

Synthesis and Characterization of New Polyimides Containing Nitrile Groups

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Introduction

Aromatic polyimides are well-accepted high-performance materials because of their excellent thermal stability, good mechanical properties as well as balanced electrical properties widely used in the fields of electronic materials. However, one of the objections is arising from their poor processability. Recently, it has been recognized that the introduction of pendant phenyl group into the polymer backbone would increase its processability.

Normally polyimides with low dielectric constant were desired for the application to advanced microelectronics. Recently polymers with high dielectric constant come to be one interesting target for researchers.

Induction of nitrile group into polymer chain is revealed to a reasonable method to increase its dielectric constant in theory due to its high molar polarization and low molar-specific volume. In addition, nitrile substituents possess rather strong bond-dissociation energy (>500 kJ/mol) to keep the polyimide excellent thermal stability [1].

In the present article we report the synthesis of a series of new polyimides bearing pendant phenyl/nitrile groups based on two novel amines, 4-[bis(4-aminophenyl)amino]benzotrile and 4-[4-(1-cyanopropoxy)phenyl]2,6-bis(aminophenyl) pyridine. Their general properties such as thermal, mechanical and electrical properties will be described herein.

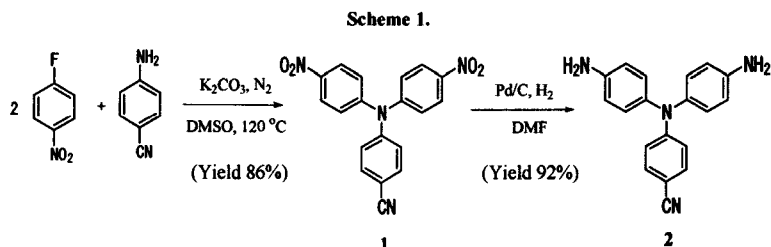
Experimental

Two new nitrile-containing diamine monomers, 4-[bis(4-aminophenyl)amino]benzotrile and 4-[4-(1-cyanopropoxy)phenyl]2,6-bis(aminophenyl) pyridine were synthesized via multi-route respectively. Diamine monomers were reacted with various tetracarboxylic dianhydrides then thermal imidization to produce a series of novel polyimides with pendant nitrile groups in the side chain. Their thermal properties, mechanical and electrical properties were evaluated. Moreover, the polyimides with no -CN groups were also prepared for comparison.

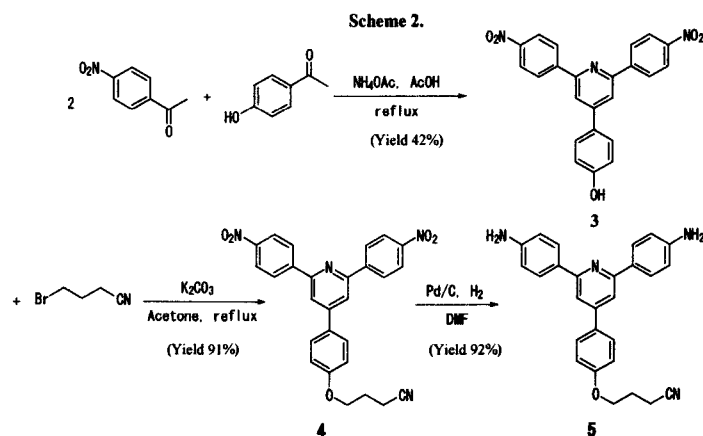
Results & Discussion

Monomer synthesis. The synthetic route of new triphenylamine and nitrile-containing diamine monomer, 4-[bis(4-aminophenyl)amino]benzotrile (**2**), was outlined in Scheme 1. The dinitro compound (**1**) was synthesized successfully by potassium carbonate-mediated condensation of 4-aminobenzotrile with 1-fluoro-4-nitrobenzene with high yield. The catalytic hydrogenation of **2** was accomplished by using

catalytic amount of Pd/C under hydrogen atmosphere. Under such mild reduction conditions, the nitrile groups kept stable, no aliphatic amine group was detected.



