Syntheses and Properties of Novel Polyimides Derived From 2-(4-Aminophenyl)-5-aminopyrimidine

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ABSTRACT: 2-(4-Aminophenyl)-5-aminopyrimidine **(4)** is synthesized via a condensation reaction of vinamidium salts and amidine chloride salts, followed by hydrazine palladium catalyzed reduction. A series of novel homo- and copolyimides containing pyrimidine unit are prepared from the diamine and 1,4-phenylenediamine (PDA) with pyromellitic dianhydride (PMDA) or 3,3′,4,4′-biphenyl tertracarboxylic dianhydride (BPDA) via a conventional two-step thermal imidization method. The poly(amic acid) precursors had inherent viscosities of 0.97–4.38 dL/g ($c = 0.5$ g/dL, in DMAc, 30°C) and all of them could be cast and thermally converted into flexible and tough polyimide films. All of the polyimides showed excellent thermal stability and mechanical properties. The glass transition temperatures of the resulting polyimides are in the range of 307–434°C and the 10% weight loss temperature is in the range of 556–609°C under air. The polyimide films possess strength at break in the range of 185–271 MPa, elongations at break in the range of 6.8–51%, and tensile modulus in the range of 3.5–6.46 GPa. The polymer films are insoluble in common organic solvents, exhibiting high chemical resistance. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 5871–5876, 2006

Key words: heteroaromatic polyimides; pyrimidine; thermal stability; mechanical property

INTRODUCTION

The quest for high temperature polymers that perform at 200°C or higher temperature began in the late 1950s to meet the demands primarily of the aerospace and electronics industries. Since then, many families of high temperature polymers have been reported.[1] The thermally stable polymers require (a) aromatic rings with high symmetry, (b) linkages bearing a large interaction between polymer chains, and (c) double strands (ladder-type structure) in their main chains.[2] Polyimides synthesized from aromatic dianhydrides and diamines with symmetric and rigid structure show outstanding thermal stability, along with high mechanical properties, and good chemical resistance and electrical properties. Therefore, they are used in widespread materials, such as coatings, films, fibers, and matrix resins for advanced composites, etc.[3–6]

The choice of heterocyclic aromatic structure in the main chain of the polymers results in imparting certain properties to the polymer.[7,8] In recent years, some researchers reported a series of novel polyimides based on heterocyclic aromatic monomers containing pyridine,[9–13] furan,[14,15] triazine,[8,16,17] pyrimidine,[18–24] pathalazinone,[25] or benzoxazole.[26] All of the polyimides had good thermal stability, for which the heterocyclic aromatic unit should have main contributions. Among these works, Russian researchers reported a series of polyimide fibers based on heterocyclic aromatic diamine holding pyrimidine ring, 2,5-bis(4-aminophenyl) pyrimidine (2,5-PRM). The pyrimidine-based polyimide fibers exhibited strength and modulus as high as 285 MPa and 6.43 GPa, respectively. These values are comparable with that of polybenzoxazole (PBO, Zylon).[18–23] The excellent properties of the polyimides were attributed to the introduction of heterocyclic aromatic diamines and the rigid linear symmetric structure of the polymer. It is shown that introduction of pyrimidine cycles into polyimides increases the strength and flexibility of fibers by improving their morphology, and enhances the thermal stability of the polyimides.

In this work, 2-(4-aminophenyl)-5-aminopyrimidine **(4)**, a new heterocyclic aromatic diamine monomer, had been synthesized successfully, and a series of novel homo- and copolyimides had been prepared by polycondensation with aromatic teracarboxylic dianhydrides PMDA and BPDA. The thermal and mechanical properties of these polyimides were also investigated.

