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Dedicated to the memory of
Professor Mircea D. Banciu (1941–2005)

AROMATIC POLYIMIDES CONTAINING POLAR NITRILE GROUPS

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A series of polyimides containing nitrile groups has been synthesized by solution polycondensation reaction of two aromatic diamines having nitrile group and two ether linkages with various aromatic dianhydrides, namely 4,4'-oxidiphthalic dianhydride, benzophenonetetracarboxylic dianhydride and hexafluoroisopropylidene-diphthalic dianhydride. The polymers were easily soluble in polar organic solvents, such as N-methylpyrrolidone, N,N-dimethylformamide and N,N-dimethylacetamide, and gave flexible thin films by casting their solution. They present high thermal stability, with decomposition temperature being above 438°C. The polymers exhibited a glass transition temperature in the range of 203-284°C, with reasonable interval between glass transition and decomposition temperature.

INTRODUCTION

High performance polymers are used in applications demanding service at enhanced temperatures while maintaining their structural integrity and an excellent combination of chemical, physical and mechanical properties. Wholly aromatic polyimides are generally the polymers of choice for these applications due to their many desirable characteristics including good thermooxidative stability and excellent mechanical properties.[1-3] However, the commercial use of these polymers is often limited because of their poor solubility and too high softening or melting temperatures. Conventional aromatic polyimides must be processed at their precursor stage, poly(amidic-acid)s, which are unstable at room temperature and must be stored at a lower temperature. The imidization process should be carried out in the final materials, at high temperature (250-300°C). This process has some inherent limitations like the generation of water, which would create voids in those materials.[4]

To overcome these problems, much research effort has been focused on the synthesis of soluble polyimides in fully imidized form, without deterioration of their own excellent properties. Polyimides that are soluble in organic solvents may be prepared through the so called one step or single-stage method. In this procedure, the dianhydride and diamine are stirred in a high boiling-point organic solvent at a temperature above 180°C. Under these conditions, chain growth and imidization essentially occur spontaneously.[5-8] Several approaches to soluble polyimides including the incorporation of flexible linkages or bulky substituents have been developed. Incorporation of short bridges such as $-CH_2-$, $-SO_2-$, -CO-, $-C(CF_3)_2-$ into the polyimide chains has proved particularly beneficial to increase solubility.[9-15] It has been generally recognized that aromatic ether linkages inserted in aromatic main chains provide them with a significantly lower energy of internal rotation. In general, such a structural modification leads to lower glass transition temperature and crystalline melting temperatures as well as significant improvement of solubility and other processing characteristics of the polymers without greatly sacrificing other advantageous polymer properties.[16, 17]

Recently, the research of some polyimides containing pendent polar groups led to development of promising high temperature piezoelectric materials. Up to now, however, the piezoelectric properties of polyimides have been by one order of magnitude lower than those required by practical use.[18, 19]

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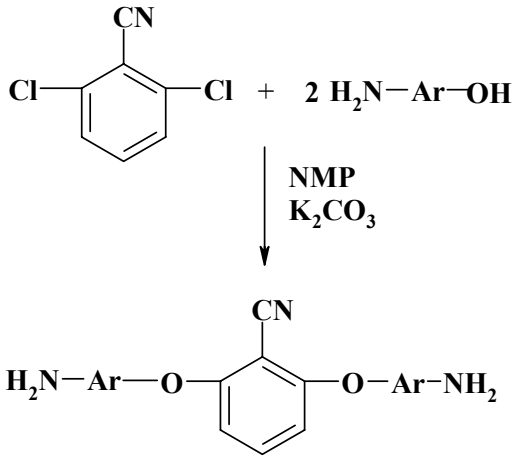
The present work is a continuation of our research on preparing processable high temperature polymers. In this article we present the synthesis of aromatic polyimides containing polar nitrile groups by solution polycondensation of two aromatic diamines having a nitrile group and two ether linkages with different aromatic dianhydrides incorporating flexible units, such as ether, carbonyl or hexafluoroisopropilidene (6F). The properties of these polymers, such as solubility, inherent viscosity, thermal stability, glass transition temperature have been studied.

