New soluble polyamides and polyimides containing polar functional groups: pendent pyrazole rings with amino and cyano groups

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ABSTRACT
A series of aromatic polyamides and polyimides containing pendent pyrazole rings with amino and cyano groups were prepared from a new monomer, 1-(2,4-diaminophenyl)-3-phenyl-4-cyano-5-aminopyrazole, which was prepared from (chloromethylene)propanedinitrile and 2,4-dinitrophenyl hydrazine with two steps. In addition, model compounds were synthesized and characterized by elemental analyses, Fourier transform infrared (FTIR), and nuclear magnetic resonance (NMR) spectroscopy. The amino and cyano groups on the pyrazole ring were not affected during the polymerization process. The synthesized polymers, with intrinsic viscosities of 0.33–0.53 dL/g, were soluble in various organic solvents. They showed no Tg values before degradation, and the 5% weight loss temperature of the polyamides and the polyimides occurred at approximately 420 and 470 ºC, respectively. They also underwent no thermal transitions, such as degradation or crosslinking, up to 440 ºC in spite of the presence of pendent amino and cyano groups.

Introduction
Thermally stable organic polymers have been the subjects of numerous studies in an effort to extend the range of applications of organic materials in harsh conditions. Among the thermally stable organic polymers, the outstanding properties of aromatic polyamides and polyimides, such as their excellent thermooxidative and thermomechanical stability levels as well as their superior chemical resistance have allowed them to be used in many applications.[1,2]

In general, thermally stable organic polymers are insoluble and intractable or only processable under extreme conditions due to the presence of strong enthalpic interactions and the minimal increase in the conformational entropy associated with their dissolution and melting due to their rigid-rod-like characteristics.[3] Given these processing problems, a great deal of research on aromatic polyamides and polyimides has been conducted to increase their processability with minimal effects on the thermal stability and to improve their specific properties over the last few decades.[4–8] For example, polyamides and polyimides containing trifluoromethyl groups show a high modulus, a low thermal expansion coefficient as well as good solubility,[9–21] and the incorporation of heterocyclic units into polyimide chains increases the glass transition temperature and thermal stability.[22–27] Also, soluble polyamides and polyimides containing crosslinkable pendent groups represent useful methods in many applications.[28,29]

Introducing stable functional groups as substituents is interesting because they can be used to impart special functionalities to polymers and to improve their processability. Previously, thermally stable and soluble polypyrazoles containing amino and cyano groups were synthesized from monomers containing the 1-chloro-2,2-dicyanovinyl moiety with dihydrazine monomers by means of a vinylic nucleophilic substitution reaction.[30,31] We also synthesized polyamides and polyimides containing pyrazole rings with amino and cyano groups in the polymer main chain.[32,33] The polymers showed high thermal stability, and the amino and cyano groups on the pyrazole ring were inert to acid chloride and acid anhydride. However, the pyrazole ring-containing polyimides showed limited solubility, though the pyrazole ring-containing polyimides showed higher thermal stability than the corresponding polyamides.

The present work deals with the synthesis and characterization of new, wholly aromatic polyamides and polyimides which have pendent pyrazole rings with amino and cyano groups. The incorporation of bulky pyrazole rings...
and the introduction of polar functional groups as pendant groups into the polymer main chain can be expected to enhance the degree of solubility in organic solvents while maintaining their high thermal stability.

**Experimental**

**Materials**

(Chloromethylene)propanedinitrile was prepared following a previously reported procedure.[34] 2,4-Dinitrophenyl hydrazine, purchased from Aldrich, was used as received. 1,4-Diazabicyclo[2,2,2]octane (DABCO) was sublimed in vacuo at 75.1 °C. Terephthaloyl chloride (TPC) and isophthaloyl chloride (IPC) were recrystallized from acetic anhydride and then dried in vacuo at 150 °C for 24 h. 1,3,5-Dimethylacetamide (DMAC), N,N-dimethylformamide (DMF) and N-methyl-pyrrolidinone (NMP) were stirred in the presence of P2O5 overnight and then distilled under reduced pressure. Chlorobenzene was stirred in the presence of P2O5 overnight and then distilled under nitrogen. Other commercially available reagent grade chemicals were used without further purification.

