

## **The Dielectric Behavior of Cyano-Substituted Polyimides**

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### **ABSTRACT**

**A number of amorphous polyimides containing polar functional groups, cyano group, have been synthesized and investigated for potential use as high temperature piezoelectric sensors. The piezoelectric constants are related to the polarization. The remanent polarization and hence piezoelectric response of a material is determined by dielectric relaxation strength which is the difference in dielectric constant at the glass transition temperature vicinity. The intent of this work is to clarify the mechanism and key components required for developing piezoelectricity in amorphous polymers and further to apply this understanding in designing a unique high temperature piezoelectric polyimide. In this paper, experimental investigations of dielectric constant of piezoelectric cyano-substituted polyimides have been tested as a function of temperature to measure the dielectric relaxation strength in the glass transition temperature region.**

***Keywords: Piezoelectricity; Polyimide; Dielectric Relaxation Strength.***

### **INTRODUCTION**

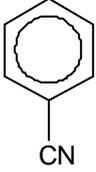
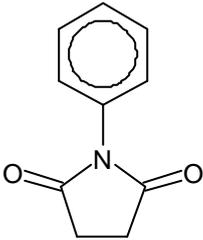
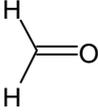
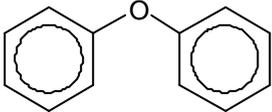
High performance piezoelectric polymers are of interest as they may be useful for a variety of aerospace and aircraft applications. Currently, semicrystalline polyvinylidene-fluoride (PVDF) and its copolymers are the only commercially available piezoelectric polymers<sup>(1)</sup>. However, this family of vinyl polymers does not possess the thermal stability dictated by high temperature aerospace applications. Polyimide polymers, on the other hand, have high thermal resistance, and excellent mechanical and electrical properties. Due to their exceptional thermal, mechanical, and electrical properties, amorphous piezoelectric polyimides are already widely used as composite matrix materials in aircraft and as dielectric materials in microelectronic devices<sup>(2)</sup>. Early molecular modeling coupled with chemical synthesis and characterization indicated the potential of forcing piezoelectricity in amorphous polyimides by adding dipole functionalities to the polymer backbone<sup>(3,4)</sup>. This was the impetus for synthesizing a series of polyimides to investigate their potential piezoelectric response as a function of nitrile dipoles. Fundamental structure-piezoelectric property insight will enable the molecular design of polymers possessing distinct improvements over state-of-the-art piezoelectric polymers including enhanced polarization, polarization stability at elevated temperatures, and improved processability. The remanent polarization ( $P_r$ ) is basically the polarization during poling process minus the electronic and atomic polarizations that relax at room temperature once the applied electric field is removed. The remanent polarization and the piezoelectric response of a material is determined by dielectric relaxation strength (?? Dielectric relaxation strength is measured experimentally from the relation between the dielectric constant with temperature. Dielectric relaxation strength (??) is the difference between dielectric constant after and before the glass transition temperature ( $T_g$ ). Dielectric relaxation strength is calculated by incorporating Maxwell

equation, Clausius-Mossotti equation, and Onsager local field <sup>(4)</sup>. This study focuses on characterization of high temperature potentially piezoelectric polyimides containing polar functionalities such as nitrile ( $-CN$ ), ether ( $-O-$ ), ( $-CO$ ) and ( $-CF_3$ ) groups as given in Table 1. The effect of structural changes on the dielectric behavior, including variations in the nature and concentration of dipolar groups, is examined. The dielectric measurements yield the dielectric relaxation strength ( $\Delta\epsilon$ ). The importance of it lies in that it is directly proportional to the piezoelectric behavior for amorphous polymers as represented by the calculated remanent polarization ( $P_r$ )<sup>(4,5)</sup>. Investigating the dielectric behavior of this series of CN-substituted polyimides will identify structures that have the potential to develop a permanent polarization, and hence be piezoelectric response.

