POLYIMIDES CONTAINING NITRILE GROUPS AND NANOCOMPOSITES BASED ON THEM

Elena HAMCIUC,[*] Corneliu HAMCIUC and Irina BACOȘCĂ

"Petru Poni" Institute of Macromolecular Chemistry, Aleea Gr. Ghica Vodă 41 A, Iași 700487, Roumania

This article presents literature data regarding the synthesis and properties of aromatic polyimides containing nitrile groups and some materials based on them. The polymers were synthesized by polycondensation reaction of various diamines having nitrile groups with different dianhydrides. The nanocomposites were prepared starting from poly(amic acid)s and a soluble precursor of barium and titanium oxides or carbon nanotubes. The properties, such as solubility, thermal and piezoelectric behavior are discussed in correlation with their chemical structure. Some applications of these polymers are also shown.

INTRODUCTION

Polyimides have attracted much attention of researchers regarding the high performance applications, due to their attractive combination of properties as well as due to the easy design for specific uses. Some properties such as chemical resistance, dielectric constant, color, glass transition or melting temperature, thermooxidative stability and solubility can be controlled by the chemical structure of the polymer.[1,2] In the last years, the use of the polyimides as matrix for composite materials having special properties received a great importance because of their good behavior at high frequencies, low conductivity, durability, and especially due to the possibility to be processed in different shapes required by specific applications.[3-5]

Aromatic polyimides having nitrile groups are promising materials with piezoelectric properties for use at high temperature.[6-9] The large dipole moment of nitrile group (4.18 D) provides a strong interaction with the applied electric field.[10,11]

Moreover, the introduction of nitrile groups into the polymer chains maintains a high thermal stability. Nitrile substituents possess strong bond dissociation energy, which keeps the excellent thermal stability of the polyimide. The pendent nitrile group on aromatic ring appears to promote adhesion of the polymer to many substrates, possibly through polar interaction with other functional groups; it also serves as a potential site for polymer cross-linking.[12-14]

According to the literature concerning piezoelectric polymers, the semi-crystalline poly(vinylidene fluoride) (**PVDF**) and its copolymers with trifluoroethylene and tetrafluoroethylene show a large piezoelectric response.[15,16] To date **PVDF** is the only commercially available piezoelectric polymer. However, this polymer has low chemical stability in harsh environments and cannot be used in high temperature applications. Therefore, there is great interest in developing other classes of piezoelectric amorphous polymers for high temperature applications.

[*] Corresponding author: ehamciuc@icmpp.ro

POLYIMIDE BASED ON 2,6-BIS(3-AMINOPHENOXY)BENZONITRILE AND 4,4′-OXYDIPHTHALIC ANHYDRIDE

Recently, much research has been made on the synthesis and characterization of polyimides containing pendent nitrile polar groups, especially with the aim to develop new high temperature piezoelectric materials for sensor and actuator fabrication.[17] The most important factors for designing an amorphous piezoelectric polymer are the dipole functionality, which means the presence of a sufficient concentration of dipoles, the ability to orient these dipoles and to lock in this alignment, and the ability to sufficiently strain the polymer. Also, the glass transition temperature of the polymer is very important because it determines the range of temperature applications. Particularly interesting is the potential use of electroactive polyimides in microelectromechanical systems (MEMS) devices due to their outstanding thermal stability and chemical resistance which satisfy the criteria for conventional MEMS processing.[18]

One of the most studied polymer as high-temperature piezoelectric material was the polyimide **m-CNDA/ODPA** prepared by polycondensation reaction of 2,6-bis(3-aminophenoxy)benzonitrile (**m-CNDA**) with 4,4′-oxydiphthalic anhydride (**ODPA**), in two steps (Scheme 1).[19,20] In the first step a poly(amic acid) **PAA-m-CNDA/ODPA** was obtained, at room temperature, in N-methyl-2-pyrrolidone (NMP) as solvent. In the second step, the resulting poly(amic acid) was cyclodehydrated to the corresponding polyimide structure by thermal or chemical procedures. The diamine **m-CNDA** was synthesized by the reaction of 2,6-dichlorobenzonitrile with *m*-aminophenol, in polar solvents such as NMP or N,N-dimethylacetamide (DMAc) in the presence of K_2CO_3.[21]

