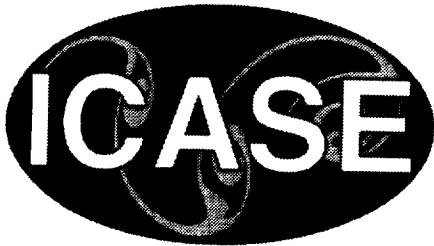


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STRUCTURE-PROPERTY STUDY OF PIEZOELECTRICITY IN POLYIMIDES

ZOUBEIDA OUNAIES¹, CHEOL PARK², JOYCELYN S. HARRISON³, JOSEPH G. SMITH³, AND JEFFREY HINKLEY³

Abstract. High performance piezoelectric polymers are of interest to NASA as they may be useful for a variety of sensor applications. Over the past few years research on piezoelectric polymers has led to the development of promising high temperature piezoelectric responses in some novel polyimides. In this study, a series of polyimides have been studied with systematic variations in the diamine monomers that comprise the polyimide while holding the dianhydride constant. The effect of structural changes, including variations in the nature and concentration of dipolar groups, on the remanent polarization and piezoelectric coefficient is examined. 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.

Key words. piezoelectric, polymer, polyimide, polarization

Subject classification. Physical Sciences

1. Introduction. This work is motivated by NASA's interest in developing high performance piezoelectric polymers as an enabling materials technology for a variety of high temperature aerospace applications. Due to their exceptional thermal, mechanical, and dielectric properties, polyimides are already widely used as composite 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 piezoelectric vinyl polymers such as polyvinylidene fluoride (PVDF) do not possess the chemical resistance or thermal stability necessary to withstand conventional MEMS processing.

Early molecular modeling by NASA scientists indicated the potential of forcing piezoelectricity in amorphous polyimides by adding dipoles to the polymer structure. This was the impetus for the current study in which we have synthesized a series of polyimides to investigate the potential piezoelectric response resulting from adding various dipoles into the structure. Table 1 lists the dipole moments of several groups that can be easily incorporated into polyimide structures.

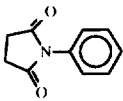
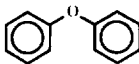

This study chronicles the synthesis, processing, and characterization of novel high temperature, potentially piezoelectric polyimides containing polar functionalities such as nitrile (-CN), ether (-O-) and sulfone (-SO₂-) groups. Measurements of the piezoelectric coefficients are presented to demonstrate the relationship between dipole concentration and the level of piezoelectricity for these materials. An understanding of the effect of such factors as dipole concentration and dipole location in the polymer on the piezoelectric properties will enable the molecular design of polymers possessing distinct improvements over state of the art piezoelectric polymers. A detailed computational and experimental analysis on the polarization of one of the promising polyimide structures is provided elsewhere [1,2].

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TABLE 1.
Values of dipoles used.

Dipoles	Dipole Moment μ (Debye)
	2.34
	1.30
	4.18
$-\text{SO}_2-$	5.20

2. Experimental

2.1. Polymer synthesis. A series of five polyimides were synthesized with pendant nitrile (-CN) and main chain ether (-O-) and sulfone (-SO₂) dipoles. As seen in Table 1, the added dipoles can be either pendant to the polymer backbone (such as the nitrile dipole) or residing within the main chain (such as the sulfone and anhydride dipoles). Polyimides containing polar groups were prepared via the amide acid in N,N-dimethylacetamide (DMAc) according to Figure 1. The diamine monomers used are: 1,3-bis(3-aminophenoxy)benzene (APB), 2,6-bis(3-aminophenoxy) benzonitrile ((2,6 β -CN) APB), 2,4-bis(3-aminophenoxy)benzonitrile ((2,4 β -CN) APB), 3,5-diaminobenzonitrile (DAB), and 3,3-diaminodiphenylsulfone (DDS). The appropriate diamine was dissolved in dimethylacetamide (DMAc) solvent at ambient temperature followed by the addition of the dianhydride, 4,4'-oxydiphthalic anhydride (ODPA), as a slurry in DMAc to the stirred mixture. The solids content was adjusted to approximately 16% w/w with additional solvent and the solution was stirred for approximately 24 hrs at room temperature under a nitrogen atmosphere. The inherent viscosity (η_{inh}) of the polyamic acids ranged from 0.4 to 0.7 dL/g. Prior to film casting, the solutions were filtered through a 0.2 micron filter using a high pressure filtration apparatus to remove any particulates from the solution. The solutions were cast onto a clean, dry glass plate using a doctor's blade in a low-humidity chamber. The cast films were dried in a chamber to form tack-free films at room temperature overnight. The tack-free films were cured at least 20°C above the glass transition temperature (T_g) in an oven purged with nitrogen at a heating rate of 2°C/min.