EXPERIMENTAL

Materials

Pyromellitic dianhydride (PMDA; Beijing Chemical Reagents Corp., China), 3,3′,4,4′-biphenyl tertracarboxylic dianhydride (BPDA, prepared in our laboratory), and 1,4-phenylenediamine (PDA, Shanghai Chemical Reagents Corp.3, China) were purified by sublimation just before use. N,N-dimethylacetamide (DMAc, Tianjing Chemical Reagents Corp., China) was dried over CaH_2 and then fractionally distilled under reduced pressure and stored over 4-Å molecular sieves. 1,3-Bis(piperidinyl)trimethinium tetrafluoroborate was prepared from piperidine and 1,1,3,3-tetramethoxypropane (4MP) in our laboratory. p-Nitrobenzonitrile (Acros) and other reagents and solvents (from various commercial sources) were used as received.

Syntheses of diamine containing pyrimidine unit

Synthesis of 2-(4-nitrophenyl)-5-nitropyrimidine (3)

Triethylamine (50 mL) was added dropwise to a solution of p-nitrobenamidine chloride salt 1 (40.44 g, 0.2 mol) and 2-nitro-1,3-bis(piperidyl)trimethinium tetrafluoroborate 2 (68.71 g, 0.2 mol) in 67 mL of acetonitrile at room temperature. After the mixture was stirred at room temperature for 3 h, the solid was filtered. The crude product was washed with water and ethanol, dried under reduced pressure to give 42.55 g (86.48%) of 3 as pale gray crystal solid. mp 250–252°C. ^1H NMR (300 MHz, DMSO-d_6, δ): 9.64 (s, 2H), 8.63 (d, 2H, J = 8.7 Hz), 8.36 (d, 2H, J = 8.7 Hz) ppm. ^{13}C NMR (75 MHz, DMSO-d_6, δ): 165.43, 154.57, 150.64, 142.54, 141.70, 131.07, 125.10 ppm. IR (KBr pellet): 3055, 1588, 1565, 1525, 1430, 1342, 853 cm^{-1}. Elemental Anal. Calcd for $C_{10}H_6N_4O_4$: C, 48.79; H, 2.46; N, 22.76. Found: C, 48.88; H, 2.56; N, 22.26.

Synthesis of 2-(4-aminophenyl)-5-aminopyrimidine (4)

Hydrazine hydrate (56 mL) (≥80%) was added to a refluxing suspension of 12.3 g (0.05 mol) of 3 and 4.0 g of 10% palladium–charcoal catalyst (Pd/C) in 900 mL of THF under nitrogen atmosphere. After the addition, the reaction proceeded for another 5 h under refluxing and then was cooled to room temperature. The Pd/C was filtered and the mother liquid was evaporated to dryness in vacuum. The residue was washed with water and cold ethanol, and dried under reduced pressure to yield 8.59 g (92.2%) of light yellow crystal solid. mp 210–211°C. MS (EI): m/z = 187.0 (M$^+$). ^1H NMR (300 MHz, DMSO-d_6, δ): 8.02 (s, 2H), 7.80 (d, 2H, J = 8.7 Hz), 6.48 (d, 2H, J = 8.7 Hz), 5.28 (s, 2H), 5.23 (s, 2H) ppm. ^{13}C NMR (75 MHz, DMSO-d_6, δ): 153.60, 149.39, 142.06, 139.79, 127.32, 125.36, 113.41 ppm. FTIR (KBr pellet): 3438, 3331, 3213, 1633, 1616, 1540, 1520, 850, 789 cm^{-1}. Elemental Anal. Calcd for $C_{10}H_{10}N_4$: C, 64.49; H, 5.41; N, 30.09. Found: C, 64.18; H, 5.32; N, 29.13.

General procedure for the syntheses of polymers

The polyimides were synthesized from the diamine 4 with PMDA or BPDA via a conventional two-step thermal imidization method. The synthesis of PI-3 is described as an example of the general synthetic route for the polyimides. To a solution of 0.3724 g (2 mmol) of 4 and 0.2162 g (2 mmol) of PDA in 15 mL of CaH_2-dried DMAc under nitrogen atmosphere, 0.8728 g (4 mmol) of PMDA was added in one portion. The mixture was stirred at ambient temperature for about 24 h under nitrogen atmosphere to afford a highly viscous poly(amic acid) solution. The inherent viscosity of the resulting poly(amic acid) was 2.9 dL/g, as measured in DMAc at a concentration of 0.5 g/dL at 30°C.