The polyimide **m-CNDA/ODPA** was soluble in organic solvents like NMP, DMAc, and N,N-dimethylformamide (DMF) due to the presence of ether flexible linkages and side nitrile groups which disturb the packing of the polymer chains and facilitate the diffusion of small solvent molecules between the macromolecules. This polymer was easily processed into thin films by casting from solution. It was thermally stable up to 400°C. The differential scanning calorimetry measurements showed no evidence of crystallization or melting which proves an amorphous morphology.
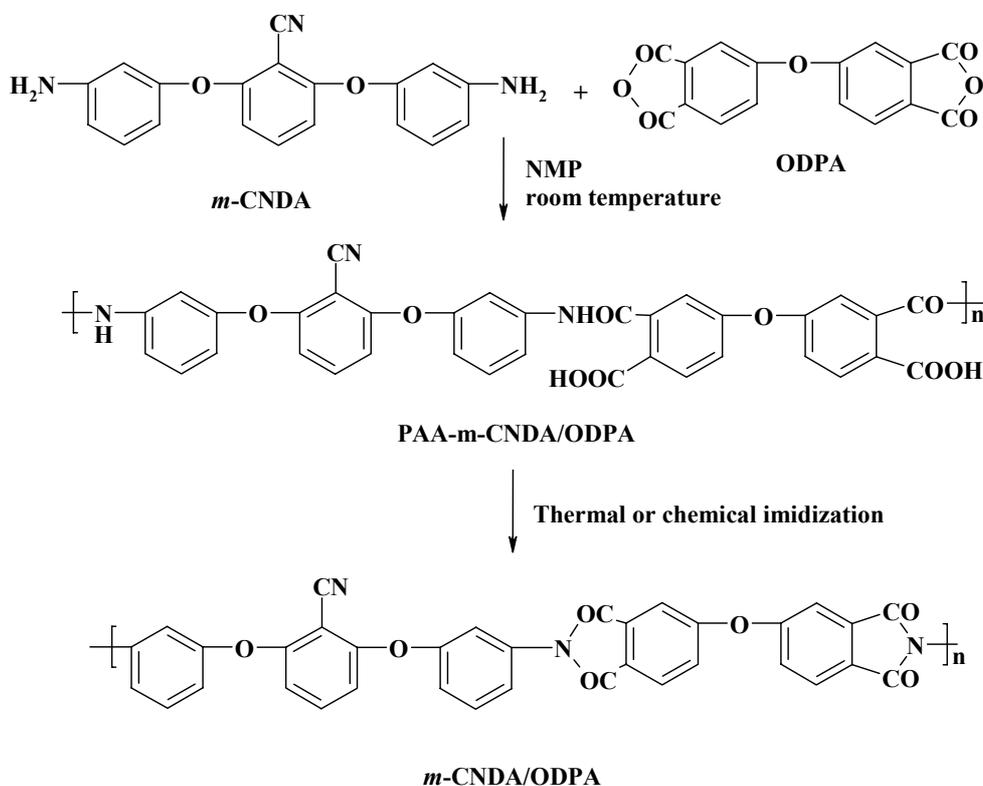
Scheme 1 – Synthesis of polyimide **m-CNDA/ODPA**.

The influence of the cyclization process on the piezoelectric properties of this polyimide was investigated. Thin films were prepared using polyimides synthesized by both thermal and chemical procedures. Two different thermal cyclization processes were used: a) standard thermal cyclization, in which the polymer film was heated at 100°C, 200°C and 300°C, for 1 h each; b) relative thermal cyclization, in which the polymer film was heated at 50°C, 150°C, 200°C and T_g+20°C, for 1 h each.

The chemical imidized films were obtained by casting a solution of polyimide powder (prepared by chemical cyclization) in NMP, followed by removing the solvent using the relative thermal cyclization conditions. No significant difference in piezoelectric response was observed for the polymer films prepared by the two thermal cyclization procedures (standard and relative cyclization). Small differences were noticed for remanent polarization (P_r) and piezoelectric constants (d_{31} and g_{33}) values of polymers prepared by thermal or chemical cyclization. Piezoelectric properties of polyimide obtained by chemical imidization procedure were better at 95°C than at room temperature. The thermal stability was evaluated by measuring the P_r which was lost in polyimide **m-CNDA/ODPA** when it is heated from 30°C to 240°C. The polymer retained 94% of its P_r at 150°C and over 80% of P_r at 200°C. It retained more than 50% of its room temperature P_r, at 150°C for 500 h. The thermal piezoelectric stability of this polyimide makes it more attractive than **PVDF** for high temperature applications. However, the piezoelectric response of this polyimide was found an order of magnitude lower than the required value for practical utility in devices.[22] **Polyimide-polydimethylsiloxane copolymers containing nitrile groups**, **1**, (Fig. 1) were prepared by polycondensation reaction of **ODPA** with a mixture of **m-CNDA** and bis(aminopropyl)oligodimethylsiloxane of controlled molecular weight (1120 g/mol), in different ratios.[23] The copolymers were soluble in polar organic solvents such as NMP, DMAc, DMF and pyridine. Compared to polyimide **m-CNDA/ODPA**, these copolymers were soluble in less polar solvents such as chloroform and tetrahydrofuran due to the presence of flexible polydimethylsiloxane segments and copolymerization effect which increased the solubility. They exhibited high thermal stability having the T_g in the range of 149-219°C. Some of them were processed into thin flexible films, following published procedures.[24] The dynamic contact angles with water increased by the introduction of the polydimethylsiloxane segments into the polyimide structure. This is because the low surface energy of the polydimethylsiloxanes provides a thermodynamic driving force for their migration to the copolymer-air interface.[25,26] As a result, during the samples preparation as films or membranes by solvent casting, the polydimethylsiloxane segments will segregate on the surface in order to minimize the surface free energy. Composite polymer films were prepared by casting a dispersion of polymer and pyrite ash powder in chloroform onto glass plates. The films were studied in order to obtain nanometric displacements, when an electric voltage was applied on their surface. The nanodisplacement field was of 300-400 nm, at 5 V dc, with flexible thin electrodes. This result is a very distinct parameter for microelectromechanical (MEMS) or nanoelectromechanical (NEMS) systems.
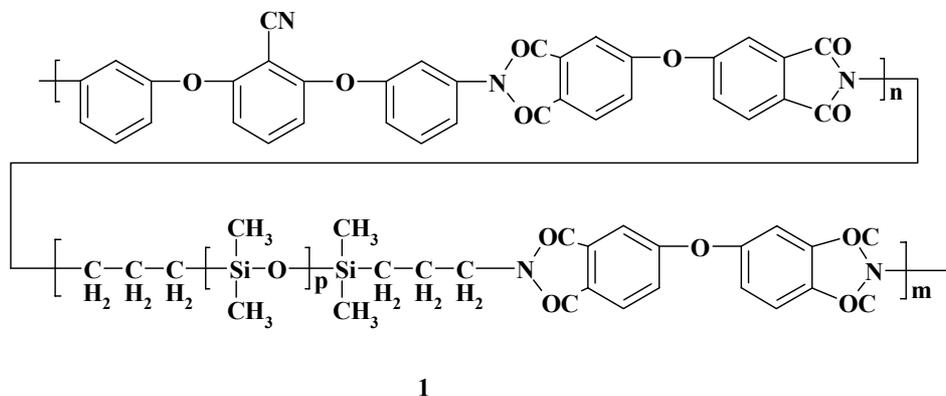

