Synthesis and Characterization of Novel Polyimides Derived from 2-Amino-5-(4-aminophenyl)-thiazole

Xin Zhao, Yan-Feng Li, Yu Shao, Tao Ma, Chen-Liang Gong, Cong-Shu Huang

State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Institute of Biochemical Engineering & Environmental Technology, Lanzhou University, Lanzhou 730000, China

ABSTRACT: A new kind of aromatic unsymmetrical diamine monomer containing thiazole ring, 2-amino-5-(4-aminophenyl)-thiazole (AAPT), was synthesized. A series of novel polyimides were prepared by polycondensation of AAPT with various aromatic dianhydrides by one-step polyimidation process. The synthesized polyimides had inherent viscosity values of 0.36–0.69 dL/g and were easily dissolved in highly dipolar solvents. Meanwhile, strong and flexible polyimide films were obtained, which have good thermal and thermo-oxidative stability with the glass transition temperatures (T_g) of 276.7–346.1°C, the temperature at 5% weight loss of 451–492°C in nitrogen and 422–440°C in air, as well as have outstanding mechanical properties with the tensile strengths of 94–122 MPa, elongations at breakage of 5–18%. These films also had dielectric constants of 3.12–3.38 at 10 MHz. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 3119–3126, 2008

Key words: high-performance polymers; thiazole-containing polyimides; unsymmetrical diamine; thermal properties; dielectric properties

INTRODUCTION

Aromatic polyimides generally possess excellent thermal and mechanical, electrical, and chemical properties. Therefore, they are being used in many applications such as electrics, coatings, composite material, and membranes.[1,2] However, the commercial use of these materials is often limited because of their poor solubility, and high softening or melting temperatures.

To overcome these problems, many efforts have been devoted to enhancing the solubility of polyimides, and this has included the introduction of noncoplanar groups,[3] or unsymmetrical structure into the polymer backbone.[4]

The formation of noncoplanar unit through the introduction of heteroaromatic rings with rigid structure into the polyimide backbones keeps the advantages of the rigid rod like polyimides with planar structure, such as interlevel dielectrics, and packaging applications including low thermal expansion and excellent mechanical strength.[5]

Introducing unsymmetrical structure into the main chain of the polyimide can lead to the improvement in solubility and melt processability and other desirable properties.[6–12] In addition, introducing heteroaromatic rings, such as the thiazole unit, into the main chain of a synthetic polymer is expected to impart certain properties such as chemical stability, thermal and thermo-oxidative stability. Also, the heteroaromatic rings can interact with metal, and may enhance the adhesion of the polymer chains to metal. However, to our knowledge, there have been very few studies concerning polyimides containing thiazole rings.[13–15]

In this article, a new kind of thiazole-containing unsymmetrical diamine monomer, 2-amino-5-(4-aminophenyl)-thiazole, has been synthesized, successfully. It was designed as a potentially convenient condensation monomer for polyimides, capable of imparting thermal and thermo-oxidative stability, as well as good solubility. A new thiazole-diamine monomer was synthesized and copolymerized to form a series of thiazole-containing polyimides. This monomer and subsequent polyimides were characterized by FTIR, ^{1}H-NMR, ^{13}C-NMR, DSC, TGA, wide-angle X-ray diffraction, and elemental analysis methods.

EXPERIMENTAL

Materials

4-Nitroacetophenone (Shanghai Chemical reagents Corp., China), hydrazine monohydrate (Beijing Chemical reagents Corp., China), bromine (Fuchen Chemical reagents Corp., Tianjin, China), and 5% Pd/C (Acros) were used without further purification. 4,4′-(Hexafluoroisopropylidene)diphthalic anhydride (6FDA, Aldrich), 4,4′-Oxydiphthalic anhydride

*Correspondence to:* Y.-F. Li (liyf@lzu.edu.cn).

(ODPA, Shanghai Nanxiang Chemical Co., China), and 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA, Beijing Chemical Reagents Corp., China) were recrystallized from acetic anhydride before use. Pyromellitic dianhydride (PMDA, Beijing Chemical Reagents Corp., China) was purified by sublimation at 200–220°C. N-Methyl-2-pyrrolidone (NMP) and m-cresol were distilled under reduced pressure over CaH_2 and P_2O_5, respectively. All other solvents were obtained from various commercial sources and used without further purification. The purities of these solvents are: chloroform (99%), ethanol (99.5%), and absolute ethanol (99.95%).

Syntheses of diamine containing thiazole unit

Synthesis of α-bromo-4-nitroacetophenone (BNAP)

To a solution of 4-nitroacetophenone (0.1 mol, 16.51 g) in chloroform (100 mL), bromine (0.1 mol, 5.10 mL) was added dropwise into the stirred solution at room temperature within 1 h. After complete addition, the mixture was stirred for another 2 h. Excess chloroform was evaporated, and the remaining yellow powder was recrystallized from ethanol. The total product yield is 80% while melting point is 93–94°C.