The glass transition temperatures (T_g) of the films were measured by differential scanning calorimetry using a Shimadzu DSC-50 with a heating rate of 10°C/min in air. The T_g was taken as inflection point of the shift of the baseline of the DSC scan. The results are presented in Table 2.

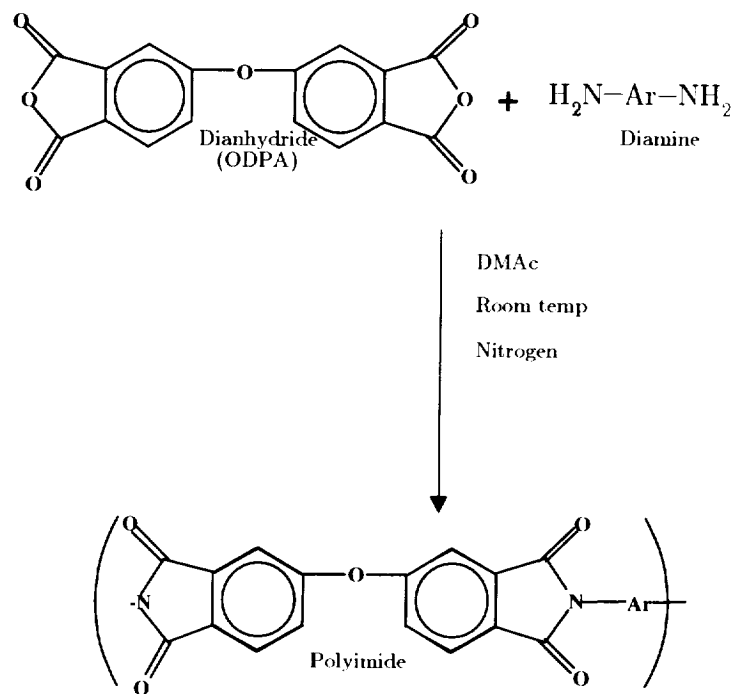


FIG. 1. Polyimide synthesis scheme

TABLE 2.

Polymer name, identification, diamine structure (-Ar-) and glass transition temperature.

Polyimide	ID	Diamine Structure (-Ar-)	T_g ($^{\circ}C$)
APB/ODPA	P1		185
(2,6- β -CN) APB/ODPA	P2		220
(2,4- β -CN) APB/ODPA	P3		205
DAB/ODPA	P4		258
DDS/ODPA	P5		246

2.2. Evaluation of polymers

2.2.1. Dielectric measurements. The dielectric constant and loss as a function of temperature and frequency were evaluated on unpoled polyimide samples using a Hewlett Packard 4192A Impedance Analyzer. The measurements were done at temperatures ranging from ambient to 300°C at 5 Hz, 10 Hz, 100 Hz and 1 kHz. These measurements yield the dielectric relaxation strength $\Delta\epsilon$, which is the change in dielectric constant as it traverses the glass transition temperature region. As pointed out by a number of researchers, $\Delta\epsilon$ is the parameter of greatest interest in designing amorphous polymers with large piezoelectric activity.

2.2.2. Poling. A thin silver layer was evaporated on either side of the film, typically around 2000 Å to establish electrical contact. The next step involved poling the polymers is to orient the dipoles. This was achieved by applying a strong electric field (E_p) at an elevated temperature ($T_p \geq T_g$) in a dielectric medium (silicone oil). After allowing sufficient time (t_p) for the dipoles to orient, the temperature was lowered in the presence of E_p in an attempt to freeze-in the orientation. Upon removal of the field E_p , partial retention of the orientation was achieved. This is known as orientation polarization. To evaluate the P_r in the poled samples, a thermally stimulated current (TSC) analysis was used; a Keithley 6517 electrometer was connected to the sample to record the short-circuit current while the sample was heated at a constant rate of 1-2°C/min from room temperature to $T_g + 20^\circ\text{C}$. The current was created as the material depolarized with increasing temperature. Integrating this current with respect to time yields the remanent polarization P_r , an indication of the degree of piezoelectricity.