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Fig. 1 – Chemical structure of polyimide-polydimethylsiloxane copolymers **1** containing nitrile groups.

It is known that the incorporation of metallic additives into polyimides improves their properties.[27-30] **Hybrid polyimide films based on barium and titanium oxides** were prepared starting from the poly(amic acid) **PAA-*m*-CNDA/ODPA** and a soluble precursor **BTL**.[31] First, a precursor of barium and titanium oxides, **BTL**, was prepared from $BaCO_3$, titanium *n*-butoxide and lactic acid.[4] **BTL** with various ratios of **BTL**/polymer was added to a poly(amic acid) solution and stirred up to **BTL** dissolved completely in polymer solutions. The resulting solutions were cast onto glass plates and gradually heated up to 375°C to obtain flexible films having different concentration of metal oxides. The presence of metal oxides decreased the thermal stability of the polyimide and increased T_g. Thus, the temperature at which a hybrid polymer film lost 5% weight decreased from 541°C, for the polymer without metal oxides, to 517°C for the polymer containing 5.66% metal oxides. The study of nanoactuation properties revealed that a hybrid film containing 3.47% barium and titanium oxides showed nanometric displacements in the range of 20-30 nm at 10 V dc with flexible thin electrodes. The reference film, not containing metal oxides, did not show displacement in the condition of the same experiment. **Polyimide nanocomposites based on carbon nanotubes** (CNT) were developed due to the increasing demand for the new polymeric materials as sensors and actuators for use in high temperature applications. CNT can be embedded into polymer matrices to produce composites suitable for structural applications. The incorporation of CNT into an electroactive polymer increases the electrostrictive properties. There are two types of CNT: single walled nanotubes (SWNT) with only one wall, and multi walled nanotubes (MWNT) which have many concentric tubes where the walls of the tubes are held together by weak van der Waals forces. CNT exhibit excellent mechanical, electrical, and thermal properties. They have extremely low electrical resistance and their thermal conductivity is about twice as high as that of diamond.[32]

Composites based on SWNT dispersed in a nitrile functionalized polyimide matrix showed excellent stability with respect to reaggregation of the nanotubes.[33] A charge transfer interaction between the nanotubes and polymer matrix was evidenced by FTIR and Raman spectroscopy. By comparison, the dispersion of SWNT in similar polyimides without nitrile groups was stable only for short periods of time.

Polyimide nanocomposites containing SWNT were investigated with the aim to develop electroactive polymeric materials as sensors and actuators for high temperature applications.[34] The introduction of SWNT into electroactive polyimides improved their electrostrictive strain, mechanical properties and chemical stability. The effects of various types and concentrations of SWNT on the dipole orientation and piezoelectricity were studied. It was found that the barely modified SWNT gave a significant increase in the *Pr* by comparing with SWNT highly modified. The *Pr* and the piezoelectric strain coefficient, d_{31}, increased with the concentration of SWNT. However, excessive loading of SWNT showed a reduction in *Pr* which was attributed to decreased poling field due to a large leakage of current.

