determine the effect of the pendant nitrile group on the piezoelectric response. Each of the diamines is reacted with 4,4' oxdiphthalic anhydride (ODPA) resulting in the two polyimides shown in Figure 1. The influence of cure cycle and thermal versus chemical imidization on the piezoelectric properties is investigated for the nitrile substituted polyimide. Two different thermal imidization cycles are used: 1) *standard*-1 hour each at 100, 200, and 300°C and 2) *relative*- 1 hour each at 50, 150, 200, and $T_g$ + 20°C. The chemically imidized films [5] are cast from a solution of polyimide powder in NMP solvent and the solvent is removed using the relative thermal cycle. As shown in Table 1, the chemically imidized polyimide has a slightly lower $T_g$ and thermal stability than the thermally imidized films.



APB/ODPA



(β-CN)-APB/ODPA

Figure 1. Chemical structures of polyimides studied.

Table 1. Thermal properties of polyimide films.

| (β-CN)-APB/ODPA | $T_g$ (°C)[1] | TGA, (°C)[2] |
|---|---|---|
| Standard thermal cure | 225 | 480 |
| Relative thermal cure | 222 | 484 |
| Chemical imidization | 199 | 459 |
| APB/ODPA | 185 | 431 |

[1]$T_g$ measured by DSC at 20°C/min.
[2]Temperature of 5% weight loss by TGA in air at 2.5°C/min.

*Poling*

A silver electrode is evaporated onto each side of the film for electrical contact. For this study all polymers are poled at the polymer's $T_g$ at a field strength of 80 MV/m for 30 minutes unless otherwise indicated. The 80 MV/m field strength is used because it yields films which are best suited for piezoelectric measurements.

*Characterization*

Three techniques are used to characterize the dielectric and piezoelectric properties of the polymers. To evaluate the $P_r$ in the poled samples, a thermally stimulated current (TSC) method is used. A Keithley 6517 electrometer is used to measure the discharged current as temperature is ramped at 1°C/min from room temperature to $T_g$ +20°C.

The $d_{31}$ is measured by mounting the polymer sample on a load frame and applying a stress parallel to the electrodes. The charge (Q) is measured using an electrometer and $d_{31}$ is given by:

$$d_{31} = Q/AX_1 \tag{1}$$

where A is the area of the electrodes and $X_1$ is the applied stress. A linear response is obtained for each of the polymers in the range from 2 to 10 newtons of force.

The $g_{33}$ coefficient is given by:

$$g_{33} = V_o / X_3 t , \tag{2}$$

where $V_o$ is the open circuit voltage, $X_3$ is the applied stress normal to the surface, and t is the film thickness. A ceramic piezoelectric actuator applies a 10 Hz force to the polymer film sample normal to the surface. A calibrated piezoelectric load cell located beneath the sample measures the force applied to the sample. An electrometer is used to measure the voltage developed across the sample in response to the applied force.

## RESULTS

A summary of the remanent polarization and piezoelectric properties for the polyimides studied is presented in Table 2. Each of the materials demonstrates a piezoelectric response although lower than previously reported [6]. The $P_r$ values and room temperature piezoelectric coefficients are low relative to other known piezoelectric polymers.

Table 2. Polarization and piezoelectric properties of polyimide films.

| (β-CN)-APB/ODPA | $P_r$ ($mC/m^2$) | $-d_{31}$ (pC/N)[1] | $-g_{33}$ (mVm/N)[1] |
|---|---|---|---|
| Standard thermal cure | 9.6 | 0.12 | 16 |
| Relative thermal cure | 10.8 | 0.15 | 20 |
| Chemical imidization | 11.5 | 0.14 | 14 |
| APB/ODPA | 3.7 | 0.01 | 6 |

[1]Measured at 25°C.

The influence of cure temperature on the piezoelectric properties is investigated for the nitrile substituted polyimide. Previous work [7] indicates that optimum mechanical film properties are obtained by limiting the ultimate cure temperature to $T_g$ + 20°C. Based on the measurements completed in this study, there is no significant difference in the piezoelectric response for the different (standard or relative) cure cycles. Likewise, the small differences in $P_r$, $d_{31}$, and $g_{33}$ values for the chemically and thermally imidized polyimides are within the experimental uncertainty of each of the methods.

