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Wholly Aromatic Polyimides Containing Pendent Amino and Cyano Groups

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Introduction

Thermally stable organic polymers have been the subject of numerous studies in order to extend the application of organic materials in harsh conditions. Of thermally stable organic polymers, the outstanding properties of aromatic polyimides such as excellent thermooxidative stability and superior chemical resistance led to the use of polyimides in many applications, such as insulating materials for electronics, semipermeable membranes for gas separation, and high-temperature adhesives and coatings.[1] In general, rigid-rod-like polymers are insoluble and intractable or only processable under extreme conditions due to strong enthalpic interactions and the minimal increase in conformational entropy associated with their dissolution and melting.[2] A great deal of research effort on the polyimides has been concentrated on increasing processability with minimal effect on thermal stability as well as improvement of their specific properties.[3] For example, polyimides containing trifluoromethyl groups showed a high modulus, low thermal expansion coefficient, and good solubility,[4−7] and incorporation of heterocyclic units into polyimide chains increased the glass transition temperature and thermooxidative stability.[8−11]

Introducing stable functional groups as substituents is interesting because they can be used to impart special functionality to polymers as well as to improve processability. Previously, polypyrazoles with amino and cyano groups were synthesized from monomers containing the 1-chloro-2,2-dicyanovinyl moiety and dihydrazines by vinylic nucleophilic substitution reaction,[12] and we reported the preparation of polyamides containing substituted pyrazole rings which show good solubility and a high glass transition temperature.[13]

In this paper, we report the synthesis and characterization of new wholly aromatic polyimides which have a rigid but kink-catenated pyrazole ring with amino and cyano functional groups.

Experimental Section

Materials. Pyromellitic dianhydride (PMDA), 3,3′,4,4′-benzophenone tetracarboxylic dianhydride (BTDA), and 4,4′-oxydiphthalic anhydride (ODPA) were recrystallized from acetic anhydride/methyl ethyl ketone (v/v = 3/1) and then dried in vacuo at 150 °C for 24 h. *N*-Methylpyrrolidone (NMP) and *N*,*N*-dimethylacetamide (DMAc) were stirred in the presence of P_2O_5 overnight and then distilled under reduced pressure. Xylene was stirred in the presence of CaH_2 overnight and then distilled under nitrogen. Other commercially available reagent grade chemicals were used without further purification.

Synthesis of Monomer 1. The diamine monomer, 1,3-bis(*p*-aminophenyl)-4-cyano-5-aminopyrazole (PYA), was prepared from 4-nitrobenzoyl chloride by following the previously reported method.[13,14]

Synthesis of Model Compound 2. A 25-mL round-bottomed flask was charged with PYA (0.462 g, 1.59 mmol), phthalic anhydride (0.471 g, 3.18 mmol), and 9 mL of DMAc. This mixture was stirred under N_2 at room temperature for 3 h. To this solution, acetic anhydride (0.487 g, 4.77 mmol) and pyridine (0.263 g, 2.39 mmol) were added to form an imide ring. After addition of acetic anhydride and pyridine, the solution was stirred at room temperature another 6 h. Within 3 h, an orange precipitate was formed. The reaction mixture was poured into 50 mL of distilled water, filtered, washed with hot water and MeOH repeatedly, and dried in vacuo (0.821 g, 93.8%): mp 400−402 °C. (DSC) Anal. Calcd for $C_{32}H_{18}N_6O_4$ (MW = 550.53): C, 69.81; H, 3.30; N, 15.27. Found: C, 68.94; H, 3.39; N, 14.92.

Polyimide 3 from PMDA and PYA. PMDA (0.7513 g, 3.444 mmol) was added in one portion to a solution of PYA (1.000 g, 3.444 mmol) in 17 mL of DMAc at room temperature. After stirring for 12 h, the viscous solution was cast on a glass plate. The glass plate was preheated in vacuo at 80 °C for 12 h to remove DMAc. Then the poly(amic acid) film was heated from 40 to 340 °C for 2 h, and the temperature was held at 340 °C for 1 h under a flow of N_2. The film was removed from the plate, washed with water and MeOH, and dried in vacuo at 100 °C for 12 h.