For amorphous polymers where the piezoelectricity is based on freezing-in of permanent dipoles, a number of researchers <sup>(6,7)</sup> showed that  $P_r$  and  $\Delta\epsilon$  are related by the equation

$$P_r = \Delta\epsilon \cdot \epsilon_0 \cdot E_p \quad (1)$$

The measured dielectric relaxation strength  $\Delta\epsilon$  is taken as the difference in dielectric constant in the  $T_g$  vicinity. Where  $\Delta\epsilon$  is the dielectric relaxation strength,  $\epsilon_0$  is the permittivity of vacuum ( $8.85 \times 10^{-12} \text{F/m}$ ),  $E_p$  is the applied electric field. In this study,  $\Delta\epsilon$  is determined experimentally and theoretically. The Dielectric relaxation strength ( $\Delta\epsilon$ ) is measured experimentally as the difference between the dielectric constant after and before glass transition temperature ( $T_g$ ). The Dielectric constant after ( $T_g$ ) is defined as the low frequency state and below the glass transition temperature ( $T_g$ ) is defined as the high frequency state. Consequently, ( $\Delta\epsilon$ ) is the difference between the low and the high frequency state.

Dipoles	Dipole Moment (Debye)
	4.18
	2.34
	2.00
	1.30

**Table 1. Values of dipoles used**

Equation 1 will be used to calculate ( $P_r$ ) which is the measure of piezoelectricity<sup>(6,7)</sup> Dielectric relaxation strength ( $\Delta e$ ) is also calculated theoretically using Onsager equation which relates permanent dipoles moment of the molecule to the electrical permittivity to get insight into the effect of the dipoles location, and density of the dipoles. After substituting Maxwell equation 2 in Clausius-Mosotti equation the resultant equation for calculated ( $\Delta e$ ) will be equation 3 and the calculated remanent polarization formula is given by equation 4<sup>(6)</sup>.

$$n = e^2 \quad (2)$$

$$\Delta e = \left(\frac{N m^2}{3kT e_0}\right) \left(\frac{n^2 + 2}{3}\right)^2 \left(\frac{3e(0)}{2e(0) + n^2}\right)^2 \quad (3)$$

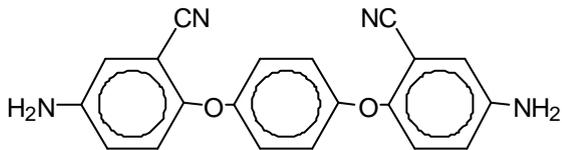
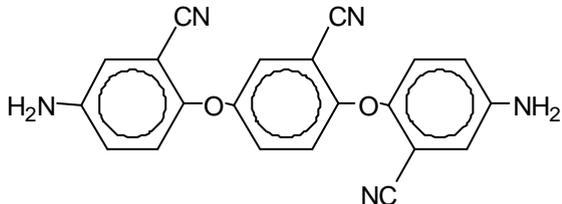
$$P_r = \left(\frac{N m^2}{3kT}\right) \left(\frac{n^2 + 2}{3}\right)^2 \left(\frac{3e(0)}{2e(0) + n^2}\right)^2 . E_p \quad (4)$$

Where  $n$  is the refractive index,  $N$  is the concentration of dipoles per unit volume (# dipoles/m<sup>3</sup>),  $m$  is dipole moment (C.m),  $k$  is Boltzmann's constant ( $1.38 \times 10^{-23}$  J/atom.K),  $T$  is the glass transition temperature (K) and  $e(0)$  is the dielectric constant at low frequency.

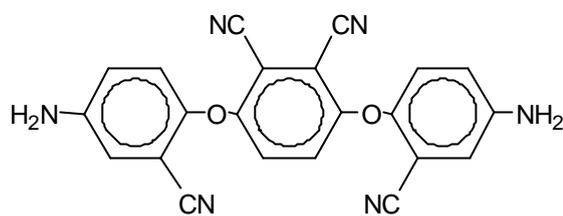
### EXPERIMENTAL

A series of cyano-substituted polyimide have been tested in this work. The series has two different structures considering the number of cyano-substituted group in the diamine portion and dianhydride portion. The diamines used in this study are given in Table 2 and, the dianhydrides are given in Table 3.