To determine the effect of the pendant nitrile group on the piezoelectric response the unsubstituted APB/ODPA was evaluated. From Table 2 it is seen that APB/ODPA exhibits an extremely low but measurable remanent polarization and piezoelectric response. Approximately 40% of the $P_r$ in the nitrile substituted polyimide is attributed to the polarization of the dianhydride portion of the polyimide [4]. This indicates that incorporating more polar groups in the dianhydride may yield polyimides with improved remanent polarizations.

An objective of this work is to develop polyimides with useful, stable piezoelectric properties at elevated temperatures. Figure 2 is a plot of the calculated $g_{33}$ coefficients for each of the polyimides as a function of temperature. The $g_{33}$ values increase with temperature in the range from 25 to approximately 95°C.

In Table 3 the piezoelectric properties at 95°C for a chemically imidized polyimide poled at an $E_p$ of 100 MV/m is compared to PVDF. At this temperature the $g_{33}$ and $d_{33}$ values of the polyimide are three times greater than those at room temperature but are still an order of magnitude lower than PVDF. For most polymers significant enhancement in piezoelectric activity is achieved by altering the morphology of the polymer through uniaxial stretching prior to poling [8,9]. Hence, with improvements in polymer design and processing it is conceivable that piezoelectric activity in polyimides will approach a range feasible for practical use in high temperature applications.

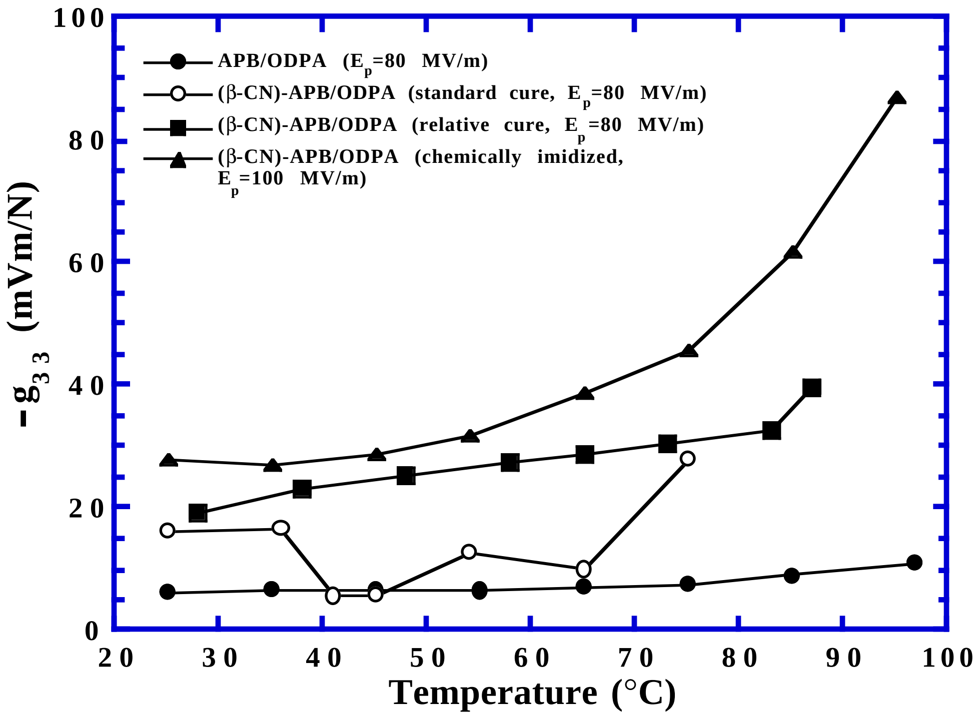



Figure 2. Temperature dependence of the piezoelectric coefficient.

Table 3. Comparison of piezoelectric properties of chemically imidized polyimide at 95°C and PVDF.

| Polymer | $-g_{33}$ (mVm/N) | $-d_{33}$(pC/N) |
|---|---|---|
| (β-CN)-APB/ODPA[1] | 87 | 2.7 |
| PVDF[2] | 339 | 33 |

[1] $g_{33}$ measured and $d_{33}$ calculated by $d_{ij} = \varepsilon\, \varepsilon_o\, g_{ij}$ [9].

[2] Piezoelectric $g_{33}$ and $d_{33}$ coefficients are from [10].