Polyimide 4 from BTDA and PYA. The above procedure was repeated with the following quantities of reagents: BTDA (1.1073 g, 3.436 mmol), PYA (0.9977 g, 3.436 mmol), and 20 mL of DMAc. IR (film, cm^{-1}) 3348, 3226 (NH_2), 3080 (aromatic C−H), 2214 (CN), 1778, 1726 (C═O of imide), 1674 (C═O of ketone), 1626, 1520 (aromatic); 1369 (C−N stretching); 721 (C═O bending).

Polyimide 5 from ODPA and PYA. The above procedure was repeated with the following quantities of reagents.: ODPA (0.5196 g, 1.675 mmol), PYA (0.4862 g, 1.675 mmol), and 10 mL DMAc.: IR (film, cm^{-1}): 3346, 3227 (NH_2); 3078 (aromatic C−H); 2214 (CN), 1777, 1721 (C═O of imide), 1618, 1517 (aromatic), 1368 (C−N stretching), 1259 (C−O−C), 744 (C═O bending).

Preparation of Polyimide 4′ with a Chemical Imidization Method. BTDA (0.4575 g, 1.420 mmol) was added in one portion to a solution of PYA (0.4122 g, 1.420 mmol) in 9 mL of DMAc at room temperature. After the mixture was stirred for 12 h, acetic anhydride (0.435 g, 4.26 mmol) and pyridine (0.168 g, 2.12 mmol) were added to the solution. The solution was stirred at room temperature another 6 h. Within 3 h, the yellow precipitate was formed. The product was mixed with 50 mL of distilled water, filtered, washed with hot water and hot MeOH repeatedly, and dried in vacuo at 100 °C for 24 h (0.809 g, 98.8%): [η] 1.86 dL/g (in DMSO); IR (KBr, cm^{-1}) 3348, 3226 (NH_2), 3080 (aromatic C−H), 2214 (CN), 1778, 1726 (C═O of imide), 1674 (C═O of ketone), 1626, 1520 (aromatic), 1369 (C−N stretching), 721 (C═O bending).

Preparation of Polyimide 5′ with a Solution Imidization Method. ODPA (0.5463 g, 1.761 mmol) was added in one portion to a solution of PYA (0.5113 g, 1.761 mmol) in 10 mL of DMAc at room temperature. The temperature was raised to 190 °C slowly, and the reaction mixture was stirred for 8 h at 190 °C. Xylene was periodically removed from the Dean−Stark trap and replaced with dry xylene to ensure cyclodehydration. Within 3 h at 190 °C, a brown gel was formed. The product was mixed with 50 mL of distilled water, filtered, washed with hot water and hot MeOH repeatedly, and dried in vacuo at 100 °C for 24 h (0.952 g, 95.8%): [η] 2.12 dL/g (in NMP containing 5% LiCl); IR (KBr, cm^{-1}) 3346, 3227 (NH_2), 3078 (aromatic C−H), 2214 (CN), 1777, 1721 (C═O of

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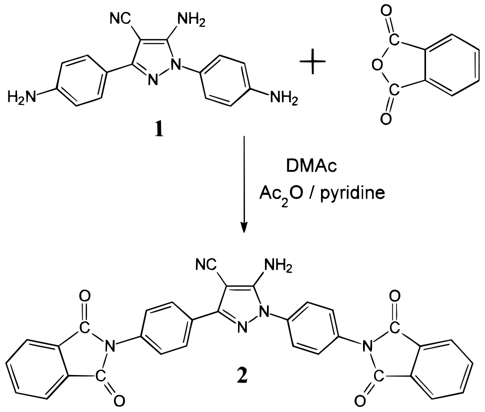
Scheme 1



imide), 1618, 1517 (aromatic), 1368 (C−N stretching), 1259 (C−O−C), 744 (C=O bending).