**General measurements**

The Fourier transform infrared (FTIR) spectra of the compounds were obtained with a Bruker EQUINOX-55 spectrophotometer using KBr pellets or film. The 1H NMR and 13C NMR spectra of the synthesized compounds were recorded on Bruker Fourier Transform AM 300 (300 MHz for 1H and 75.1 MHz for 13C) spectrometers. The chemical shift of nuclear magnetic resonance (NMR) was reported in parts per million (ppm) using tetramethylsilane as an internal reference. Splitting patterns were designated as s (singlet), d (doublet), t (triplet), dd (doublets of a doublet), m (multiplet), and br (broadened). Elemental analyses were carried out with a FISONS EA 1108 analyzer. The inherent viscosity data were obtained with a Cannon-Ubbelohde viscometer at 30 °C. Differential scanning calorimetry (DSC) and a thermogravimetric analysis (TGA) were performed on a TA 2200 thermal analyzer system. The melting points (m.p.) of the synthesized compounds and the T_g values of the polymers were obtained with the DSC instrument at a heating rate of 10 °C/min in N2. TGA measurements were taken at a heating rate of 10 °C/min in N2 or air.

**Monomer synthesis**

1-(2,4-Dinitrophenyl)-3-phenyl-4-cyano-5-aminopyrazole (1)

A 250 mL round-bottomed flask was charged with 2,4-nitrophenyl hydrazine (7.21 g, 36.4 mmol), DABCO (4.09 g, 36.4 mmol), and 50 mL of NMP. A solution of (chloromethylene)-propanedinitrile (6.87 g, 36.4 mmol) in 60 mL of NMP was added slowly to this solution. The reaction mixture was stirred under N2 at 70 °C for 12 h, cooled to room temperature, and then poured into water to precipitate. This precipitation was filtered, washed with cold water and methanol repeatedly, and then dried in vacuo (11.20 g, 87.8% yield); m.p. 253–256 °C. FTIR (KBr, cm⁻¹): 3430, 3320, 3220 (–NH₂); 3080 (aromatic C–H); 2219 (–CN); 1648, 1610, 1500 (aromatic); 1539, 1346 (NO₂). 1H NMR (DMSO-d₆, ppm): 8.92 (d, 1H, J = 2.07 Hz); 8.68 (dd, 1H, J = 8.73 Hz, J = 2.17 Hz); 8.14 (d, 1H, J = 8.77 Hz); 7.82–776 (m, 2H); 7.51–7.42 (m, 3H); 7.33 (s, 2H, –NH₂ on the pyrazole ring). 13C NMR (DMSO-d₆, ppm): 154.62, 152.14, 146.84, 145.02, 134.65, 130.47, 130.41, 129.64, 128.92, 128.66, 126.06, 121.26, 115.03, 71.40. Elemental Analysis for C₁₆H₁₄N₆O₄ (MW = 350.29): C, 54.9%; H, 2.9%; N, 24.0% (Calculated); C, 54.8%; H, 3.0%; N, 23.9% (Found).

1-(2,4-Diaminophenyl)-3-phenyl-4-cyano-5-aminopyrazole (2)

A slurry of 1 (10.50 g, 30.0 mmol), SnCl₂ (47 g, 248 mmol), and 180 mL of 95% ethanol was stirred while 80 mL of concentrated HCl was added slowly. After the addition of HCl was over, the mixture was refluxed for 12 h. Excess ethanol was evaporated and the remaining solution was poured into 300 mL of ice water. The solution was basified with a 10% NaOH solution and the precipitate was filtered off, washed with hot water and cold methanol, and then recrystallized from acetone / H₂O (v/v = 3:1) to give deep yellow product (7.49 g, 86.0% yield): m.p. 194–196 °C. FTIR (KBr, cm⁻¹): 3430, 3320, 3220 (–NH₂); 3080 (aromatic C–H); 2219 (–CN); 1648, 1610, 1500 (aromatic); 1539, 1346 (NO₂). 1H NMR (DMSO-d₆, ppm): 7.85–7.76 (m, 2H); 7.51–7.36 (m, 3H); 6.72 (d, 1H, J = 8.75 Hz); 6.22 (s, 2H, –NH₂ on the pyrazole ring); 6.06 (d, 1H, J = 2.03 Hz); 5.95 (dd, 1H, J = 8.81 Hz, J = 2.01 Hz); 5.09 (s, 2H), 4.66 (s, 2H, –NH₂). 13C NMR (DMSO-d₆, ppm): 153.69, 150.38, 149.73, 145.14, 131.80, 128.73, 128.71, 128.30, 125.87, 116.19, 111.28, 103.80, 100.20, 95.89. Elemental Analysis for C₁₆H₁₄N₆ (MW = 290.32): C, 66.2%; H, 5.0%; N, 28.8% (Calculated); C, 66.2%; H, 5.0%; N, 28.8% (Found).