**Table 2. Diamines tested in the study**

Diamine Structure Nomenclature		
Unsubstituted		0CN
Nitrile-substituted		2CN
Nitrile-substituted		3CN

Nitrile-substituted



4CN

Table 3. Series of Dianhydride

Structure	Nomenclature
	bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride (BisADA)
	Isopropylidene dianiline (IPDA)
	Oxydiphthalic dianhydride (ODPA)
	Hexafluoroisopropylidene Bisphthalic Dianhydride (6FDA)

The glass transition temperatures ( $T_g$ ) of the films were measured by differential scanning calorimetry (DSC) using TA instrument (Q-1000) and a heating rate of 10 C/min. The glass transition temperature ( $T_g$ ) was assigned at the inflection point, the point between the onset point (the intersection of the first and second tangents) and the end point (the intersection of the second and the third tangents).

Dielectric spectroscopy probes are the interaction of polymer segments to a time dependent electric field coupled with a temperature change. For example, dielectric constant can provide information about the rotation of permanent dipoles in the polymer. The resulting relaxation, expressed as a complex dielectric constant. The dielectric constant( $\epsilon^*$ ) is given by equation 5.

$$\epsilon^* = \epsilon' + i\epsilon'' \quad (5)$$

Where  $\epsilon'$  is the real part of the dielectric constant and it generally refers to the dielectric constant of the material and where  $\epsilon''$  is the imaginary part, or the dielectric loss.

One advantage of using dielectric spectroscopy is the broad frequency range (20 Hz-1 MHz). After each frequency scan, the temperature was increased to better probe relaxation phenomena. A low external AC electric field (rmsV=0.005-1.0 Volts) was applied across the capacitor plate configuration where the material being tested. An HP4284A Precision LCR meter and a Sun Systems Environmental Chamber were used to perform the dielectric spectroscopy experiment. Labview VI was the software of choice to control both frequency and temperature. It records the capacitance and loss tangent, and converts the raw data into dielectric constant and dielectric loss. The measurements were taken at temperatures ranging from ambient to 350 C and the following three frequency readings: 20 Hz, 100 Hz and 1 kHz. These measurements allowed to determine the dielectric relaxation strength ( $\epsilon''/\epsilon'$ ).

## RESULTS AND DISCUSSION

In this study, the dielectric relaxation strength ( $\epsilon''/\epsilon'$ ) is used as a quantitative measure of piezoelectricity to select the polyimide with the most potential for piezoelectric applications. As mentioned in the introduction, the dielectric relaxation strength can predict the presence of piezoelectricity, and it also indicates dipole motion within the polymer, whether it is a free rotation or cooperative motion of the dipoles. Moreover, the higher ( $\epsilon''/\epsilon'$ ), the higher the piezoelectricity since it arises solely from dipolar orientation. Therefore,  $\epsilon''/\epsilon'$  is a practical criterion to use when designing piezoelectric amorphous polymers. Presence, addition and location of dipoles affect the glass transition temperature ( $T_g$ ). As the number of CN dipoles increases in the diamine portion, the  $T_g$  increases as it is given in Table 4. In all cases, adding CN dipole to the backbone increases  $T_g$ . Introduction of flexible linkages in the dianhydride portion of a polyimide has a greater impact on lowering  $T_g$  than the presence of the same flexible segment in the diamine<sup>(2)</sup>. The  $T_g$  of polyimides is lowered by a decrease in the rigidity of the chain throughout flexible linkages or by a reduction of interchain-interactions. The shorter and the more flexible linkages require less thermal energy (kT) for the motion<sup>(2,6)</sup>. At the initial stages of the experiment, it appears that the structures of the polyimides area clear indication that the more flexible the structure the lower  $T_g$  is. For example, BisADA structure produced the lowest ( $T_g$ ) as given in Table 4. Moving from a flexible and light structure to a rigid and heavy structure increased ( $T_g$ ). This trend has been observed when bis [4-(3,4-dicarboxyphenoxy)phenyl] propane dianhydride (BisADA), Isopropylidene dianiline (IPDA), Oxydiphthalic dianhydride (ODPA), and Hexafluoroisopropylidene Bisphthalic Dianhydride (6FDA) polyimides structure were tested.