Results and Discussion

The diamine monomer, PYA, was prepared from 4-nitrobenzoyl chloride as previously reported.[13] The model reaction was conducted to investigate the reactivity of the amine group on the pyrazole ring and to obtain a model compound that can be used as a reference for structural and thermal characterization of corresponding polymers as shown in Scheme 1. PYA was reacted with monofunctional phthalic anhydride to produce di(amic acid), and then this intermediate was subsequently cyclodehydrated at room temperature with condensation reagent, acetic anhydride, and pyridine, to give the orange diimide model compound **2** with quantitative yield.

During the model reaction, the amino group on the pyrazole ring was not reacted with phthalic anhydride and the cyano group on the pyrazole ring was not affected. The chemical structure of the model compound was confirmed by IR and ^{1}H NMR spectra. The ^{1}H NMR spectrum of **2** shows a peak at 7.02 ppm corresponding to unreacted amine on the pyrazole ring, and the IR spectrum of **2** shows absorption bands at 1781, 1720, 1372, and 715 cm^{-1} corresponding to the C=O imide asymmetric and symmetric stretching, C−N imide stretching, and C=O imide bending, respectively, as well as absorption bands at 2212 cm^{-1} corresponding to CN stretching and 3438 and 3335 cm^{-1} corresponding to primary amine (−NH$_2$) stretching. The thermal behavior of the model compound was examined by TGA and DSC. The model compound showed no weight loss up to 390 °C in nitrogen and no thermal transition except melting at 402 °C. These results reveal remarkable stability of the amino and cyano groups attached to pyrazole rings, which is attributed to conjugation between the electron-donating amine and the electron-withdrawing cyano group through the pyrazole ring.

New pyrazole rings containing polyimides were prepared from PYA and commercially available aromatic dianhydrides, such as PMDA, BTDA, and ODPA, through ring-opening polyaddition and subsequent cyclodehydration as shown in Scheme 2.

First, the polyimides were prepared by a conventional thermal curing method (**3**, **4**, **5**). The ring-opening polyaddition in DMAc at room temperature yielded viscous poly(amic acid) solutions. The inherent viscosities of poly(amic acid)s were 0.87−1.36 dL/g (Table 1). They were cast on a glass plate and then preheated in vacuo at 80 °C for 12 h to give the films of the poly(amic acid)s. Thermal conversion to polyimides was carried out by successive heating of the films to 340 °C under a flow of N$_2$. Brownish, transparent, and fingernail creasable films were obtained. The polyimides prepared by thermal curing did not dissolve in any organic solvents except concentrated sulfuric acid, while corresponding polyamides previously reported were well dissolved in polar aprotic solvents.[13]

Scheme 2

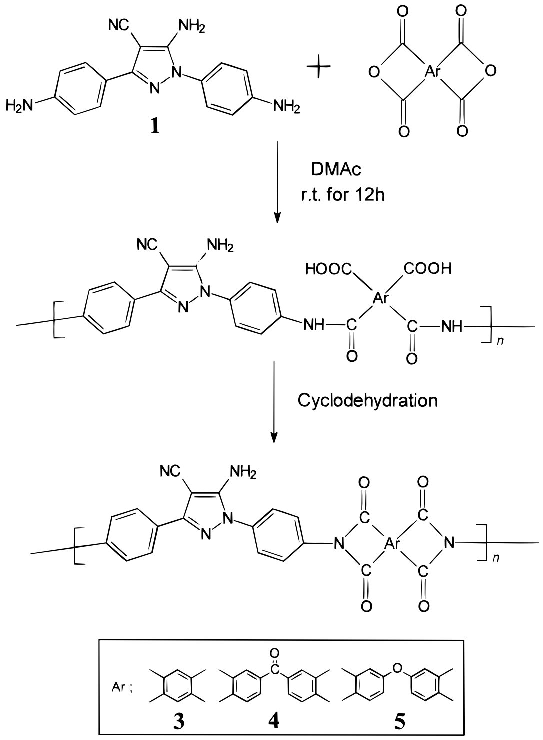


Table 1. Thermal Properties of the Pyrazole Ring Containing Polyimides

polymer	η_{inh}[a] (dL/g)	T_g[b] (°C)	T_d[c] in N_2 (°C)	T_d[c] in air (°C)	CTE[d] (ppm/°C)
3	1.36	411	518	511	8.61
4	1.18	405	523	511	28.1
5	0.87	322	517	504	47.2