Another new diamine monomer bearing pyridine heterocyclic unit and nitrile group, 4-[4-(1-cyanopropoxy)phenyl]2,6-bis(aminophenyl) pyridine (**5**) was synthesized via a 3-step method as demonstrated in Scheme 2. The nitro-precursor (**3**) was prepared by the reaction of 4-hydroxybenzaldehyde and *p*-nitroacetophenone at the presence of excess ammonium acetate in glacial acetic acid as solvent. This route was a well known Chichibabin method [2], one the best way for preparation of pyridine ring. The following synthesis introduced nitrile-group into the backbone by reacted with 4-bromobutyronitrile using potassium carbonate as a base. This Williamson reaction proceeded well even without removing the water by Dean-stark instrument in advance. Finally, the catalytic hydrogenation was carried out just the same with compound **1**. Based on IR, ^1H and ^{13}C NMR assignments, it was confirmed the formation of diamine monomers **1** and **5** with expected structure.



Polymer synthesis. Polyimides were prepared via the polyaddition of diamine and tetracarboxylic dianhydrides with subsequent thermal imidization as shown in Scheme 3.

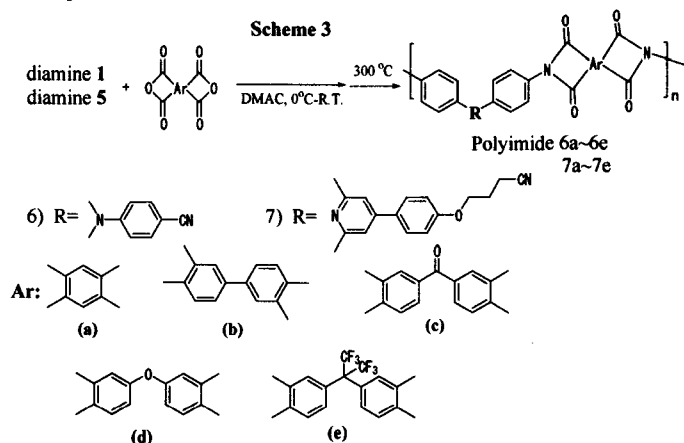
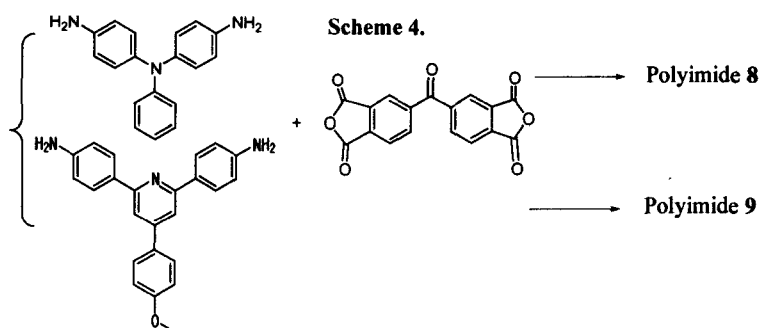


Table 1 demonstrates the thermal and electrical properties of polyimides. The polymers were fairly stable up to a temperature around or above 400 °C and lost 10% weight in the range of 500-590 and 470-580 °C in nitrogen and air, respectively. It was found that these polymers showed high glass transition temperatures between 305 and 360 °C, which suggested that the induction of unique units, triphenylamine, nitrile group or pyridine ring into the backbone would increase the T_g of polyimides. Similar results were reported before by Prof. Liaw for the polyimides bearing 3,4-dimethyl triphenylamine in the side chain with high T_g between 254 and 326 °C [3]. In order to check the effect of nitrile group upon the electrical property of polyimides, corresponding polymers **8** and **9** with no -CN groups were also prepared (Scheme 4). Diamine compound 4,4'-diamino-4''-nitrotriphenylamine was synthesized by the condensation of aniline with 1-fluoro-4-nitrobenzene then followed by catalytic reduction. Because there was no aniline substituted by electron-withdrawing groups on *p*-position used here, sodium hydride was selected as strong base instead of potassium carbonate to elevate its reactivity.