Recently, a novel all-organic actuator fabricated with SWNT electrodes was reported.[35] The SWNT film was obtained by filtering a SWNT solution through an anodized alumina membrane. The dielectric properties of polyimide *m*-CNDA/ODPA sandwiched by the SWNT electrodes over a broad range of temperature (from 25 to 280°C) and frequency (from 1 kHz to 1 MHz) were studied. The all-organic actuator with the SWNT electrodes showed a larger electric field-induced strain than that with metal electrodes, under identical measurement conditions.

An approach to enhance the piezoelectricity of polyimides through the addition of lead zirconate titanate (PZT) particles and SWNT was reported.[36] The effect of the fillers on the properties of the nanocomposites was evaluated. It was found that the SWNT increased the dielectric, piezoelectric, and mechanical properties of the polyimide matrix. The incorporation of the SWNT in the PZT/polyimide composites facilitates polarization and produces an increase of the piezoelectric properties of the resulting material.

The effect of SWNT on the enhanced piezoresistive sensitivity of polyimide nanocomposites from below to above percolation was investigated.[37] The maximum piezoresistive stress coefficient of $1.52 \ 10^{-3}$ MPa^{-1} was found at just above the percolation threshold concentration (~ 0.05 wt %) of SWNT. This value is higher than those of metallic piezoresistive materials by two orders of magnitude ($4.25 \ 10^{-5}$ MPa^{-1} for aluminum). The piezoresistive properties are due to change in intrinsic resistivity of the composite as a result of variation of tunneling distance between conducting SWNT particles under compression or tension.

The dielectric constant of two types of nanocomposites, based on SWNT and a polyimide matrix containing hexafluoroisopropylidene groups or nitrile units, could be predicted using the Bruggemann model.[38] The results were compared with the experimental values of the dielectric constant. A significant increase in the electrical conductivity and dielectric constant was noticed at low content of SWNT fillers with a percolation threshold at 0.06 vol %. Using the Bruggeman model modified by Giordano, a reasonable agreement for SWNT contents under the percolation threshold and a SWNT dielectric constant of 2000, comparing with the experimental values, was found.

OTHER POLYIMIDES CONTAINING NITRILE GROUPS

Poly(ether imide)s having triphenylamino-cyano groups, **2**, were synthesized from 4-[bis(4-aminophenyl)-amino]benzonitrile and different bis(ether-anhydride)s (Fig. 2).[39] 4-[Bis(4-aminophenyl)-amino]benzonitrile was prepared by hydrogenation of the compound resulting from the reaction of 1-fluoro-4-nitrobenzene with 4-aminobenzonitrile, in the presence of K_2CO_3. Bis(ether-anhydride)s were synthesized by the sequence of reaction starting with aromatic nucleophilic substitution of 4-nitrophthalonitrile with various bisphenols.[40,41] The polymers showed good solubility in organic solvents such as NMP, DMF, DMAc, pyridine, chloroform and were easily processed into thin films. They exhibited good thermal stability up to 510°C, having T_g in the range of 224-279°C. The polymer film **2a** and the corresponding composite film containing 20% pyrite ash powder were investigated in order to evaluate the nanometric displacement when an electric voltage was applied on their surface. The composite film showed nanometric displacements in the range of 300 - 400 nm under a force of 2.2 N. The polymer film **2a** not containing pyrite did not show nanoactuation.
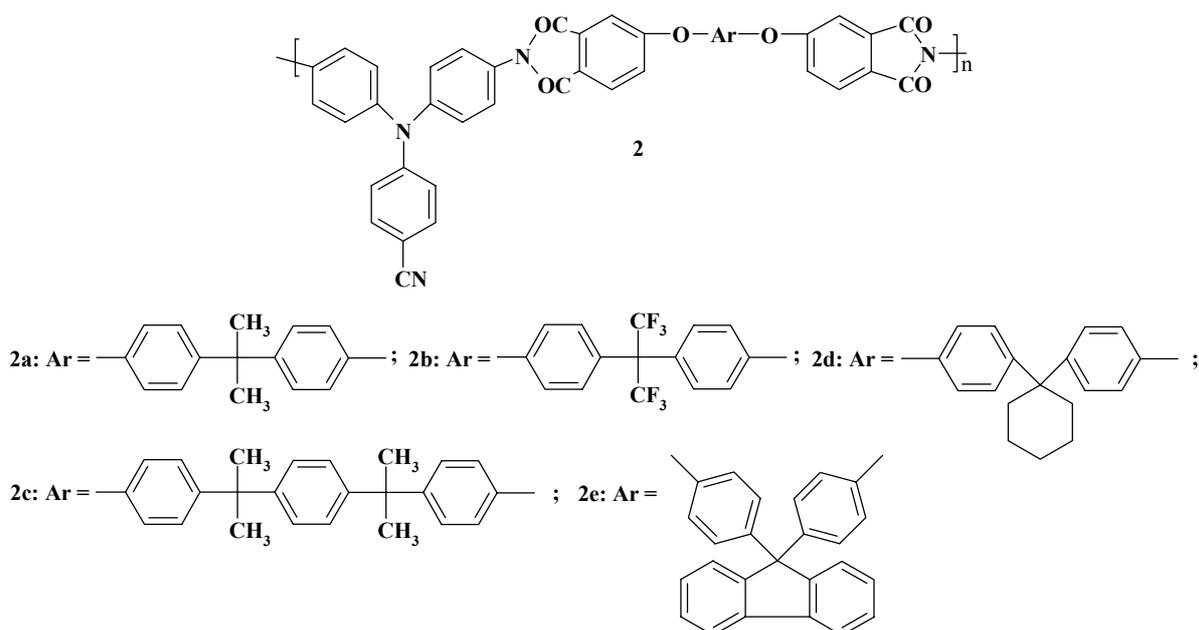