**Model reactions**

**Model compound of the polyamide (3)**

A 25 mL round-bottomed flask was charged with 2 (0.361 g, 1.24 mmol), benzoil chloride (0.349 g, 2.48 mmol), and 7 mL of DMAC. The mixture was stirred under N₂ at 0 °C for 3 h. To this solution, pyridine (0.272 g, 2.48 mmol) as an acid acceptor was added. After the addition of pyridine, the solution was stirred at room temperature for 10 h and poured into water to precipitate a colorless solid that was filtered, washed with hot water and methanol repeatedly,
and dried in vacuo at 70 °C (0.610 g, 98.7% yield): m.p. 270–272 °C. FTIR (KBr, cm⁻¹): 3343, 3221, 3178 (NH₃ on the pyrazole ring); 3309 (NH₂ of amide); 3062 (aromatic C–H); 2215 (CN); 1669 (C=O of amide); 1605, 1561, 1513 (aromatic). ¹H NMR (DMSO-d₆, ppm): 10.56 (s, 1H), 10.00 (s, 1H, –C(=O)–NH–); 8.57 (d, 1H, J = 2.28 Hz); 8.04–8.00 (m, 2H); 7.85–7.75 (m, 5H); 7.60–7.35 (m, 10H); 6.72 (s, 2H, –NH₂ on the pyrazole ring). ¹³C NMR (DMSO-d₆, ppm): 165.78, 165.07, 151.76, 151.75, 131.08, 129.11, 128.72, 128.37, 127.32, 127.29, 126.98, 124.56, 117.15, 116.60, 115.58, 70.80. Elemental Analysis for C₃₀H₂₂N₆O₂ (MW = 498.54): C, 72.3%; H, 4.4%; N, 16.9% (Calculated); C, 72.1%; H, 4.5%; N, 17.0% (Found).

Model compound of polyimide (4)

A 25 mL round-bottomed flask was charged with 2 (0.341 g, 1.17 mmol), phthalic anhydride (0.347 g, 2.34 mmol), and 7 mL of NMP. The temperature was increased to 190 °C slowly and the reaction mixture was stirred for 12 h at this temperature. Chlorobenzene was periodically removed from a Dean-Stark trap and replaced with dry chlorobenzene to ensure cyclodehydration. The solution was poured into water to precipitate a deep yellow solid that was filtered, washed with hot water and methanol repeatedly and dried in vacuo at 70 °C (0.612 g, 95.0% yield): m.p. 360–362 °C. FTIR (KBr, cm⁻¹): 3400–3150 (broad, NH₂ on the pyrazole ring); 3060 (aromatic C–H); 2227 (CN); 1781 (C=O of imide); 1635, 1512 (aromatic); 1370 (C–N bending); 723 (C=O bending). ¹H NMR (DMSO-d₆, ppm): 8.70 (br, 2H, aromatic of the BTDA moiety); 7.94 (br, 1H), 7.86 (br, 2H, aromatic attached amide linkage); 7.50–7.20 (br, 3H, aromatic of pendent phenyl); 6.60 (s, 2H, –NH₂ on the pyrazole ring). ¹³C NMR (DMSO-d₆, ppm): 165.00, 164.52 (–C(=O)–NH–) ppm: 107.4, 10.66 (1H), 10.18, 10.14 (1H, –NH₂ of amide); 8.53 (t, 1H), 8.21 (s, 1H), 8.16 (d, 1H); 8.11–7.75 (m, 5H), 7.60–7.40 (m, 4H), 6.71 (s, 2H, –NH₂ on the pyrazole ring). ¹¹B NMR (DMSO-d₆, ppm): 150.59, 144.29, 143.04, 139.78, 134.95, 134.80, 134.62, 133.99, 131.07, 129.00, 128.62, 127.19, 126.12, 125.84, 125.30, 117.64, 117.28, 115.63, 70.73 (C–N).
Results and discussion