The addition of a single polar nitrile group, the length of the chain, the dipole density and, the type of the dipole, the use of flexible and relatively non-polar bridging groups in the dianhydride affect the dielectric relaxation strength ( $\epsilon''/\epsilon'$ ) and consequently remanent polarization  $P_r$ <sup>(8)</sup>. A linear relationship exist between the dielectric relaxation strength ( $\epsilon''/\epsilon'$ ) and the remanent polarization ( $P_r$ ), as it may be concluded from equation 1. Keeping the dianhydride constant, and changing the diamine with varying concentrations of nitrile dipoles were also studied.

**Table 4. Calculated and measured values of  $\epsilon_e$  and  $P_r$ .**

<i>Polyimide Structure</i>	<i>T<sub>g</sub></i> (°C)	<i>Calculated</i> <i><math>\epsilon_e</math></i>	<i>Measured</i> <i><math>\epsilon_e</math></i>	<i>Calculated</i> <i>P<sub>r</sub></i> (mC/m <sup>2</sup> )	<i>Measured</i> <i>P<sub>r</sub></i> (mC/m <sup>2</sup> )
<b>0CN-BisADA</b>	201	3.56±0.08	2.88±1.09	1.58	1.32
<b>2CN-BisADA</b>	220	17.53±0.37	15.61±1.19	7.76	6.91
<b>3CN-BisADA</b>	227	26.47±0.44	17.33±1.00	12.33	8.24
<b>4CN-BisADA</b>	231	45.83±5.08	42.29±1.13	18.71	16.74
<b>0CN-IPDA</b>	237	2.03±0.04	1.60±0.22	0.90	0.71
<b>2CN-IPDA</b>	246	13.57±0.26	12.50±2.50	6.01	5.53
<b>3CN-IPDA</b>	248	29.97±0.58	18.95±1.60	13.26	8.38
<b>4CN-IPDA</b>	261	44.28±1.16	35.74±2.24	19.59	15.81
<b>0CN-ODPA</b>	241	1.18±0.02	0.56±0.19	0.52	0.38
<b>2CN-ODPA</b>	247	12.98±0.25	11.94±2.21	5.74	5.28
<b>3CN-ODPA</b>	253	22.60±0.43	18.46±2.95	10.00	8.17
<b>4CN-ODPA</b>	272	31.12±0.85	19.74±3.23	13.77	8.65
<b>0CN-6FDA</b>	270	1.108±0.02	0.59±0.23	0.49	0.26
<b>3CN-6FDA</b>	277	14.69±0.27	9.21±1.82	6.50	4.08
<b>4CN-6FDA</b>	289	20.92±0.53	14.87±2.76	9.26	6.58

Figure 1 shows the dielectric values for 0CN, 2CN, 3CN, 4CN-BisADA polyimides as a function of temperature. The value of the dielectric relaxation strength constant ( $\epsilon''$ ) increases, as the nitrile functionality increases. The value of ( $\epsilon''$ ) increases from 2.88 to 15.61 to 20.2 to 45.83 as the CN group increases from 0CN to 2CN to 3CN to 4CN; for BisADA dianhydride. This is a clear indication of the contribution of the dipoles to the dielectric constant. The same trend is found for the results. Table 4, which compares the dielectric behavior for 0CN, 2CN, 3CN, and 4CN for BisADA, IPDA, ODPA, and 6FDA respectively. Therefore, it is expected that 4CN exhibits the highest piezoelectric performance compared to 3CN, 2CN and 0CN.

