Synthesis and Characterization of Polyimides Derived From Cyano-Containing 1,4-Bis(4-aminophenoxy)benzene Monomers

Daniel J. Klein1(✉), Crystal C. Topping2, and Robert G. Bryant3

1Current address: Ashland Performance Materials, 5200 Blazer Parkway, Dublin, Ohio 43235
2Applied Technologies and Testing Branch, NASA Langley Research Center, Hampton, VA 23681-2199
3Advanced Materials and Processing Branch, NASA Langley Research Center, Hampton, VA 23681-2199
E-mail: djklein@ashland.com; Fax: (614) 790-6409

Received: 2 September 2006 / Revised version: 3 February 2007 / Accepted: 5 February 2007
Published online: 28 February 2007 – © Springer-Verlag 2007

Summary
A series of three new cyano-containing diamines based upon 1,4-bis(4-aminophenoxy)benzene was synthesized and polymerized with six different dianhydrides to yield 18 different polyimides. Due to the high dipole moment of the cyano group, it was believed that these polymers would display differing degrees of electroactivity depending upon the degree and position of cyano substitution. The type of dianhydride bridging group and length are also factors that affect the electroactivity of polyimides. Polyimides based upon 1,4-bis(4-aminophenoxy)benzene were used as reference materials by which the respective cyano-containing analogs were compared. As the degree of cyano group substitution increased, the glass transition temperature increased. As cyano substitution increased, the polymer chain flexibility decreased due to hindered rotation about the phenyl-ether-phenyl linkages in the diamine portion of the polymer. The tensile moduli ranged from 2.97 to 4.57 GPa and ultimate tensile strengths from 79 to 156 MPa, which are typical values of aromatic polyimides.

Keywords
polyimides, glass transition, piezoelectric, cyano, mechanical properties, thermal properties, synthesis

Introduction
In 1969 Kawai first reported that polyvinylidene fluoride (PVDF) exhibited a high piezoelectric response when drawn and poled [1]. This response is due to dipole orientation taking place in the presence of an electric field. There has been only limited study of piezoelectric polymers since this discovery, with poly(vinylidene cyanide) [2,3], polyurethanes [4,5], polyureas [4,6,7], nylons [8-10], and PVDF/trifluoroethylene copolymers [11-13] being those most frequently studied.
The use of PVDF is somewhat limited by its upper use temperature, whose piezoelectric activity starts to decrease above 80°C due to loss of polarization [14]. Nylons display higher remnant polarizations than PVDF, but the moisture absorption of nylons is detrimental to poling and the dielectric properties. Although nylons have low glass transition temperatures ($T_g$s) the upper use temperatures of nylons should be 150°C or higher due to orientation stabilization occurring through intermolecular hydrogen bonding [8]. Hence, the stabilization of orientation of polar groups by intermolecular forces or increased $T_g$s may enhance the inherent electroactivity of polar polymers.

This work focuses on the synthesis of polyimides from a series of cyano-substituted 1,4-bis(4-aminophenoxy)benzene monomers. Polyimides not only display low moisture uptake, but also will have high $T_g$s that will enable higher use temperatures than PVDF. The cyano content and position of these polar cyano groups on the diamine monomer will allow for a determination of how much effect the dipole concentration and dipole position have on the piezoelectric properties.

Experimental

Materials

2,3-Dicyanohydroquinone, hydroquinone, 2-chlorobenzonitrile, 10% palladium on carbon, pyridinium hydrochloride, N-methyl-2-pyrrolidinone (NMP), and hydrochloric acid (HCl) (Aldrich Chemical Co.) were used as received. Dimethylsulfoxide (DMSO) and dimethylformamide (DMF) (Fisher Chemical Co.) were distilled from phosphorus pentoxide. 2,5-Dimethoxybenzonitrile (Maybridge Chemical Co.) was used as received. Potassium carbonate (Fisher Chemical Co.) was ground and dried at 100°C under reduced pressure overnight. 5-Nitro-2-chlorobenzonitrile (I) was prepared according to the literature [15]. 4,4’-Oxydiphthalic anhydride (ODPA) and isophthaloyl dianhydride (IPDA) (Imitech) were used as received. 3,3’,4,4’-Benzophenone tetracarboxylic dianhydride (BTDA) (Chriskev Co.) was recrystallized from acetic anhydride. 2,2’-Bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) (Clariant Corp.) was recrystallized from acetic anhydride. 4,4’-Bisphenol A dianhydride (BisADA) (GE Plastics) was recrystallized from acetic anhydride. 2,2’-Bis(3,4-dicarboxyphenyl)dimethylsilyl dianhydride (SiDA) was prepared according to the literature [16]. 1,4-Bis(4-aminophenoxy)benzene (TPE-Q) (Chriskev Co.) was used as received.

Characterization

Differential scanning calorimetric (DSC) measurements were performed under air at a heating rate of 10°C/min using a Shimadzu TA-501 Thermal Analyzer equipped with a Shimadzu DSC-50 cell. Thermogravimetric analyses (TGA) were performed in nitrogen and air at a heating rate of 2.5°C/min using a Perkin Elmer TGA. Proton nuclear magnetic resonance ($^1$H NMR) spectra were obtained with a Bruker AVANCE 300 NMR spectrometer at 300 MHz. Carbon nuclear magnetic resonance ($^{13}$C NMR) spectra were obtained with a Bruker AVANCE 300 NMR spectrometer at 75 MHz. Tetramethylsilane was used as the reference for $^1$H and $^{13}$C NMR analyses. The reference peaks were assigned at 0 ppm. Infrared spectra (IR) were obtained with a Nicolet Magna-IR Spectrometer 750. Melting points were determined using an Electrothermal 9200 melting point apparatus and are uncorrected. Inherent viscosities