A diamine monomer containing a pyrazole ring with amino and cyano functional groups was prepared according to the reaction sequence of Scheme 1. The formation of the pyrazole ring was done by reacting (chloromethylene)propanedinitrile with 1,4-dinitophenyl hydrazine in the presence of DABCO as an acid acceptor. In the synthesis of dinitro compound 1, only one product was obtained with a high yield. Dinitro compound 1 was reduced with SnCl₂ and HCl to give the corresponding diamine monomer 2. During this reduction process, the amino and the cyano groups on the pyrazole ring were not affected, and 2 was obtained with a high yield. The overall yield of the two steps was 76%.

The structure of the diamine monomer containing pyrazole ring (2) was confirmed by spectroscopic data, and the FTIR and ¹H NMR spectra of 1 and 2 are shown in Figures 1 and 2, respectively. The FTIR spectrum of 2 showed absorption bands at 3425 and 3341 cm⁻¹ corresponding to primary amines, 3216 cm⁻¹ for the hydrogen bonding characteristics of the primary amines, and 2208 cm⁻¹ for CN stretching. The ¹H NMR spectrum of 2 showed values of 5.09 and 4.66 ppm corresponding to four protons of the two primary amines on the phenyl ring, a value of 6.22 ppm corresponding to two protons of the primary amine on the pyrazole ring, and values of 7.85–5.95 ppm corresponding to the eight protons of the phenyl rings. All 14 carbon peaks were detected in the ¹³C NMR spectrum, and the elemental analysis results were in good agreement with the calculated values.

Model reactions were conducted to investigate the amine reactivity on the pyrazole ring and to obtain model compounds that can be used as references for the structural and thermal characterization of the corresponding polymers. 2 was reacted with benzyol chloride and phthalic anhydride to give the model compounds 3 and 4, respectively, as shown in Scheme 2.
analyses of the model compounds were in good agreement with the calculated values.

The thermal behavior of the model compounds was also examined by TGA and DSC. Model compounds 3 and 4 showed no weight loss up to 350 °C in nitrogen and no thermal transition except for melting transitions at 271 and 360 °C, respectively.

The new polyamides and polyimides containing a pyrazole ring with amino and cyano groups were prepared from 2 with commercially available aromatic dicarboxylic acid chlorides and dianhydrides, respectively, in the same manner used for the model reaction.

The polyamides were synthesized from the diamine monomer 2 with TPC and IPC in DMAc at room temperature for 12 h, as shown in Scheme 3. The polymers formed colorless flakes upon pouring of the reaction mixture into water which was being stirred. In all cases, the polymers were obtained with quantitative yields. The intrinsic viscosities of PA1 and PA2 were 0.53 and 0.48 dL/g, respectively. The polymers gave transparent and flexible films upon casting.

The formation of polyamides was confirmed by spectroscopic data, and the FTIR and 1H NMR spectra of the model compound 3 and PA1 are shown in Figures 3 and 4, respectively. The FTIR spectra of the polyamides showed characteristic amide absorption bands at 3320 and 1670 cm⁻¹. The 1H NMR spectra of the polyamides showed two peaks corresponding to amide protons and carbons. Moreover, it was confirmed that the amino and the cyano groups on the pyrazole ring remained intact during the polymerization process. The FTIR spectra
The intrinsic viscosities of PI₁ and PI₂ are 0.33 and 0.38 dL/g, respectively, and the resulting polymers gave somewhat brittle films upon casting. The relatively low molecular weight is presumably due to the steric hindrance of the pendent pyrazole ring during imidization. Because it is known that amic acid formation is reversible, effective and fast imidization is necessary to obtain polyimides with high molecular weights.[35,36]