2.2.3. Piezoelectric strain coefficient measurements, d_{31} . Measurements of the d_{31} coefficient were made using a modified Rheovibron. As the sample was strained in the 1-direction by the application of a force, F , a charge, Q , forms across its electrode. The piezoelectric strain coefficient was calculated according to the following equation below:

$$(2.1) \quad d_{31} = \frac{(Q / wl)}{(F / wt)}$$

where w is the width of the sample, l is the length and t is the thickness. The coefficient d_{31} was measured as a function of frequency at 0.1 Hz, 1 Hz, 10 Hz, and 100 Hz and temperature from 25°C to 250°C.

2.3. Polarization calculations. The maximum degree of polarization that can be achieved in an amorphous polymer depends on the concentration of dipoles, their strength, and the geometry of the polymer chain. Two different measures of this quantity were used. The first measurement yields the ultimate polarization P_u of a polymer, and it is given by:

$$(2.2) \quad P_u = N \cdot \mu$$

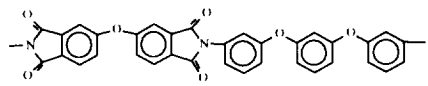
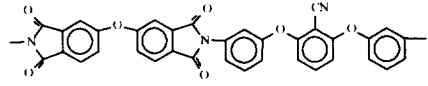
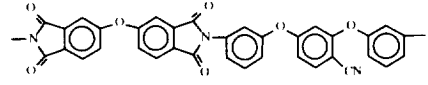
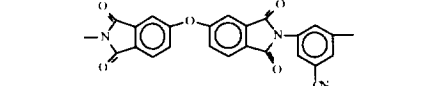
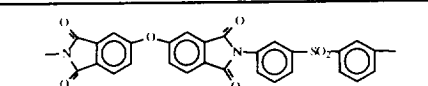
where μ is the dipole moment and N is the number density of dipolar groups. Equation (2.2) is for a rigid dipole model and gives a maximum value for the polarization that assumes all dipoles are perfectly aligned with the poling field.

The mean square dipole moment per gram is calculated from a model of a freely rotating chain and therefore takes into account intramolecular correlations enforced by the chain architecture [3]. This calculation results in P_{theo} , which will be presented along with P_u in the results section.

3. Results and Discussion. Key to the development of a piezoelectric response in amorphous polymers is the ability to align and lock-in a preferred orientation of the dipoles within the polymer. This orientation is influenced by the inherent flexibility of the polymer chains. Factors such as steric hindrances and inter- and intra-molecular interactions can impede or enhance the overall orientation polarization. For the APB/ODPA polyimide, the diphenylether linkage (-O-) in both the dianhydride and diamine segments of the polymer permits torsional rotation and facilitates dipole alignment. The addition of a single, polar nitrile pendant group to APB/ODPA increases the polarization and also T_g as indicated by Table 2. In addition to the presence of a dipole, the location of the nitrile group also affects the orientation dynamics as evidenced by the difference in T_g for the β -CN isomers P2 and P3 polymers. Glass transition temperatures in polymers tend to decrease with increasing segment flexibility. This is apparent from an examination of the P4 polyimide that has a significantly higher T_g due to the absence of the flexible ether linkages.

Table 3 lists the dielectric properties of the various polyimide structures studied. As mentioned earlier, the dielectric relaxation strength or $\Delta\epsilon$ can predict the presence of piezoelectricity since it indicates dipole motion within the polymer [4], whether due to free rotation or cooperative motion. As explained in the poling section, piezoelectricity arises in amorphous polymers by freezing these dipoles in a given direction; therefore, $\Delta\epsilon$ is a practical criterion to use when designing piezoelectric amorphous polymers. Inspection of Table 3 yields a dielectric relaxation strength, $\Delta\epsilon = 4.0$, attributable to the motion of the anhydride units alone. This has been validated through computational work [5]. Adding a nitrile dipole to the phenyl ring as in P3 increases $\Delta\epsilon$ to 6.0, possibly indicating an increased piezoelectric response when compared to unsubstituted P1. Furthermore, adding a nitrile dipole to a different location as in P2 increases $\Delta\epsilon$ more. This is presumably due to additive polarization of the ether and nitrile dipoles.

TABLE 3.
Dielectric properties.