The proper quantity of the poly(amic acid) solution was cast on a glass plate and placed in an oven maintaining at 60°C overnight to remove most of the solvent. The semidried poly(amic acid) film was converted into the polyimide film by sequential heating at 80°C for 1 h, and at 150, 200, 250, 300, 350, and 400°C each for 0.5 h under vacuum. The film was removed from the glass plates by soaking in hot water.

Measurements

^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) were taken on a Varian Unity spectrometer and with tetramethylsilane as an internal standard. Fourier transform infrared (FTIR) spectra were obtained with Bio-Rad Digilab Division FTS-80 FTIR spectrometer. Elemental analyses were measured with an elemental analyzer MOD-1106 (Italyd). MS spectra were taken by a Bruker BIFLEX mass spectrometer. The melting points of the prepared monomers were determined on an XT-4 melting point apparatus (Beijing Taike Apparatus Inc.) and were uncorrected. The inherent viscosities of the polymers were measured with an Ubbelohde viscometer at a concentration of 0.5 g/dL in DMAc at 30°C. Thermo gravimetric analysis (TGA) was done with a PerkinElmer TGA-2 at a heating rate of 10°C/min under air. Dynamic mechanical thermal analysis (DMTA) was performed on a dynamic mechanical analyzer (Rheometric Scientific Inc.) using film samples in tensile mode at a heating rate of 5°C/min and a frequency of 1 Hz. The wide-angle X-ray diffraction (WAXD) measurements were undertaken on a Rigaku max 2500 V PC X-ray diffractometer (Japan) with Cu Kα radiation (40 kV, 200 mA) with a scanning rate of 2°/min from 2° to 60°. The tensile measurements were car-
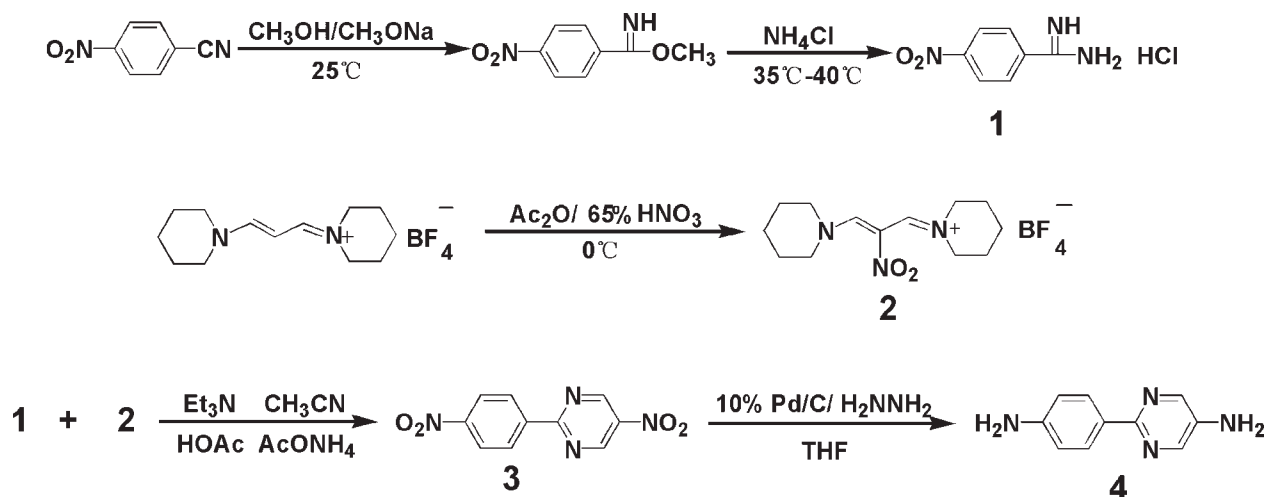
Scheme 1 The synthesis of the aromatic diamine **4**.

ried at room temperature under air using an Instron model 1122 at a drawing rate of 5 mm/min.