To illustrate the thermal stability of the polyimides, Figure 3 shows the percentage of remanent polarization which is lost in (β-CN)-APB/ODPA as it is heated from 30°C to 240°C. At 150°C the polymer retains 94% of its remanent polarization. Over 80% of the $P_r$ is retained at 200°C. This thermal stability indicates that polyimides can potentially be used for high temperature piezoelectric applications.

## CONCLUSIONS

Polarization and piezoelectric properties have been measured for APB/ODPA and its nitrile substituted derivative. The effect of polyimide synthesis method was investigated and no significant difference in piezoelectric response was observed. The level of piezoelectricity in the (β-CN)-APB/ODPA is an order of magnitude lower than what is necessary for practical utility in devices. The high temperature stability of the remanent polarization has been verified. Future efforts will concentrate on increasing the piezoelectric response through processing such as mechanical stretching and by incorporating the use of computational tools to guide synthesis of other polyimides.

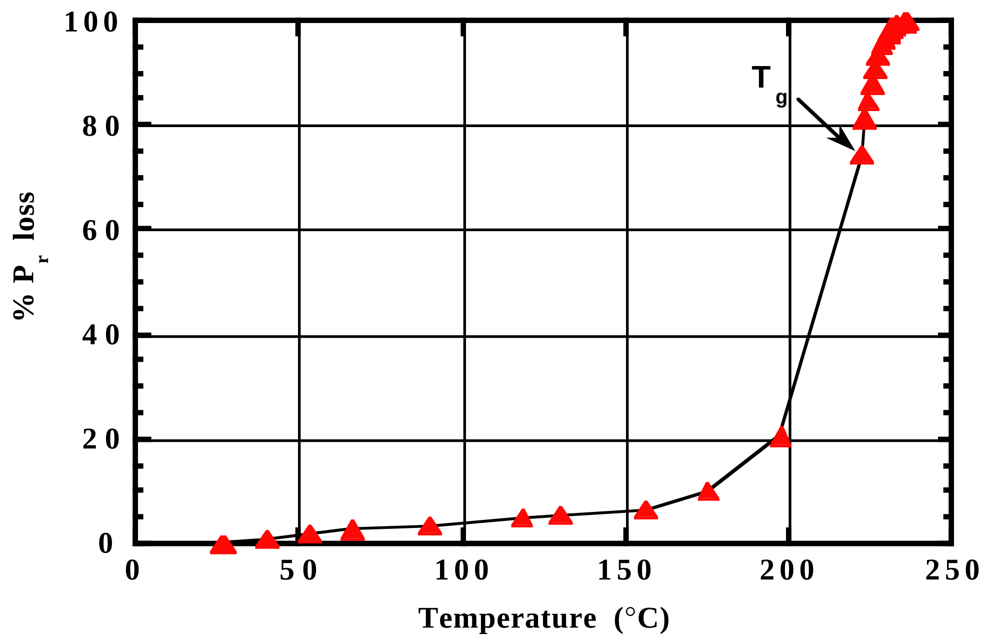



Figure 3. Percentage $P_r$ loss as a function of temperature for (β-CN)-APB/ODPA.

## ACKNOWLEDGEMENTS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## REFERENCES


1. G. Thomas Davis, in Polymers for Electronic and Photonic Applications, edited by C.P. Wong (Academic Press, Inc., Boston, 1993) pp. 435-465.

2. T. Furukawa, IEEE Trans. Elect. Insul., 21, 543 (1986).

3. B. Newman, P. Chen, K. Pae, and J. Scheinbeim, J. Appl. Phys., 51, 5161 (1980).

4. Z. Ounaies, J. Young, J. Simpson and B. Farmer, Materials Research Society Symposium Proceedings, Boston, MA, (1996).

5. A.K. St. Clair and T.L. St. Clair, US Patent No. 5,338,826 (16 August 1994).

6. J.O. Simpson, S.S. Welch, and T.L. St. Clair, Materials Research Society Symposium Proceedings, Ed. Jen, A. K-Y., 413, 351 (1996).

7. J. F. Dezern, and C.I. Croall, NASA Technical Memorandum 104178 (1991).

8. H. Ueda and S.H. Carr, Polymer J., 16, 661 (1984).

9.  G. Thomas Davis, in The Applications of Ferroelectric Polymers, edited by T. Wang, J. Herbert, and A. Glass (Blackie, London, 1988) pp. 37-65.

10.  Piezo Film Sensors Technical Manual, AMP, Inc., (1993).