Polymer Structure	Polymer ID	1 KHz		100 Hz		10 Hz	$\Delta\epsilon_{10\text{ Hz}}$
		ϵ	D	ϵ	D	ϵ	
	P1	3.4	0.0008	3.4	-	3.5	4.0
	P2	3.5	0.0031	3.5	-	3.8	11.0
	P3	3.6	0.0012	3.61	0.002	3.7	6.0
	P4	3.9	0.0076	4.0	-	4.4	9.0
	P5	3.5	0.0029	3.5	0.0038	3.8	9.0

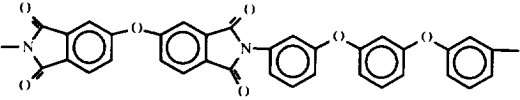
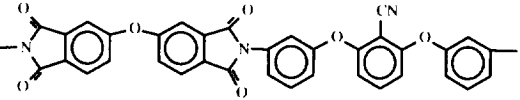
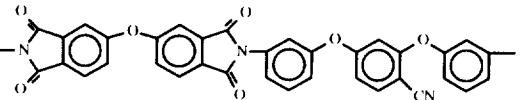
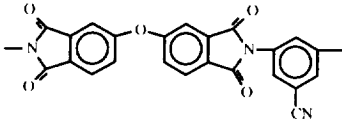
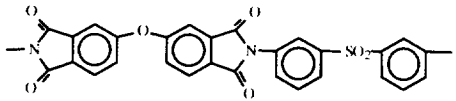
A linear relationship exists between the dielectric relaxation strength $\Delta\epsilon$ and the remanent polarization P_r , as shown below:

$$(3.1) \quad P_r = \Delta\epsilon \epsilon_0 E_p$$

Where ϵ_0 is the permittivity of free space (8.85 pF/m) and E_p is the poling field. Agreement between P_r obtained from equation (3.1) and P_r measured (using TSC) can confirm that the source of piezoelectricity in these polyimides was the non-cooperative orientation of the added dipoles. Each dipole orients independently of others to the degree allowed by the flexibility of the chain. Table 4 presents computed and measured polarization values for the polyimide series. Calculations of the ultimate and theoretical P_u values aid in screening potential piezoelectric structures. The difference between the predicted P_u and the measured P_r relates to the difficulty in orienting dipoles in an amorphous structure; hence the ratio of P_r to P_u is an indication of the efficiency with which polarization may be imparted into the polymer. Typical values for amorphous polymers that exhibit free dipolar motion do not exceed 30% [4]. The polymers with the highest dipoles (nitrile and sulfone) result in the higher P_r . Their efficiency appears to be maximized for the poling conditions given. The lower poling efficiency for the P4 may be related to the rigidity of the backbone. Unlike the other polymers, this one was poled below T_g due to a limitation of the poling apparatus.

TABLE 4.

Polymer structure and polarization calculations and measurements.

Polymer Structure	Polymer ID	P_u^a (mC/m ²)	P_{theo}^b (mC/m ²)	P_r^c (mC/m ²)	P_r/P_u (%)
	P1	22	.	5	23
	P2	40	24	14	35
	P3	40	22	6	14
	P4	57	33	4	7
	P5	48	43	13	28

^a Based on rigid dipole theory.^b Based on Mean Squared Dipole calculation.^c Based on TSC measurements.

Figure 2 shows the value of the piezoelectric charge coefficient, d_{31} , as a function of temperature for P2 and P5. That of PVDF is included for comparison purposes. For the range of temperatures examined, the polyimides are in the glassy state (i.e. below T_g), hence they do not deform readily. As the polymers approach their respective glass transition temperatures, d_{31} increases due to a decrease in the modulus. In the temperature regime from 25°C to 80°C the piezoelectric constant of PVDF is two orders of magnitude higher than that of either polyimide. Typically PVDF is not used above 80°C since at these temperatures, the polymer begins to lose its mechanical orientation imparted during processing. The material also starts degrading chemically, and aging of the piezoelectricity is precipitated at these high temperatures. Polymers P2 and P5 on the other hand are resistant to temperature effects in this range. In fact, at 150°C, the piezoelectric constant of P2 increases and is now only one order of magnitude lower than that of PVDF. That of P5 at 200°C (two times the operating temperature of PVDF) is now the same order of magnitude as PVDF. Loss of the piezoelectric effect occurs in both PVDF and the polyimides over time and temperature. For PVDF this loss is not recoverable due to loss in mechanical orientation; however, amorphous polyimides can be regenerated by re-poling.