RESULTS AND DISCUSSION

Two aromatic diamines, namely 2,6-bis(*m*-amino-phenoxy)benzonitrile, **1a,** and 2,6-bis(*p*-aminophenoxy)benzonitrile, **1b**, were prepared by the reaction of 2,6-dichlorobenzonitrile with *m*-or *p*-aminobenzoic acid, in N-methylpyrrolidone (NMP) as solvent, in the presence of potassium carbonate[20, 21], as shown in scheme 1.



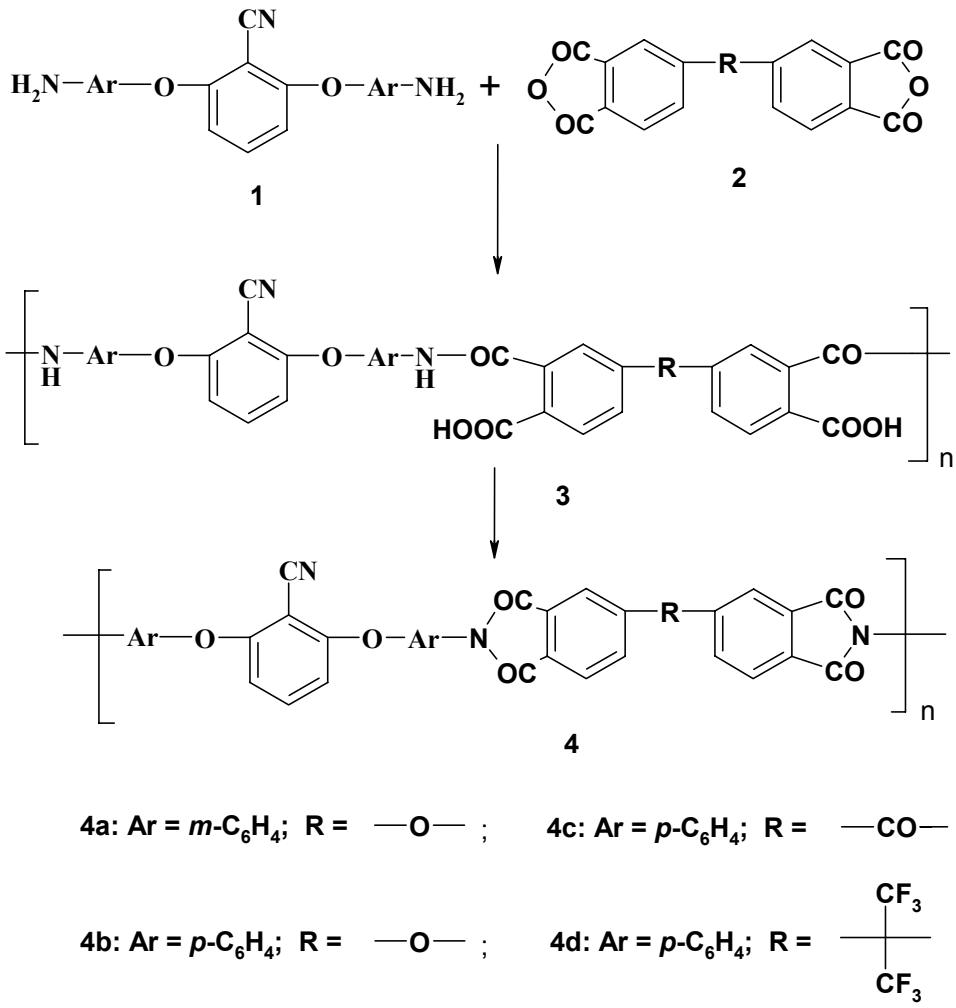
Scheme 1 – Synthesis of the diamines **1**.

1a: Ar = *m*-C_6H_4 ; **1b: Ar = *p*-C_6H_4**

The synthesis of aromatic polyimides took place in two steps, in one pot. In the first step, the polycondensation of an aromatic diamine **1** with an aromatic dianhydride **2** was performed at room temperature, leading to a poly(amidic-acid) **3** (Scheme 2 and table 1). NMP was used as solvent, and the total concentration of solids was 10-12%.