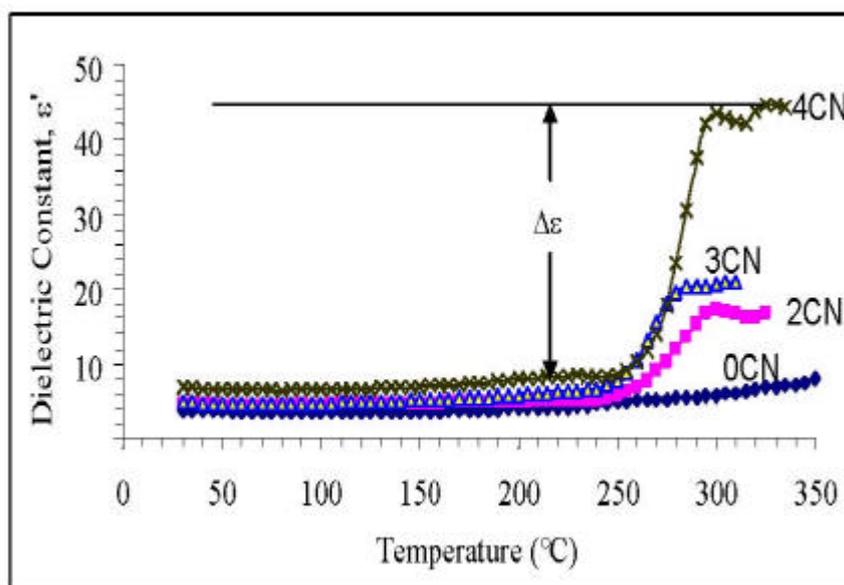


Fig. 1. Effect of adding CN dipoles to Isopropylidene dianiline (IPDA)

Figure 2 shows the variation of the dielectric behavior for 2CN-BisADA, 2CN-IPDA, and 2CN-ODPA polyimides as a function of temperature. BisADA Dianhydride structure has more flexibility than any other dianhydride structures with lower ( $T_g$ ) and consequently high ( $\epsilon'$ ). The effect of the charge transfer complex, which is an association, is somewhat stronger than ordinary Van der Waals association<sup>(2,10)</sup>. The stronger charge transfer complex means the closer with packing<sup>(2)</sup>. The electron affinity of the dianhydride and the ionization potential of diamine determine the strength of these complexes. A hinge in the dianhydride will reduce the strength of charge transfer complex because it reduces the electron affinity of the dianhydride by isolating the powerful electron withdrawing anhydride groups from each other. Charge transfer complex model effectively explains the nature of the relationship between the glass transition temperature of the polyimides and the electron affinity of the dianhydride for several polyimides. High electron affinity means high charge transfer complex which is consequently means high glass transition temperature. But, glass transition temperature seems to become insensitive to electron affinity of the dianhydride as the bridging group in the dianhydride becomes longer for example like BisADA dianhydride case.