FTIR (KBr pellet): 1641 cm^{-1} (C=O stretching), 1573, 1323 cm^{-1} (C—NO_2 stretching), 1323 cm^{-1} (C—N stretching), 843 cm^{-1} (p-substituted benzene), 573 cm^{-1} (C—Br stretching); ^{1}H-NMR (300 MHz, CDCl$_3$, δ) 8.38–8.35 (d, J = 8.1 Hz, 2H, H$_a$), 8.19–8.16 (d, J = 8.1 Hz, 2H, H$_b$), 4.47 (s, 2H, H$_c$); ^{13}C-NMR (300 MHz, CDCl$_3$, δ): 189.86(C^5), 150.58(C^1), 138.31(C^4), 130.00(C^3), 123.87(C^2), 26.92(C^6); MS(EI): 244(M$^+$). Elemental Anal. Calcd. For $C_8H_6NO_3Br$ (244.04): C, 39.37; H, 2.48; N, 5.74. Found: C, 39.40; H, 2.51; N, 5.63.
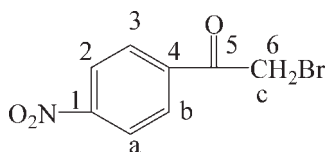
Synthesis of 2-amino-5-(4-nitrophenyl)-thiazole (ANPT)

A mixture consisting of 4.88 g (0.02 mol) of BNAP, 1.52g (0.02 mol) of thiourea, and 100 mL of absolute ethanol was put into a reaction flask. The mixture was refluxed for 2 h with stirring before being poured into 400 mL of distiller water and neutralized with ammonia water to form a precipitate. The precipitate was filtrated off, washed with water, and recrystallized from ethanol to get a yellow product. The total product yield was 75% while melting point is 278–280°C.

FTIR (KBr pellet): 3386 cm^{-1} (NH_2 stretching), 1520, 1343 cm^{-1} (C—NO_2 stretching), 1343 cm^{-1} (C—N stretching), 848 cm^{-1} (p-substituted benzene); ^{1}H-NMR (300 MHz, DMSO-d_6, δ): 8.16–8.14 (d, J = 8.1 Hz, 2H, H$_a$), 7.98–7.95 (d, J = 8.1 Hz, 2H, H$_b$), 7.34 (s, 1H, H$_c$), 7.18 (s, 2H, H$_d$); ^{13}C-NMR (300 MHz, DMSO-d_6, δ): 158.41(C^7), 137.62(C^1), 135.72(C^4), 130.69(C^6), 116.10(C^3), 113.85(C^2), 99.14(C^5); MS(EI): 221(M$^+$). Elemental Anal. Calcd. For $C_9H_7N_3O_2S$ (221.23): C, 48.86; H, 3.19; N, 18.99. Found: C, 48.84; H, 3.20; N, 18.91.
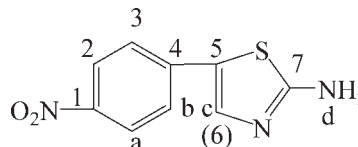
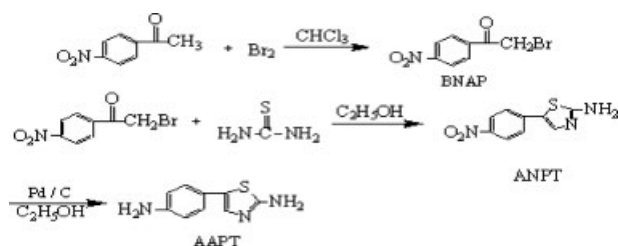### Synthesis of 2-amino-5-(4-aminophenyl)-thiazole (AAPT)

The nitrocompound ANPT (11.06 g, 0.05 mol) and 5% Pd/C (0.45 g) were suspended in 100 mL of ethanol in a 250-mL flask. The suspension solution was heated to reflux, and hydrazine monohydrate 80% (20 mL) was added dropwise to the mixture over 0.5 h. After a further 4 h of reflux, the resultant clear, darkened solution was filtered hot to remove Pd/C, and the filtrate was distilled to remove some solvent. The obtained mixture was poured into 200 mL of stirring water, giving rise to pale-yellow product that was isolated by filtration. The crude product was purified by recrystallized from ethanol to give 2-amino-5-(4-aminophenyl)-thiazole (AAPT) (7.2 g, 90% total yield) as a yellow solid with a melting point of 177–179°C.