RESULTS AND DISCUSSION

Syntheses of diamine containing pyrimidine unit

The aromatic diamine **4** was synthesized by the reactions shown in Scheme 1. The compounds **1**[27] and **2**[28,29] were prepared according to the reported methods. Reaction of vinamidinium salts with amidine salts leads to a displacement of terminal amino groups to give pyrimidines, in the presence of base.[28,30–33] The nitro compounds were converted into the diamine **4** by the Pd-catalyzed hydrazine reduction. NMR, IR spectroscopy, elemental analysis, and MS spectrometry confirmed the structures of **3** and **4**. The molecular weight of **4** determined by mass spectrometry was 187.0, which agreed with the calculated ones (M$^+$). In the FTIR spectrum, **3** displayed the absorption bands representative of the nitro group at 1525 (asymmetric stretching) and 1342 cm^{-1} (symmetric stretching). After reduction, the aromatic primary amine absorption at 3438 and 3331 cm^{-1} were identified and the bands for nitro group disappeared. Both the dinitro and diamine compounds showed the Ar—H bending band on the 2,5-disubstituted pyrimidine rings around 850 cm^{-1}. The structures of **3** and **4** were also corroborated by high-resolution NMR spectra. The ^{1}H NMR demonstrated that the nitro groups were completely converted into amino groups by the high-field shift of the aromatic protons and by the signals at 5.28 and 5.23 ppm peculiar to amino protons. In the ^{13}C NMR spectra, up field shifts of the phenyl carbon resonance were observed in diamine **4** because of the resonance effect caused by the electron-donating amino group. Thus all the spectroscopic data obtained are in good agreement with the proposed chemical structures.

Syntheses and characterization of polymers

The novel polyimides were prepared by a two-stage method. The homopolyimides were prepared by the

### TABLE I
Thermal Properties of Polyimide Films

Code	PI	η^a_{inh} of PAA (dL/g)	T_β (°C)[b]	T_g (°C)[b]	Under air[c]	
					T_5 (°C)	T_{10} (°C)
PI-1	PMDA-PDA/**4** (0/100)	4.38	Ud[d]	422	552	580
PI-2	PMDA-PDA/**4** (25/75)	3.33	Ud[d]	427	537	566
PI-3	PMDA-PDA/**4** (50/50)	2.9	Ud[d]	434	500	548
PI-4	PMDA-PDA/**4** (75/25)	2.08	Ud[d]	420	540	572
PI-5	BPDA-PDA/**4** (0/100)	1.18	179	352	573	594
PI-6	BPDA-PDA/**4** (25/75)	1.13	182	318	587	608
PI-7	BPDA-PDA/**4** (50/50)	1	198	307	592	611
PI-8	BPDA-PDA/**4** (75/25)	0.97	194	309	589	607

[a] Inherent viscosity of poly(amic acid) measured with 0.5 g/dL in DMAc at 30°C.
[b] Obtained from DMTA at a heating rate of 5°C/min at 1 Hz.
[c] 5% and 10% weight loss in air obtained from TGA at a heating rate of 10°C/min.
[d] Undetected.
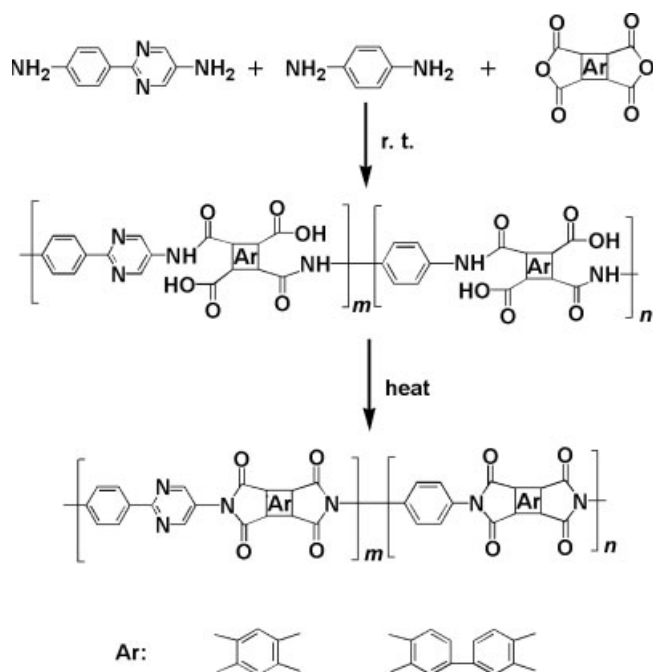
Scheme 2 The synthesis of polyimides (n/m, molar ratio).