In the second step the resulting solution of poly(amidic-acid) was heated, under nitrogen, at 180-185°C, for 4 h. The water of imidization was evacuated by a slow stream of nitrogen which was used as inert medium, at the same time.

The conversion of poly(amidic-acid) to the fully cyclized polyimide was confirmed by IR spectroscopy. Figure 1 shows the IR spectra of poly(amidic-acid) **3a** and the corresponding polyimide **4a**, as an example. The complete conversion of *o*-carboxy-amide groups to the imide ring was evidenced by the disappearance of the amidic bands at 1650-1700 cm^{-1} and 2500-3000 cm^{-1}. In all IR spectra of polymers **4** strong bands appearing at 1780-1770 cm^{-1} and 1720-1710 cm^{-1} were attributed to symmetrical and asymmetrical stretching vibrations of carbonyl groups of imide rings. Absorption band at 1380 cm^{-1} was due to C–N stretching of imide rings, and absorption band at 730 cm^{-1} was due to imide ring deformation. The absorption peak at 1230 cm^{-1} was attributed to the aromatic ether Ar-O-Ar. Aromatic C=C bands were found at 1600 cm^{-1} and 1500 cm^{-1} while C-H absorption was found at 3070 cm^{-1}. All polymers exhibited an absorption band at 2220 cm^{-1}due to the presence of CN groups. Polymers **3d** and **4d** present characteristic absorption bands at 1180 cm^{-1} and 1210 cm^{-1} due to 6F groups.



Scheme 2 – Preparation of poly(amidic-acid)s **3** and polyimides **4**.

Table 1

Preparation of polyimides **4**

Polymer	Monomers		NMP	R.T.	H.T.
	Diamine, **I** (g)	Dianhydride,**II** (g)	(mL)	(h)	(h)
4a	1.585	1.55	28	4	6
4b	1.585	1.55	28	3	8
4c	1.268	1.288	24	3	3
4d	1.585	2.220	25	4	3.5

R.T. = Reaction time at room temperature
H.T. = Reaction time at high temperature

The cyclization of poly(amidic-acid)s to the corresponding imide structures was also evidenced by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Thermogravimetric analysis of the poly(amidic-acid)s showed a first weight loss at about 100°C due to the evolution of absorbed water, a second weight loss in the range of 130-210°C which was attributed to the evolution of water resulting from the thermal cyclization to imide structure and a third weight loss above 400°C due to the degradation of the resulting polyimide. Figure 2 presents ATG and differential thermogravimetric (DTG) curves of polymers **3a** and **4a**.

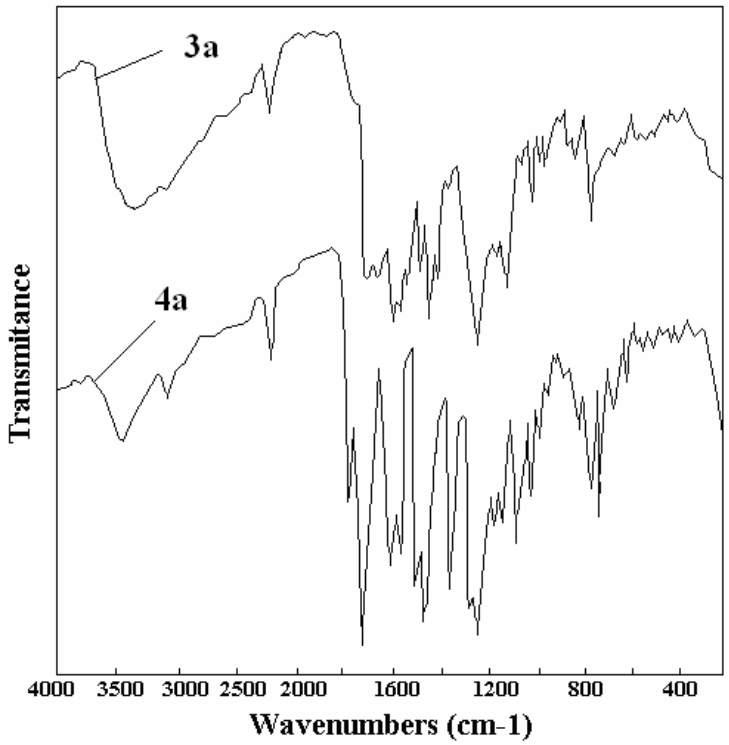


Fig. 1 – Typical IR spectra of poly(amidic-acid) **3a** and polyimide **4a**.