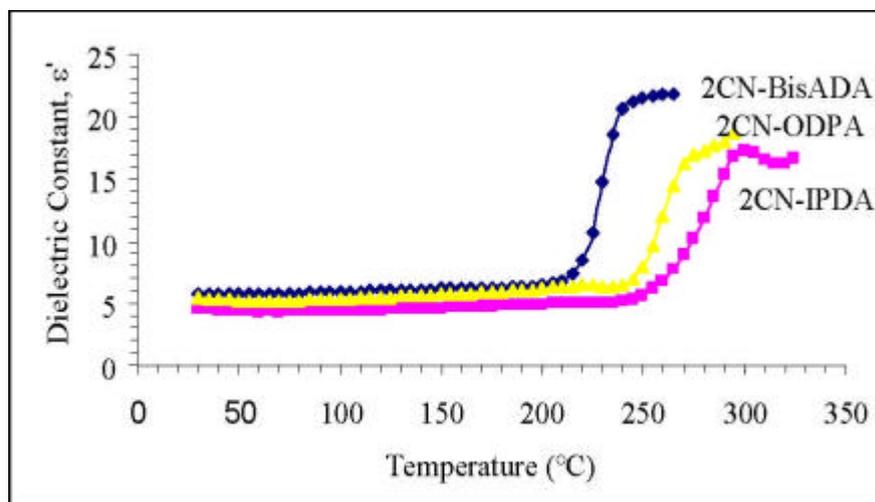


Fig. 2. Effect of varying the dianhydride for 2CN

The effect of benzene ring is very clear in glass transition temperature values, as the number of the benzene ring increases the glass transition temperature for the polyimide increases because it makes the polymer heavier<sup>(6)</sup>. IPDA dianhydride has higher glass transition temperature than BisADA dianhydride and consequently  $T_g$  which is lower than in BisADA structure. Diphenyl ether group in ODPA is flexible, so the value of  $T_g = 19.74$  is higher than 6FDA. The two trifluoromethyl groups in 6FDA have the highest value of electro-negativity due to the presence of the fluorine atoms. Insertion  $-CF_3$  group, which is heavy, to the polymer backbone leads to impede close packing and reduce the charge transfer complex. In addition,  $-CF_3$  increases the free volume percent between the polymer chains which reduce the number of polarizable groups in a unit volume, and lowers the electronic polarization because of the large electro-negativity in its bond<sup>(11)</sup>. The values of the measured ( $\epsilon'$ ,  $P_r$ ) and the calculated ( $\epsilon'$ ,  $P_r$ ) are close as it is clear from Table 4. The experimental values of  $\epsilon'$  are lower than the calculated values and this may be due to some assumptions in calculating  $\epsilon'$ . The difference between the measured and calculated values may be explained as follows; in the calculated  $\epsilon'$ , all the dipoles are counted. While in the measured values, they have some strict hindrances in the chains, therefore, not all the dipoles have been affected. This fact affects the values of  $\epsilon'$  which are required to calculate  $P_r$ .

The refractive index,  $n$ , according to Maxwell equation 3 is only applicable for high frequency  $\sim 1$  PHz) which is not the case in this experiment range (20-1000Hz). The values of dielectric constant decrease as the frequency increases, but we used the highest available frequency to calculate the dielectric constant relative to the applicable range for Maxwell equation. Consequently, that means high calculated dielectric since the frequency is low.

The dielectric constant  $\epsilon(0)$  is the value of dielectric at low frequency, these values do not make a clear plateau in Figures 1 and 2 which affect the values of calculated  $\epsilon'$ . Since  $\epsilon'$  is equal to the difference between the dielectric constant at low frequency and the dielectric constant at high frequency, therefore the experimental  $\epsilon'$  will be affected. The glass transition temperature ( $T_g$ ) is a range of temperatures and it is not a single value. This affects the values of the calculated  $\epsilon'$  because  $\epsilon'$  is a function of temperature.

## CONCLUSION

In conclusion, a new series of cyano-substituted was synthesized by reacting different dianhydride with different diamine nomenclatures. The results indicate that increasing the number of dipoles in the polyimide backbone, increases the value of dielectric relaxation strength  $\epsilon''$  and hence remanent polarization ( $P_r$ ). To align the dipoles efficiently, higher poling temperature and electric field strength are required. Factors such as steric hindrances and inter- and intra-molecular interactions can impede or enhance the overall orientation polarization.

It is clear that increasing the nitrile dipole to the polyimides increases the  $T_g$ . Polyimides derived from 4CN displayed the highest value of  $\epsilon''$  and  $P_r$  among all of the 3CN, 2CN, and 0CN. Consequently, the values of remanent polarization  $P_r$  are also high. A linear relationship was found between the dielectric relaxation strength  $\epsilon''$  and the remanent polarization  $P_r$ . The dipole moment in nitrile group is the highest among all the other used dipoles and that was a very important reason for choosing it. Adding CN dipoles to diamine increases  $\epsilon''$ , and consequently  $P_r$ , which is clear in both the experiments and the calculated values. The general trend from the experimental and calculated values of  $\epsilon''$  is, adding CN dipoles increases the  $P_r$ . As a result the lower  $T_g$  means high  $\epsilon''$  and  $P_r$ . The results showed that the highest value of dielectric relaxation strength  $\epsilon''$  and consequently  $P_r$  is for BisADA dianhydrides. The second and third best dianhydride were IPDA and ODPDA. The minimum value of  $\epsilon''$  was for 6FDA structure.

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