As Table 5 indicates, higher values of d_{31} at the high temperatures result in higher values of g_{31} , which is desirable in a sensor material. At temperatures close to T_g , some dipoles relax toward their equilibrium position, which results in a slightly lower value of d_{31} in subsequent measurements.

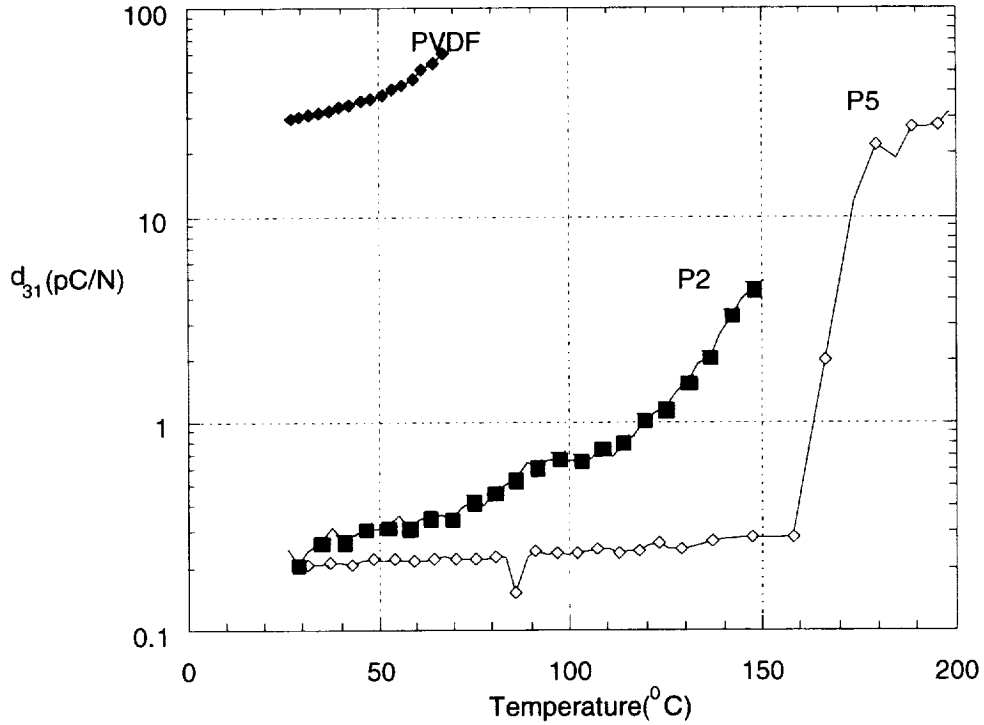


FIG. 2. Comparison of the piezoelectric charge coefficient d_{31} .

TABLE 5.
Piezoelectric coefficients.

Polymer	T = 25°C		T = 100°C		T = 150°C		T = 200°C	
	d_{31} (pC/N)	g_{31} (mV- m/N)	d_{31} (pC/N)	g_{31} (mV- m/N)	d_{31} (pC/N)	g_{31} (mV- m/N)	d_{31} (pC/N)	g_{31} (mV- m/N)
PVDF	25	235	60	565	-	-	-	-
P1	0.02	0.5	0.02	0.6	0.02	0.6	-	-
P2	0.3	7.6	0.7	22	5.0	152.7	-	-
P5	0.2	6.4	0.3	7.6	2.0	61.1	30	916

4. Conclusion. Based on this initial structure-property analysis, it is clear that flexibility of the structure and the magnitude and location of added dipoles significantly influence the level of piezoelectric response for this series of polyimides. It follows that dipole concentration should also be an important contributor; however, this is limited by practical synthesis considerations. Future work will explore the feasibility of developing new monomers and polymers with larger dipole concentrations while maintaining chain flexibility and favorable geometries.

The piezoelectric charge coefficients d_{31} increase at temperatures in excess of 100°C. However, at this point it is not clear that this may be exploited in practice. The challenge resides in the fact that as d_{31} increases, the dipoles start relaxing back to their equilibrium state, hence lowering the piezoelectric response over time. The key is to operate in a range where d_{31} is high yet dipole relaxation is minimized.

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