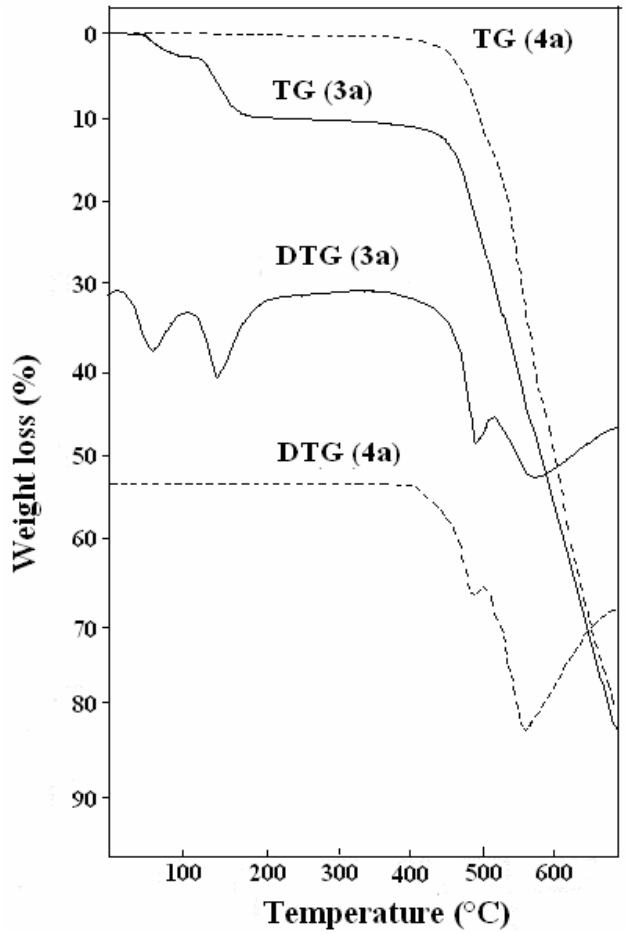


Fig. 2 – TGA and DTG curves of poly(amidic-acid) **3a** (solid line) and polyimide **4a** (dashed line).

The DSC curves of the poly(amidic-acid)s **3** exhibited a broad endotherm at about 100°C due to the evolution of absorbed water. All the samples showed an endotherm just above 140°C. According to thermogravimetric analyses, the poly(amidic-acid) underwent thermal cyclization in the same range of the DSC endotherm. Figure 3 presents the DSC curves of poly(amidic-acid) **3a** and polyimide **4a**.

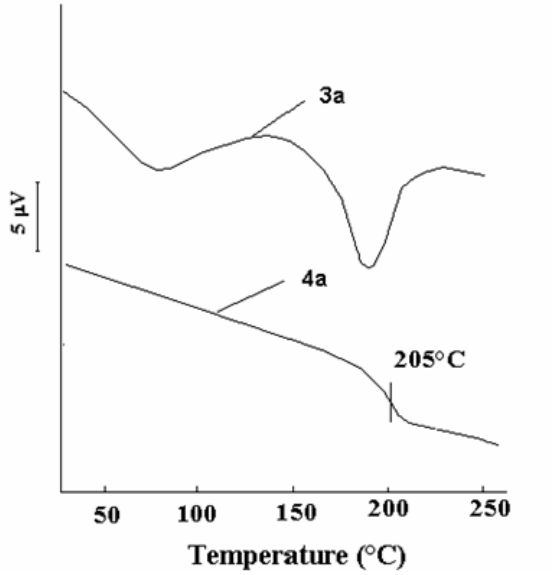


Fig. 3 – DSC curves of poly(amidic-acid) **3a** and polyimide **4a**.