polycondensation of **4** and PMDA (or BPDA). In the case of the copolymers, a mixture of diamines at a designated ratio with the added portion of PMDA or BPDA was used. The inherent viscosities of PAA precursors were in the range of 0.97–4.38 dL/g (c = 0.5 g/dL, in DMAc, 30°C). All of the PAA precursors could be cast into flexible and tough PAA films, which could be subsequently converted into tough polyimide films by extended heating at elevated temperature. The inherent viscosities of the PAA precursors are summarized in Table I, along with the thermal properties of the PI films.

The synthesis of the polyimides is shown in Scheme 2. The complete imidization was confirmed by FTIR spectroscopy, where the characteristic bands of the imide carbonyl were at around 1772–1778 cm^{-1} (asym C=O, stretching), 1707–1713 cm^{-1} (sym C=O, stretching), 1342–1350 cm^{-1} (C—N, stretching), 1071–1082 cm^{-1} and 719–735 cm^{-1} (imide ring formation). The disappearance of amide and carbonyl bands at 1700–1650 cm^{-1} and 3500–2800 cm^{-1} indicate a virtually complete conversion of PAA precursors into the PIs. The colors of the PMDA-based polyimide films were deep yellow, whereas the polyimide films based on BPDA were light yellow.
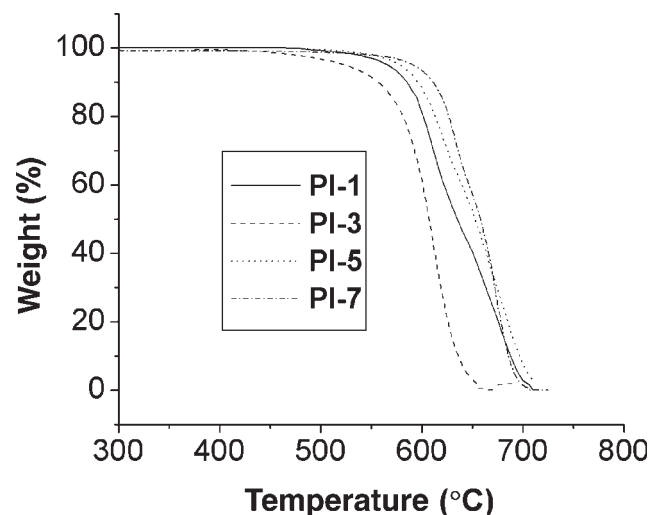
Solubility of polyimides