FTIR (KBr pellet): 3417, 3343 cm^{-1} (NH_2, stretching), 3265 cm^{-1} (associated NH_2, stretching), 1334, 1263 cm^{-1} (C—N stretching), 838 cm^{-1} (p-substituted benzene); ^{1}H-NMR (300 MHz, DMSO-d_6, δ): 7.39–7.36 (d, J = 9.0 Hz, 2H, H$_b$), 6.83 (s, 2H, H$_d$), 6.49 (s, 1H, H$_c$), 6.46–6.43 (d, J = 9.0 Hz, 2H, H$_a$), 5.11 (s, 2H, H$_e$); ^{13}C-NMR (300 MHz, DMSO-d_6, δ): 157.55(C^7), 140.59(C^1), 137.86(C^6), 116.37(C^3), 113.09(C^4), 103.43 (C^2), 86.43(C^5); MS (EI): 191 (M$^+$). Elemental Anal. Calcd. For $C_9H_9N_3S$ (191.25): C, 56.52; H, 4.74; N, 21.97. Found: C, 56.51; H, 4.76; N, 21.94.
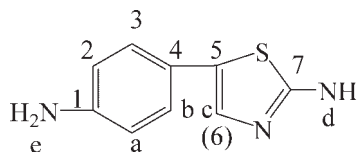
General procedure for the syntheses of polyimides

A mixture consisting of 2 mmol of dianhydride, 2 mmol of diamine, and 0.488 g of benzoic acid were added to a 250-mL, three-necked flask which was equipped with a mechanical stirrer a Dean-Stark

Scheme 1 Synthesis of 2-amino-5-(4-aminophenyl) thiazole (AAPT).

trap, a condenser, and a nitrogen inlet/outlet tube. About 12 mL of *m*-cresol was added and then the reaction mixture was heated at 80°C for 3 h and then at 180°C for 9 h. Next, 0.52 g of isoquinoline was added to the reaction, and it was heated at 180°C for another 9 h. The reaction mixture was cooled to room temperature and precipitated into an excess of methanol. The precipitated polyimide was collected by filtration and was dried in a vacuum oven at 120°C for a period of 6 h and then at 150°C for 24 h. Yields greater than 95% were obtained.

Film preparation

The polymers were dissolved in NMP at a concentration of 5–10 wt % and then filtered through sandbed filter. The filtered solutions were coated on a glass plate and dried in a temperature-controlled oven at 100°C for 24 h. The prepared films were peeled from the plates and dried in a vacuum at 100°C for 24 h.

Characterization

The inherent viscosities of the resulting polyimides were measured with an Ubbelohde viscometer at 30°C. FTIR spectra (KBr) were recorded on a Nicolet NEXUS670 fourier transform infrared spectrometer. ^{1}H-NMR (300 MHz) and ^{13}C-NMR (300 MHz) spectra were measured on a JEOL EX-300 spectrometer using tetramethylsilane as the internal reference. Elemental analyses were determined by a Perkin–Elmer model 2400 CHN analyses. The mechanical properties were measured on an Instron 1122 Tensile Apparatus with 100×5 mm specimens in accordance with GB 1040-79 at a drawing rate of 100 mm/min. The dielectric constant was determined on an Agilent 4291B instrument with 25 μm thickness specimens at a frequency of 10 MHz at 25°C. The water uptake values of the films were determined by the weighing of the changes in vacumm-dried film specimens before and after immersion in deionized water at 25°C for 24 h. Testing of differential scanning calorimetry (DSC) were performed on a Perkin–Elmer differential scanning calorimeter DSC 7 or

Pyris 1 DSC at a scanning rate of 20°C/min in flowing nitrogen (30 cm^3/min), and glass transition temperatures (T_g) were read at the DSC curves at the same time. Thermogravimetric analysis (TGA) was conducted with a TA Instruments TGA2050, and experiments were carried out on $\sim$ 10 mg of samples in flowing air (flowing rate = 100 cm^3/min) at a heating rate of 20°C/min. Wide-angle X-ray diffraction measurements were performed at room temperature (about 25°C) on a Siemens Kristalloflex D5000 X-ray diffractometer, using nickel-filtered CuKα, radiation (λ = 1.5418 E, operating at 40 kV and 30 mA).

RESULTS AND DISCUSSION

Syntheses of diamine containing thiazole unit

Novel diamine monomer, i.e., AAPT, was synthesized by a three steps procedure, respectively, as shown in Scheme 1. Firstly, α-bromo-4-nitroacetophenone (BNAP) was formed by bromination of 4-nitroacetoph-enone using chloroform as the solvent, then single nitro compound, 2-amino-5-(4-nitrophenyl)-thiazole (ANPT), was synthesized by the ring formation of BNAP with thiourea, and ANPT was converted to AAPT by reduction of the nitro groups into NH$_2$ groups by catalytic hydrogenation of them with Pd/C in ethanol. Based on the better solubility of ANPT than traditional symmetrical two nitro compounds, the diamine monomer was easily purified. The new aromatic diamine monomer is stable in air at room temperature.