The polyimides **4** were soluble in aprotic amidic solvents such as NMP, N,N-dimethylacetamide or N,N-dimethylformamide. Their good solubility allowed the imidization process to be performed in solution so that the final polymers were obtained as imidized products, which is more convenient than using poly(amidic-acid)s. The good solubility of the present polyimides is explained by the presence of flexible bridges such as ether, carbonyl, hexafluoroisopropylidene, which disturb the packing of the polymers and make the shape of the respective macromolecules to be far from a linear rigid rod that is characteristic to conventional polyimides.

The inherent viscosity of the polymers was in the range of 0.38-0.59 dL/g (Table 2).

Table 2

Properties of polyimides **4**

Polymer	η_{inh} [a] (dL/g)	T_g [b] (°C)	T_5 [c] (°C)	T_{10} [d] (°C)
4a	0.38	203	438	470
4b	0.40	234	445	477
4c	0.56	264	517	543
4d	0.59	284	484	502

[a] Measured at a concentration of 0.5 g polymer in 100 mL of NMP, at 20°C; [b] Glass transition temperature determined from DSC curve; [c] Temperature of 5% weight loss in TGA curves; [d] Temperature of 10% weight loss in TGA curve;

All these polymers possess film-forming ability. Their solutions in NMP having a concentration of about 10% were cast onto glass substrates and dried to yield free standing films having a thickness of 20-30 µm.

The thermal stability of polyimides **4** was investigated by thermogravimetric analysis. All polymers exhibited high thermal stability, with insignificant weight loss up to 420°C. They began to decompose in the range of 438-517°C, and the temperature of 10% weight loss (T_{10}) was in the range of 470-543°C (Table 2). The thermal behaviour of the present polymers is similar to the related polyimides without nitrile groups based on benzophenonetetracarboxylic dianhydride[5] and hexafluoroisopropylidene-diphthalic dianhydride.[22] The polymer **4c** containing C=O group in the dianhydride segment exhibited the highest thermal stability

(T_5 =517°C). Also, polymer **4d** containing 6F group in the dianhydride segment exhibited higher thermal stability (T_5= 484°C) when compared with polymers **4a** and **4b** which contain ether linkage in the dianhydride segment (T_5 : 438°C and 445°C, respectively).

The glass transition temperature (T_g) of the polyimides **4**, evaluated from DSC curves, was in the range of 203-284°C (Table 2). The DSC measurements showed no evidence of crystallisation or melting which proves an amorphous morphology (Figure 3). As expected the polymers **4a** and **4b** exhibited lower T_g value in the series due to the presence of additional flexible ether linkages in the dianhydride units. The polymer **4a** containing *m*-phenylene rings coming from the diamine segment had the lowest T_g (203°C). The higher T_g value of polymer **4d** (284°C) is explained by the presence of bulky 6F units in the polymer backbone. It can be noticed that there is a large interval between the glass transition and decomposition temperature which makes these polymers attractive for thermoforming processing, as well.

The nitrile group is advantageous for use in piezoelectric polymers due to its large dipole moment (4.18 D), which provides a strong interaction with the applied electric field.[23] Thus, in the case of polymer **4a**, 48% of the total polarization is due to the nitrile substituent, while the anhydride segment makes only up to 39% of the total polarization. The detailed study of the piezoelectric properties of these polymers will be reported later.

EXPERIMENTAL

Synthesis of the monomers

Aromatic diamines **1a** and **1b**, namely 2,6-bis(*m*-amino)phenoxy)benzonitrile and 2,6-bis(*p*-aminophenoxy)benzonitrile, were prepared by the reaction of *m*- or *p*-aminophenol with 2,6-dichlorobenzonitrile in NMP in the presence potassium carbonate, according to a published procedure[20,21]; they were recrystallized from a mixture of ethanol with water or DMF with water, respectively.

1a: M.p.210-213°C.

IR (KBr, cm^{-1}): 3450, 3360 (NH_2), 3060 (aromatic) 2230 (CN), 1620 (NH), 1600 (aromatic), 1240 (ether).