Fig. 2 – Chemical structures of poly(ether imide)s **2** containing triphenylamino-cyano groups.

Amorphous polyimides **3** were prepared based on **ODPA** and certain diamines having nitrile groups such as bis(3-aminophenoxy)benzonitrile, 2,6-bis(3-aminophenoxy)benzonitrile and 1,3-bis[2-cyano-3-(3-aminophenoxy)]phenoxybenzene (Fig. 3).[42] Thin films were prepared to investigate their P_r. Each sample was heated at a temperature of T_g + 20°C. During the polarization process the temperature was increased up to T_g + 10°C and was maintained at this value for 1 h. Then the polymer was cooled at room temperature in the presence of electric field in order to keep the polarization state. P_r value for sample **3a** was twice smaller than that of sample **3b** and much smaller than that of sample **3c**, depending on the number of polar nitrile groups and their position on the aromatic ring.

Polyimides **4** (Fig. 4), derived from nitrile-substituted 1,4-bis(4-aminophenoxy)benzene and different dianhydrides exhibited an increase of T_g with the number of nitrile groups from the unit structure due to the decreasing of the flexibility of the macromolecular chains.[43] The polymers based on 4,4′-(hexafluoroisopropylidene)diphthalic anhydride showed excellent mechanical properties, having elastic modulus in the domain of 3.05-3.84 GPa and tensile strength of 104-131 MPa. Polyimides containing 4 nitrile groups in the unit structure showed the highest P_r values. Particularly, the polyimide having four nitrile groups and a dimethylsilane unit exhibited the highest P_r value of 42 mC/m^2.
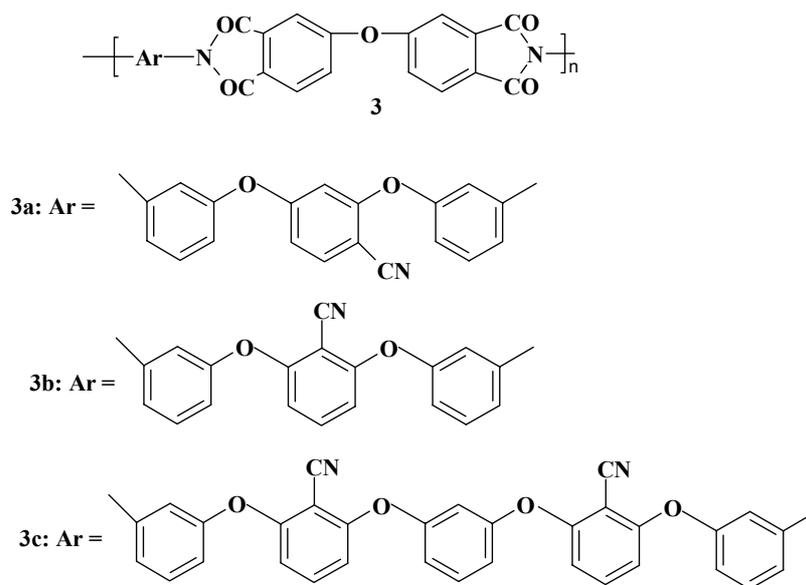

3a: Ar =

3b: Ar =

3c: Ar =

Fig. 3 – Chemical structure of polyimides **3** derived from **ODPA** and different diamines containing nitrile groups.

$$X = \ —O— \ ; \ —CO- \ ; \ —\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}— \ ; \ —O—\bigcirc—\underset{\underset{CF_3}{|}}{\overset{\overset{CF_3}{|}}{C}}—\bigcirc—O— \ ;$$

$$—OC—\bigcirc—CO- \ ; \ —\underset{\underset{CF_3}{|}}{\overset{\overset{CF_3}{|}}{C}}—$$