Polyimides derived from BTDA were selected for comparison. The corresponding polymers with -CN groups, **6c** and **7c** showed rather high T_g of 315 °C and 342 °C compared with the blank ones **8** (T_g=270 °C) and **9** (T_g=331 °C). This result indicated that the nitrile groups played a great role on the thermal property of polyimide with increasing T_g. Thus, the higher polarity makes the higher the T_g of the polymers.



The polyimides **6** and **7** showed dielectric constants of 3.10-3.73. Compared with the blank polyimides **8** ($\epsilon=3.16$) and **9** ($\epsilon=3.02$) without nitrile groups, it was found that the dielectric constant increased which contributed to its high molar polarization ($P_M=11.0 \text{ cm}^3\text{mol}^{-1}$) and low molar-specific volume ($V_M=19.5 \text{ cm}^3\text{mol}^{-1}$) of -CN group [1].

Table 1. Thermal and electrical property of polymers

Polymer code	T _g ^a (°C)	T ₅ ^b (°C)		T ₁₀ ^b (°C)		Dielectric constant ^c
		In N ₂	In air	In N ₂	In air	
9a	353	558	549	581	578	3.58
9b	358	569	562	593	588	3.23
9c	315	539	527	571	567	3.73
9d	304	560	548	583	575	3.29
9e	321	523	516	547	538	3.10
10a	345	461	437	503	488	3.63
10b	360	467	448	532	509	3.18
10c	342	467	446	526	504	3.62
10d	315	462	418	504	473	3.54
10e	339	471	501	517	501	3.19

^aFrom DSC measurements conducted at a heating rate of 20 °C min⁻¹.

^bTemperature at 10% weight loss (T₁₀) was determined by TGA at a heating rate of 10 °C min⁻¹.

^cFrequency: 10 GHz

All polyimide films prepared by thermal cyclodehydration showed tough, transparent and flexible nature. The mechanical property of polyimides were studied as summarized in Table 2.. These tough and flexible polyimide films had a tensile strength of 80-130 MPa, an elongation at break of 4-12%, and a tensile modulus of 1.5-3.0 GPa.

Table 2. Mechanical properties of various polymer films ^a

Polymer Code	Initial modulus (GPa)	Elongation-at-break (%)	Tensile strength (MPa)
9a	2.15	5.9	112
9b	1.18	6.7	80
9c	1.16	7.9	92
9d	1.84	11.2	105
9e	2.30	6.4	117
10a	1.54	5.6	86
10b	1.32	4.3	94
10c	2.21	7.5	119
10d	1.94	9.6	104
10e	1.37	6.7	97

^a Film cast from polymer solution of DMAc

Among these polyimides, PI-a and PI-b showed poor solubility due to the presence of rigid phenylene and naphthalene units. However, polymers derived from ODPa and 6FDA exhibited better solubility than the others because of their kink units in the backbone, they were readily soluble in a variety of solvents such as DMF as well as in less polar solvents such as pyridine, *m*-cresol at room temperature or upon heating. Moreover, polyimides from 6FDA even could dissolve in THF at room temperature.

Polymers 9 exhibited high molecular weights with average *M_n* ranging from 114,000 to 182,000 g mol⁻¹ with polydispersities around 1.3. While polymers 10 bearing pyridine heterocyclic ring exhibited moderate molecular weights with average *M_n* ranging from 41,100 to 21,400 g mol⁻¹ with *M_w*/*M_n* around 1.2-1.3 by GPC measurement. It revealed that the reactivity of diamine 2 is higher than that of diamine 5.

Conclusions

Two new diamine monomers containing pendant nitrile group and their polyimides with various dicarboxylic dianhydrides were successfully prepared. Polymers showed high glass transition temperatures, excellent thermal stability and tensile properties. Results presented herein also demonstrated that incorporating nitrile group into polymer backbone would enhance their dielectric constants and glass transition temperatures.

Reference

- [1] Van, D.W. Krevelen: Properties of Polymers, Elsevier 1990; Chapter 11.
- [2] Weiss, M.J. Am. Chem Soc 1952, 74, 200.
- [3] Liaw D J, Hsu P N, Chen W H and Lin S L *Macromolecules* 2002, 35, 4669.