The solubility behavior of the polyimides generally depends on the structure of macromolecules and intermolecular interactions and their chain packing density, which are affected by the rigidity, symmetry, and regularity of the molecular backbone. All of the films are almost insoluble in such common organic solvents as chloroform, methanol, acetone, DMF, DMAc, NMP, DMSO, p-chlorophenol, m-cresol, and acetic acid, exhibiting high chemical resistance. This nature can be explained by the strong interaction between polymer chains that are highly stacked on each other because of their planar structure and rigid-rod chain. All of the PI films based on BPDA can dissolve in concentrated sulfuric acid at room temperature. In the case of PI films prepared from PMDA, after being immersed in the H$_2$SO$_4$ at room temperature for 3 days, the films of PI-1 and PI-2 dissolved completely, while PI-3 was broken into small pieces and PI-4 was just softened. The difference in solubility behavior of the copolyimides may be caused by the concentration of the pyrimidine units in the backbone. The basicity of the pyrimidine makes it easier to be dissolved in the sulfuric acid.
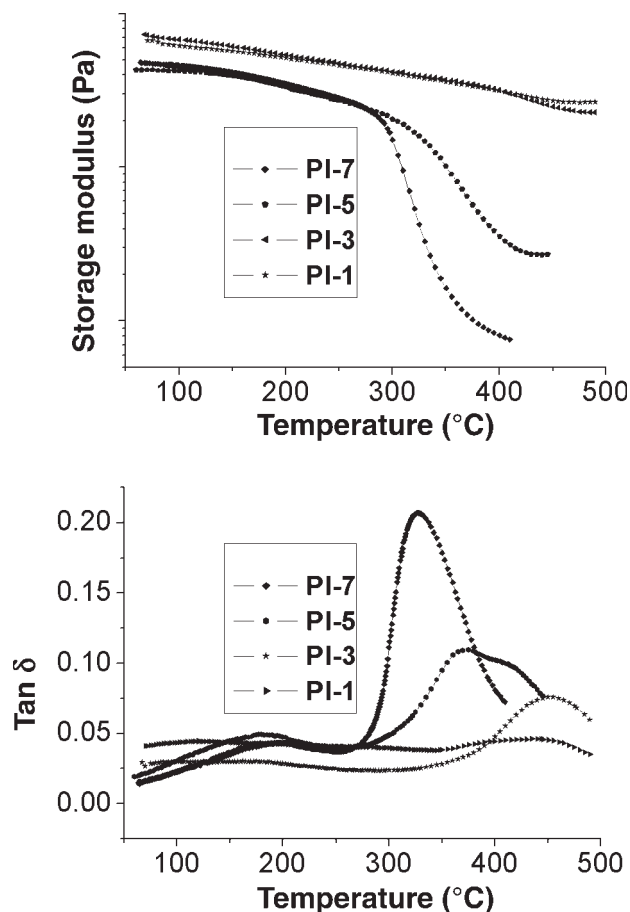
Thermal properties of polyimides

The thermal stability of the polyimide films is estimated by the 5% ($T_{5\%}$) and 10% ($T_{10\%}$) weight loss temperature measured by a thermal gravimetric analyzer (TGA) at a heating rate of 10°C/min under air atmosphere (Fig. 1). The polyimides have a $T_{10\%}$ in range of 548–611°C under air, while some of them show $T_{5\%}$ above 590°C (Table I), showing high thermooxidative stability. But $T_{5\%}$ and $T_{10\%}$ do not change much with the increase of the molar ratio of rigid, rod-like PDA, confirming that the pyrimidine units may have critical influence on the thermal stability of the polymer.

The glass transition temperature (T_g) is determined under air using dynamic mechanical thermal analyzer (DMTA) at a heating rate of 5°C/min under air (Fig. 2). The results are listed in Table I. The

Figure 1 Typical TGA curves of polyimides.

Figure 2 Typical dynamics mechanical thermal analysis plots for polyimides.

cernible glass transitions on the DSC thermograms, possibly because of the low thermal effect during the transition of some rigid-rod polyimides and their high packing density.

Mechanical properties of polyimides

The mechanical properties of the polyimides are determined using a tensile machine and are evaluated using their stress–strain profiles. The results are reported in Table II. The polyimides have strength at break of 181–271 MPa, elongations at break of 6.5–51%, and tensile modulus of 3.55–5.93 GPa, indicating that the PIs containing pyrimidine have excellent mechanical properties. As shown in Table II, the elongations and the strength of BPDA-based polyimides are much higher than those of the PMDA-based polyimides while there is no obvious difference between the polyimides based on the same dianhydride, implying the dianhydride component have contributions for the difference. From the DMTA curves (Fig. 2), it can be seen that the storage modulus decreases slightly at high temperature, especially for the polyimides prepared from PMDA, and the polyimides without PDA moiety exhibit the highest storage modulus above 400°C, indicating that the pyrimidine component has significant influence on the mechanical properties of polyimides at high temperature.