4a: R1=R2 = R3 = H
4b: R1 = CN; R2 = R3 = H

4c: R1 = R2 = CN; R3 = H
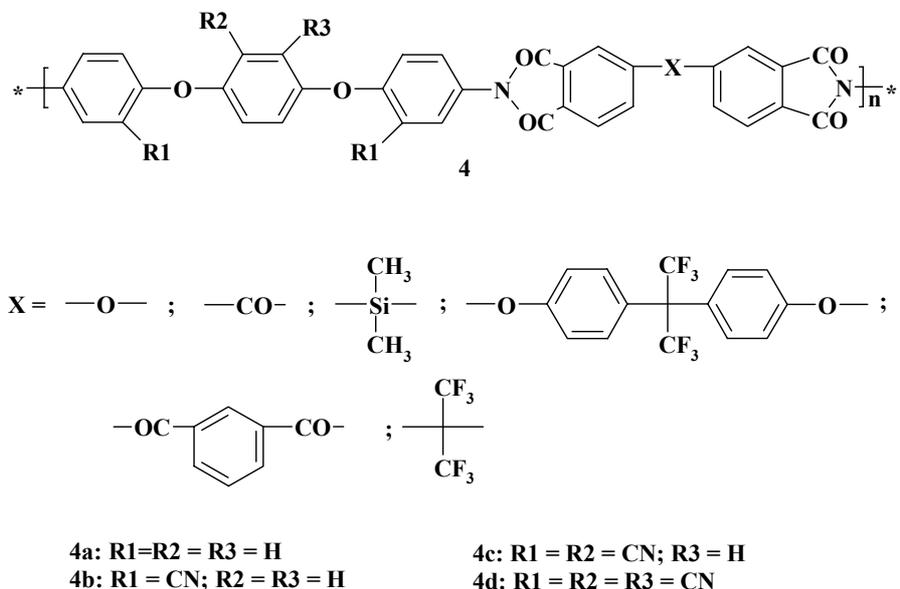**4d: R1 = R2 = R3 = CN**

Fig. 4 – Chemical structure of polyimides **4**.

Polyimides derived from 2,6-bis(4-aminophenoxy)benzonitrile or 2-cyano-4,4′-diaminodiphenylether and different dianhydrides were reported.[44,45] These polymers exhibited high thermal stability and good solubility in aprotic polar solvents. T_g values varied depending on the

dianhydride structure. The presence of nitrile groups lead to an increase of dielectric constant (ε).

Fluorinated polyimide **5** containing nitrile groups, compared with similar polymers not containing such groups, showed high values of ε (Fig. 5).[46] Thus, the polymer **5a** had $\varepsilon = 2.88$ at 0%

relative humidity, and 3.41 at 70% relative humidity, while the polymers **5b** and **5c** showed higher values for ε, of 3.03 and 3.14, respectively, under dry conditions, and 3.95 and 4.47 at 70% relative humidity. These polymers exhibited high thermal stability up to 500°C.

5a: R$_1$ = H; R$_2$ = H   **5b: R$_1$ =CN; R$_2$ = H**   **5c: R$_1$ = H; R$_2$ = CN**
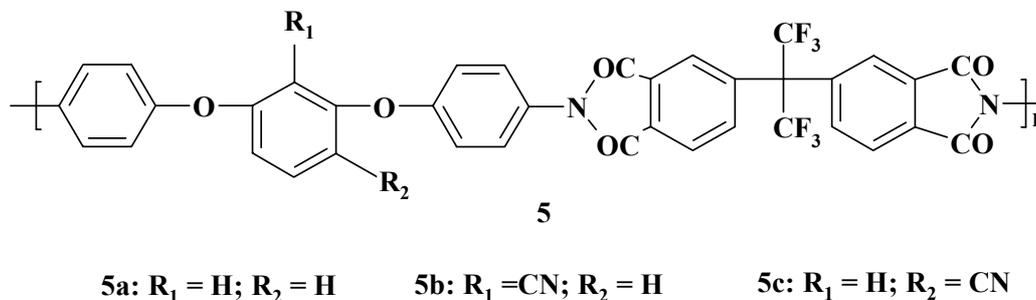
Fig. 5 – Chemical structure of fluorinated polyimides **5**.

Aromatic polyimides were synthesized by solution polycondensation of 2,6-bis(3-aminophenoxy)-benzonitrile with different dianhydrides such as pyromellitic dianhydride, benzophenonetetracarboxylic dianhydride, biphenyltetracarboxylic dianhydride, and 4,4′-(hexafluoroisopropylidene)diphthalic anhydride.[47] The polymers showed good solubility in polar amidic solvents and high thermal stability. Some of them showed good film forming ability giving flexible and resistant films from solutions. Other polyimides derived from two diamines which contain nitrile groups, 4-[bis(4-aminophenyl)-amino]benzonitrile and 4-[4-(1-cyanopropoxy)phenyl]-2,6-bis(4-aminophenyl)-pyridine, and various aromatic dianhydrides exhibited good solubility in polar solvents, thermal stability up to 400°C, T_g in the range of 305-