[a] Inherent viscosity of corresponding poly(amic acid), 0.5 g/dL in DMAc at 30 °C. [b] Measured by DSC with a heating rate of 10 °C/min. [c] The 5% weight loss temperature. [d] Measured by TMA at temperature range from 50 to 250 °C.

The formation of polyimides was confirmed by FTIR spectroscopy. FTIR spectra of the model compound and polyimide **3** are seen in Figure 1, where they show similar patterns. FTIR spectra of the polymers show the absorption bands at 1780, 1720, 1370, and 720 cm^{-1} corresponding to characteristic imide bands. It was also confirmed that the amino and cyano groups on the pyrazole rings remained intact after thermal curing. They show absorption bands at 2210 cm^{-1} (CN stretching) and 3445 and 3350 cm^{-1} (−NH$_2$ stretching).

Chemical imidization was carried out in the case of polymerization of PYA and BTDA (**4′**), and solution imidization using NMP as a solvent and xylene as an azeotroping reagent was also carried out for polymerization of PYA and ODPA (**5′**). Precipitation occurred during imidization in the former case, and gelation occurred during imidization in the latter case. **4′** is soluble in DMF, DMSO, and NMP at elevated temperature, but **5′** is soluble in NMP containing LiCl. The

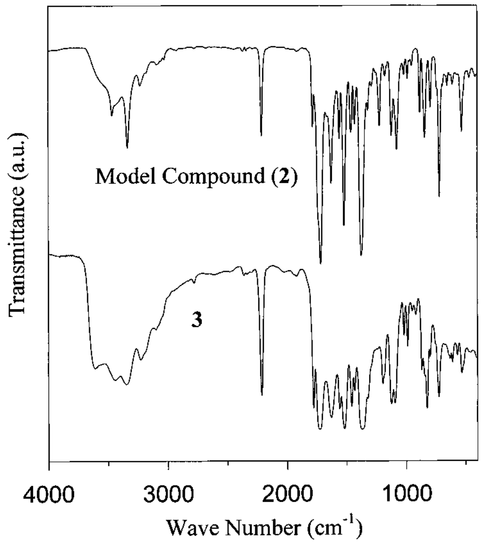


Figure 1. FTIR spectra of model compound (top) and **3** (bottom).

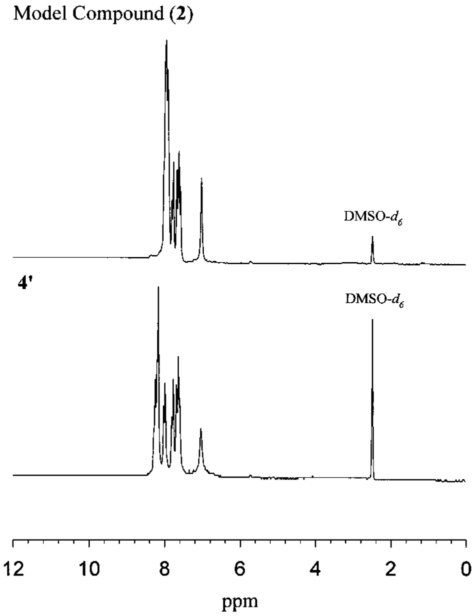


Figure 2. ^{1}H NMR spectra of model compound (top) and **4′** (bottom).