X-ray diffraction data of polyimides

The crystallinity of the prepared polyimides was evaluated by WAXD scans. The representative WAXD patterns of the thermally cured polyimide films are presented in Figure 3. As expected, all of the polyimides reveal a strong peak reflection at 2θ values of about 20°, which indicated that these polyimides have a high packing density and high-level crystallinity. These results confirm the rigid structure of the polyimides; they also offer an explanation for their poor solubility and high T_g values.

BPDA-based polyimides show the T_β and the T_g ranging from 179 to 198°C and from 307 to 352°C, respectively. Meanwhile the PMDA-based polyimides exhibit T_g ranging from 420 to 434°C, but the T_β is not obvious. As expected, all of the PMDA-derived polyimides reveal a higher T_g in comparison with those of the corresponding BPDA-derived ones, because of the higher rigidity of the polymer chains. All of the homo- and copolyimides do not show dis-

TABLE II
Mechanical Properties of Polyimide Films[a]

Code	PI	Elongation at break (%)	Strength at break (MPa)	Tensile modulus (GPa)
PI-1	PMDA-PDA/**4** (0/100)	7.7	195	5.93
PI-2	PMDA-PDA/**4** (25/75)	6.8	185	4.59
PI-3	PMDA-PDA/**4** (50/50)	11.3	188	3.92
PI-4	PMDA-PDA/**4** (75/25)	6.5	181	4.24
PI-5	BPDA-PDA/**4** (0/100)	42	248	3.55
PI-6	BPDA-PDA/**4** (25/75)	47	271	4.12
PI-7	BPDA-PDA/**4** (50/50)	51	253	3.59
PI-8	BPDA-PDA/**4** (75/25)	47	258	4.02

[a] Measured at room temperature under air using an Instron model 1122 at a drawing rate of 5 mm/min.
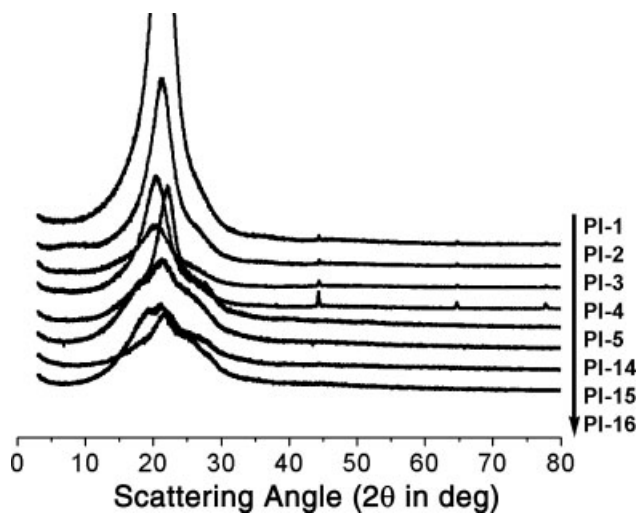
Figure 3 WAXD curves for polyimides.

CONCLUSIONS

2-(4-Aminophenyl)-5-aminopyrimidine **(4)** was synthesized by the condensation reaction of vinamidium salts and *p*-nitrobenamidine chloride salt, followed by hydrazine palladium catalyzed reduction in the reasonable high yield. The diamines were polycondensated with aromatic tetracarboxylic dianhydrides in DMAc. The polymerization proceeded homogeneously and gave the poly(amic acid)s showing the inherent viscosities in range of 0.97–4.38 dL/g ($c = 0.5$ g/dL, in DMAc, 30°C). The corresponding polyimides were obtained as flexible films by curing the semidried poly(amic acid) films. The polyimides showed excellent thermal stability and mechanical properties. The characteristics were considered to be due to the introduction of the symmetric and rigid structure containing pyrimidine into the polymer backbone. The films were insoluble in common organic solvents and exhibit high chemical resistance.

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