The polyimides were synthesized from diamine monomer 2 with PMDA and BTDA, respectively, by a solution imidization method, as shown in Scheme 4. Polymerization was carried out by reacting stoichiometric amounts of diamine monomer 2 with aromatic dianhydride at a concentration of 10 w/v % solids in NMP. The ring-opening polyaddition at room temperature for 12 h yielded a poly(amic acid) solution. After dilution of the solution to 5 w/v %, subsequent cyclodehydration by heating at 190 °C for 12 h gave fully imidized polyimides with a quantitative yield. The intrinsic viscosities of PI₁ and PI₂ are 0.33 and 0.38 dL/g, respectively, and the resulting polymers gave somewhat brittle films upon casting. The relatively low molecular weight is presumably due to the steric hindrance of the pendent pyrazole ring during imidization. Because it is known that amic acid formation is reversible, effective and fast imidization is necessary to obtain polyimides with high molecular weights.[35,36]

The formation of polyimides and their chemical structure were confirmed by FTIR and ¹H NMR spectroscopy. The
FTIR spectra of model compound 4 and PI1 are presented in Figure 5, showing similar patterns. The FTIR spectra of the polymers showed absorption bands at around 1780, 1725, 1360, 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 solution imidization at 190 °C. They showed absorption bands at 2210 cm\(^{-1}\) (CN stretching) and 3400–3150 cm\(^{-1}\) (–NH\(_2\) stretching). The \(^1\)H NMR spectra obtained at 100 °C showed a peak at approximately 6.6 ppm, corresponding to the unreacted amine group on the pyrazole ring, as shown in Figure 6.

The solubility of the synthesized polymers was tested in various solvents. The polyamides were quite soluble in tetrahydrofuran, chlorobenzene, and polar aprotic solvents, including NMP, DMAC, DMF, and DMSO at room temperature. They were slightly soluble in acetone and chloroform. Although the polyimides showed lower solubility than the polyamides, they were soluble in NMP and DMSO, whereas polyimides containing pyrazole rings in the main chain as previously reported did not dissolve in any organic solvent.[33] The enhanced solubility is presumably due to the bulky pendant pyrazole rings containing polar functional groups and their asymmetric structure.

The thermal properties of the resulting polymers were investigated by TGA and DSC analyses. The physical properties of the polymers are summarized in Table 1, and the TGA curves of the polymers are shown in Figure 7.

The 5% weight loss temperatures of PA1, PA2, PI1, and PI2 were 423, 418, 465, and 481 °C in nitrogen and 409, 407, 465, and 464 °C in air, respectively. The TGA results revealed that the polyimides have higher thermal stability levels than the polyamides. For the polyamides, the initial decomposition started at 300 °C, presumably due to the pendant pyrazole ring containing amino and cyano groups.[37] On the other hand, the polyimides were stable

**Table 1. Thermal properties of the synthesized polymers.**

| Polymer | \(\eta_{inh}\) (dL/g) | \(T_{\text{d5}}\) (°C) | Char yield at 800 °C in N\(_2\) (%) | Char yield at 800 °C in air (%) |
|---------|-----------------|-----------------|-------------------------------|------------------------------|
| PA1     | 0.33 \(^{b}\)   | 423             | 409                           | 57                           |
| PA2     | 0.48 \(^{b}\)   | 418             | 407                           | 58                           |
| PI1     | 0.33 \(^{c}\)   | 465             | 465                           | 66                           |
| PI2     | 0.38 \(^{c}\)   | 481             | 464                           | 60                           |

\(\text{Inherent viscosity, measured at 30 °C with a concentration of 0.5 g/dL.}^{a}\)

\(\text{In DMAC.}^{b}\)

\(\text{In NMP.}^{c}\)

\(\text{Measured by TGA with a heating rate of 10 °C/min.}^{d}\)
up to 400 °C in both N₂ and air. Generally, aromatic polyamides have a tendency to form a charge-transfer complex and strong interchain packing. These chains interact with each other via a charge-transfer or electronic polarization mechanism.[35,36] The amino and cyano functional groups may participate in the interactions of polyimide chains and become less vulnerable to thermooxidative reactions. None of the polymers detected the glass transition temperature (T_g) with the DSC until they degraded.

Conclusion

Wholly aromatic polyamides and polyimides containing amino and cyano functional groups in the pendent pyrazole ring were newly synthesized from a new diamine monomer. The synthesized polymers, which have a moderate molecular weight, were soluble in organic solvents and have high thermal stability. They also showed no thermal transitions, such as degradation or crosslinking, up to 440 °C in spite of the presence of pendent amino and cyano groups.

Disclosure statement

No potential conflict of interest was reported by the authors.

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