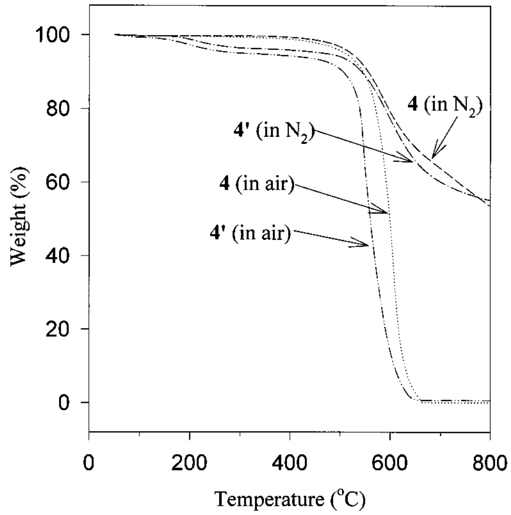


Figure 3. TGA curves of polyimide from BTDA and PYA (**4** and **4′**).

intrinsic viscosities of **4′** and **5′** were 1.86 and 2.12 dL/g, respectively. The polyimide **4′** gave pale-yellowish, transparent, and tough films on casting. The chemical structures of **4′** and **5′** were confirmed with FTIR and ^{1}H NMR spectroscopy. The FTIR spectra of **4′** and **5′** were almost the same as the FTIR spectra of the corresponding polyimide prepared by the thermal imidization method. The ^{1}H NMR spectrum of **4′** shows the peak at 7.04 ppm corresponding to the unreacted amine group on the pyrazole ring (Figure 2). In TGA measurement, a sudden small weight loss of **4′** and **5′** occurred around 220 and 290 °C, respectively, because they were not fully imidized. The degree of imidization of the polymers was determined with FTIR by comparing the intensity of the absorption band at 1370 cm^{-1} (imide C$-$N stretching), assuming 100% imidization of the polyimide obtained from conventional thermal imidization. The 1500-cm^{-1} (aromatic C=C stretching) band was used as an internal reference to normalize the intensity of the imide absorption band.[15] The degrees of imidization are 93.8 and 96.4% for **4′** and **5′**, respectively.

The thermal behavior of these polyimides was evaluated by TGA, DSC, and TMA. The Thermal properties are summarized in Table 1. The 5% weight loss temperatures are in the range of 517−523 °C in nitrogen and 504−511 °C in air. The TGA curves of **4** and **4′** are shown in Figure 3. Surprisingly, the amino and cyano groups on the pyrazole ring were stable up to 500 °C even in air. In the case of the polyamides, the amino group on the pyrazole ring was destroyed in air at 300 °C.[13] Generally, aromatic polyimides have a tendency to form charge-transfer complexes and strong interchain packing. The chains interact with each other via a charge-transfer or electronic polarization mechanism.[16] The amino and cyano functional groups may participate in the interactions of polyimide chains and become less vulnerable to thermooxidative reactions. The char yield at 800 °C in nitrogen was 54−66%, depending on the anhydride used.

All of the polyimides showed high glass transition temperatures (T_g's) and low thermal expansion coefficients (CTEs). The T_g's of these polymers are 411, 405, and 322 °C for **3**, **4**, and **5**, respectively, and the CTEs are 8.61, 28.1, and 47.2 ppm/°C for **3**, **4**, and **5**, respectively. The differences in the T_g and CTE values were caused by the differences in chain rigidity due to the different structures of the dianhydrides employed. The tensile strength of **5** was 1292 kg/cm^2 (126.6 MPa), which is comparable to that of Kapton (120 MPa).

In summary, the heterocyclic diamine monomer with amino and cyano functional groups, 1,3-bis(*p*-aminophenyl)-4-cyano-5-aminopyrazole, was converted to new high-molecular-weight polyimides with PMDA, BTDA, and ODPA. The synthesized polymers had high glass transition temperatures and high thermal stability. Surprisingly, there was no thermal transition such as degradation or cross-linking up to 500 °C despite the pendent amino and cyano groups.

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Supporting Information Available: Characterization method, characterization data for **1**, FTIR spectra of polymers

4, **4′**, **5** and **5′**, and wide-angle X-ray diffraction patterns of polymers **3**, **4′**, and **5′** (4 pages). See any current masthead page for ordering information and Internet access instructions.

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