^{1}H-NMR (DMSO-d_6, ppm): 7.2 (3H, m), 6.8 (2H, s), 6.65 (2H, s), 6.50 (2H, s), 5.10 (NH_2).

1b: M.p.: 120-122°C.

IR (KBr, cm^{-1}): 3450, 3360 (NH_2), 3060 (aromatic) 2230 (CN), 1620 (NH), 1600 (aromatic), 1240 (ether).

^{1}H-NMR (DMSO-d_6, ppm): 7.5 (3H, m), 6.9 (4H,d), 6.6 (4H, m), 5.10 (NH_2).

Aromatic dianhydrides **2a**, **2b** and **2c**, namely 4,4'-oxydiphthalic anhydride, benzophenonetetracarboxylic dianhydride and hexafluoroisopropylidene-diphthalic dianhydride, were provided by commercial sources. They were recrystallised from acetic anhydride and washed thoroughly with anhydrous diethylether. M.p. **2a**: 234-236°C; M.p. **2b**: 225-227°C; M.p. **2c**:245-247°C.

Synthesis of the polymers

Polyimides **4** were prepared by solution polycondensation reaction of equimolar amounts of aromatic diamines containing nitrile groups, **1**, with an aromatic dianhydride **2** in NMP as a solvent. Details for the preparation of polyimides **4** are given in table 1. A typical polycondensation was run as shown in the following example: In a 100 mL three necked flask, equipped with mechanical stirrer and nitrogen inlet and outlet were introduced 1.585 g (0.01 mol) of diamine **1a** and 28 mL NMP. The mixture was stirred under nitrogen to complete dissolution. Then 1.55 g (0.01 g) of dianhydride **2a** was added to the resulting solution under stirring at room temperature. The solution was maintained under stirring and nitrogen stream for 4 h. About 10 mL of the resulting poly(amidic acid) solution was precipitated into 100 mL of water. A white fibrous product resulted which was thoroughly washed twice with 200 mL water each and once with 100 mL of ethanol, filtered each time and dried under vacuum. The rest of polymer solution was heated at 180-185°C for 6 h, under a nitrogen stream, to perform the cyclization of the poly(amidic-acid) **3a** to the corresponding polyimide structure **4a**. The water evolved during imidization was removed from the reaction mixture with the slow stream of nitrogen which was used as inert medium. The flask was cooled-down to room temperature and the resulting polyimide solution was poured into water to precipitate the polymer. The solid product was filtered, washed three times with water under stirring and dried at 120°C.

Measurements

Melting points of the monomers were measured on a Melt-Temp II (Laboratory Devices) without correction.

The inherent viscosities of the polymers were determined in NMP at 20°C, at a concentration of 0.5 g/dL, by using an Ubbelohde viscometer.

Infrared spectra were recorded with a Specord M-80 Spectrophotometer by using KBr pellets.

^{1}H NMR spectra were recorded on a Jeol C-60 MHz Spectrometer for solutions in deuterated dimethylsulfoxide (DMSO-d_6) using tetramethylsilane as internal standard.

Thermogravimetric analysis was performed on a MOM derivatograph (Hungary) in air, at a heating rate of 12°C/min. The temperature at which the samples achieve a 5% weight loss (T_5) and the temperature of 10% weight loss (T_{10}) were recorded.

The glass transition temperature (T_g) of the precipitated polymers was determined with a Mettler differential scanning calorimeter DSC 12E, at a heating rate of 10°C/min, under nitrogen. Heat flow versus temperature scans from the second heating run

were plotted and used for reporting the glass transition temperature. The mid-point of the inflexion curve resulting from the typical second heating was assigned as the glass transition temperature of the respective polymer.

CONCLUSIONS

Aromatic polyimides having nitrile functional groups have been synthesized by solution polycondensation reaction of aromatic diamines incorporating nitrile groups with certain aromatic dianhydrides. The polymers are soluble in polar aprotic solvents, and possess film forming ability. They show high thermal stability with decomposition temperature being in the range of 438-517°C and a glass transition temperature in the range of 203-284°C. Preliminary investigations showed that due to the polar nitrile groups, these polymers may have potential piezoelectric properties, which will be reported later.

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