360°C, ε in the domain of 3.1-3.73 at 10 GHz, and good mechanical properties having the tensile strength of 80-120 MPa, elongation to break of 4-12% and elastic modulus of 1.2-2.3 GPa .[48]

Aromatic polyimides **6** containing amino- and cyano-substituted pyrazole groups were prepared by polycondensation reaction of 1,3-bis(*p*-aminophenyl)-4-cyano-5-aminopyrazole with several dianhydrides, such as pyromellitic dianhydride, **ODPA** and benzophenonetetracarboxylic dianhydride (Fig. 6).[49] The polymers were thermally stable having the temperature of 5% weight loss in the range of 517-523°C (in nitrogen) and 504-511°C (in air). T_g was in the interval 322-411°C. Unexpectedly, the amine and nitrile side groups were stable up to 500°C even in air atmosphere.
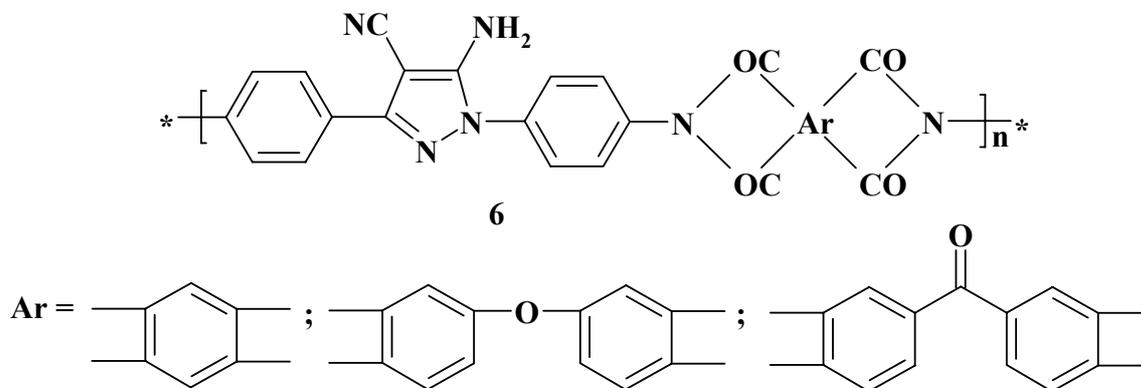

Fig. 6 – Chemical structure of polyimides which contain pyrazol rings
substituted with nitrile and amine functional groups, **6**.

Polymers with nonlinear optical properties, **7**, were synthesized by chemical modification of polyimides having hydroxy side groups with different chromophores, such as 2-(N-ethyl-4-(tricyanovinyl)aniline)ethanol or 4-(dicyanomethylen)-2-methyl-6-[4-(ethyl(2-hidroxyethyl)-amino)styril]-4H-pyran, using Mitsunobu reaction (Scheme 2).[50] The chromophore loading level in the polyimides was controlled efficiently from 0 to 50% by weight. The polymers showed excellent solubility and

processibility, high T_g values above 220°C, and thermal stability. They exhibited a large electro-optic coefficient (up to 34 pm/V at 0.63 μm and 11 pm/V at 0.83 μm) and long-term stability (>500 h at 100°C) of the dipole alignment. This method allows preparing NLO side-chain polyimides with a wide variety of pendant nonlinear optical chromophores which leads to desired physical properties of the polymeric materials.
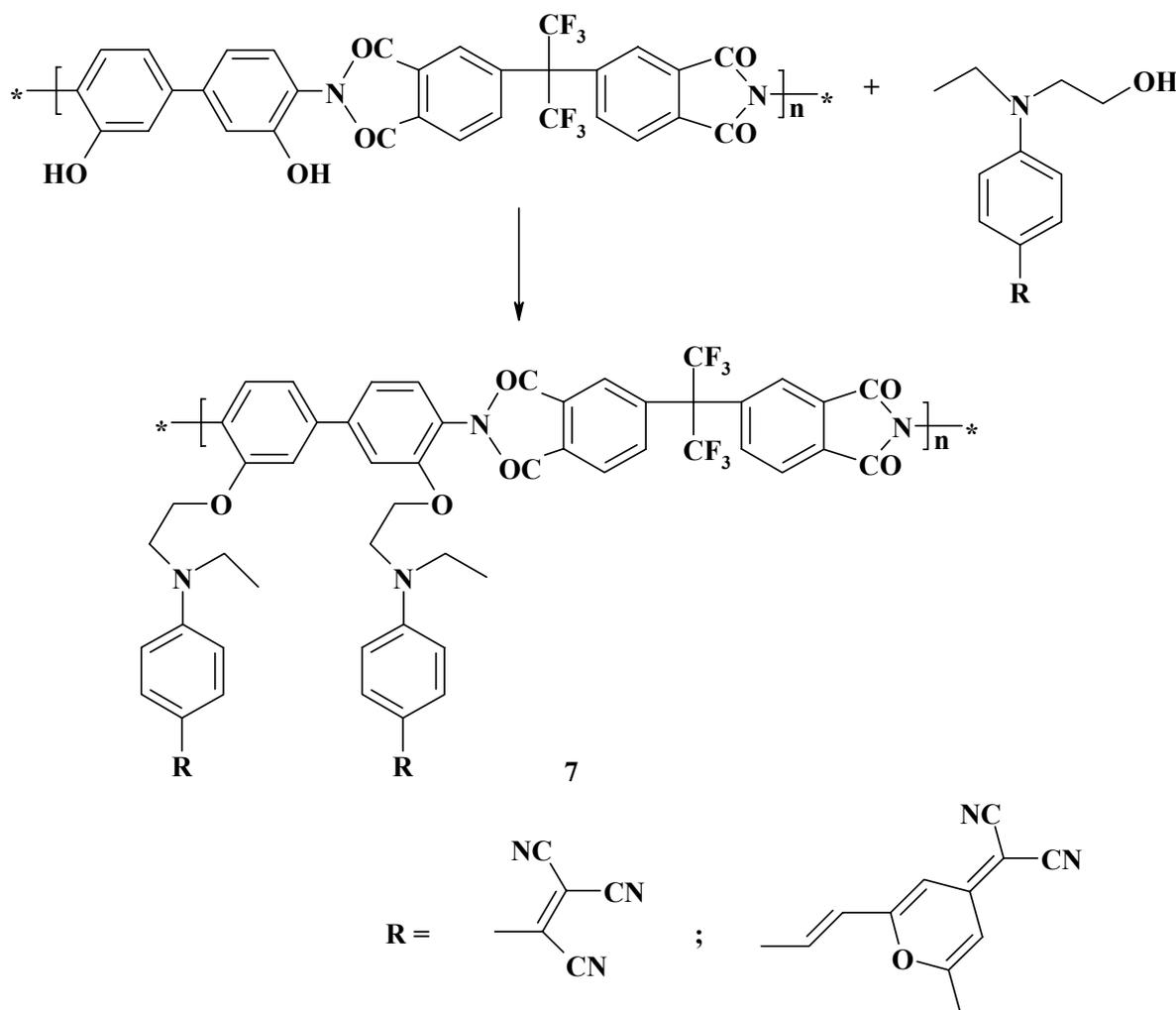
Scheme 2 – Synthesis of polyimides containing NLO side-chains, **7**.

Recently, the synthesis of a new Y-type polyimide containing 2,3-dioxybenzylidenemalonitrile chromophore groups was reported (Fig. 7).[51] The polymer exhibits the advantages of both main-chain and side-chain NLO polymers namely, stable dipole alignment and good solubility. It showed thermal stability up to 330°C and T_g of 190°C. The second harmonic generation (SHG) coefficient

(d_{33}) of poled polymer films at the 1064 nm fundamental wavelength was around 3.15 x 10⁻⁹ esu. The dipole alignment exhibited a thermal stability even at 20°C higher than the glass-transition temperature, and there was no SHG decay below 210°C, which was acceptable for nonlinear optical device applications.
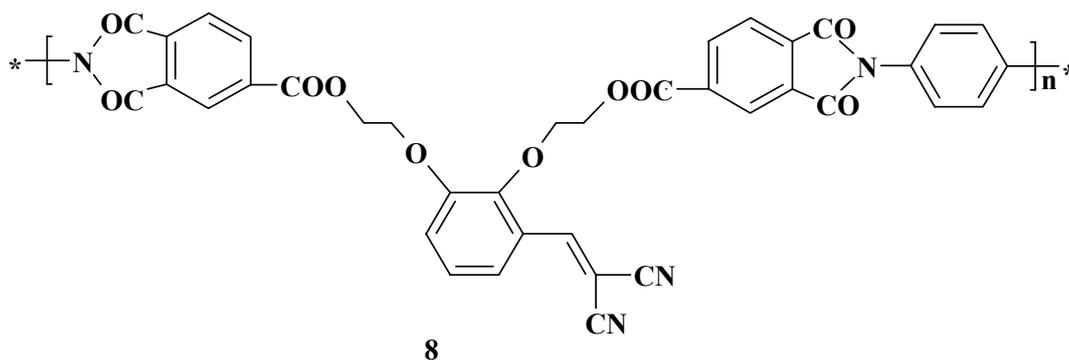
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Fig. 7 – Chemical structure of Y-type polyimide containing pendant NLO chromophores, **8**.

CONCLUSIONS

The introduction of the nitrile groups into the polyimide structure leads to materials with piezoelectric properties, with potential applications at high temperatures. The piezoelectric properties are significantly influenced by the flexibility and conformation of polymer chains, the magnitude and dipole positions. The dipole concentration in the unit structure of the polymers is an important factor which contributes to the increase of the piezoelectricity. Remarkable results were obtained with polymer nanocomposites containing carbon nanotubes. Also, nonlinear optical polyimides containing side nitrile groups in the chromophore segment were obtained.

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