FTIR, NMR, and elemental analysis were used to confirm the structures of the intermediate BNPT, ANPT, and the diamine monomer (AAPT). The FTIR spectra of BNAP gave a characteristic band at 573 cm^{-1} (C—Br stretching). After the ring formation of BNAP, the resulting nitro compound ANPT gave two characteristic bands indicating asymmetric and symmetric stretching of NO$_2$ group at 1520, 1343 cm^{-1}, especially. The diamine monomer (AAPT) obtained by reduction of ANPT illustrates that there are characteristic absorption of the amino group showed a pair N—H stretching bands in the region of 3417–3343 cm^{-1} and a associated N—H stretching band at 3265 cm^{-1}. Furthermore, the corresponding absorption bands of the nitro group have disappeared. The FTIR spectra confirm the reaction mechanism shown in Scheme 1.

Figure 1 shows the ^{1}H-NMR and ^{13}C-NMR spectra of the diamine AAPT, and clearly identify its chemical structure. As shown in Figure 1(a), the absorption peaks appeared at 5.1 and 6.8 ppm in the ^{1}H-NMR are assigned to the amino protons of benzene and thiazole ring, which indicated the presence of unsymmetrical structure. All intermediate compounds and the diamine were also confirmed by
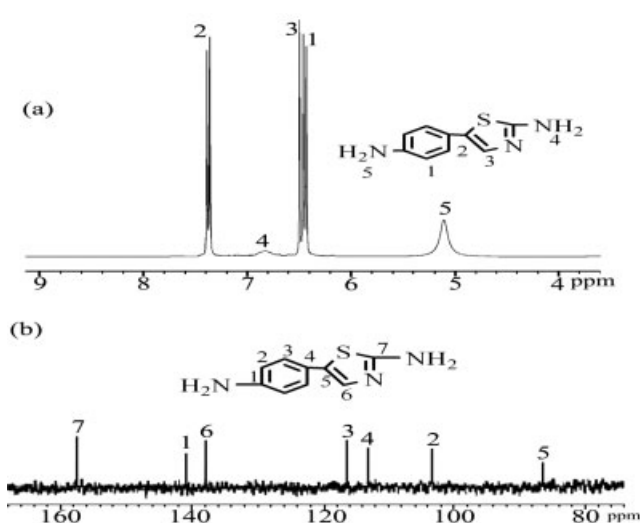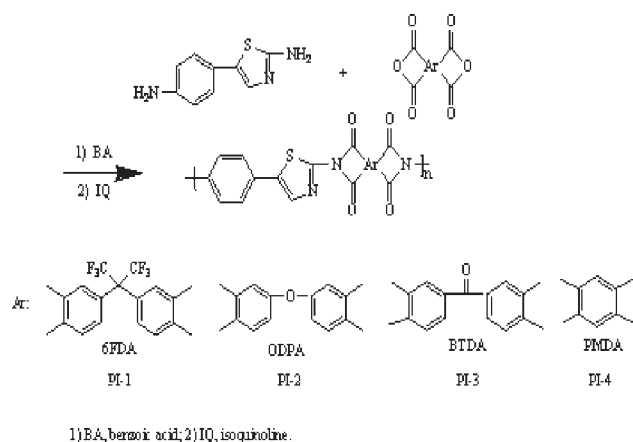
Figure 1 NMR spectra of AAPT: (a) ^{1}H-NMR; (b) ^{13}C-NMR (300 MHz, DMSO-d_6).

Figure 2 FTIR spectra of the polyimides films.

elemental analysis, which were in good agreement with the calculated values, as reported in earlier section. The results indicate that the design and synthesis of novel diamine monomer AAPT should be successful and feasible in this work.

Synthesis chemistry of polyimides

A series of polyimides were prepared from the poly-condensations of diamine monomer AAPT with various commercially available aromatic tetracarboxylic dianhydrides including 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA), 4,4'-Oxydiphthalic anhydride (ODPA), 3,3',4,4'-benzophenonetetracar-boxylic dianhy-dride (BTDA), pyromellitic dianhy-dride (PMDA), via one step synthetic method, as shown in Scheme 2. These polyimides were prepared by high temperature polycondensation reactions in a high boiling solvent (m-cresol) at 180–190°C. The for-

mation of the trans-isoimide was promoted by the acidic catalyst which was added in the first step. Then, the conversion of the trans-isoimide to poly-imide needed a basic catalyst.[16,17] The inherent viscosity of the polyimides were significantly affected by the nature of the catalysts, mole ratio of the catalysts and dianhydrides, and addition order of the catalysts.[18] The most effective catalyst was benzoic acid (2 mol) that with dianhydride (1 mol) added at the beginning of the reaction, and then isoquinoline (2 mol) was added after a few hours. The structural features of the polyimides were identified with FTIR and ^{1}H-NMR. FTIR spectra of these polyimides are illustrated in Figure 2. It could be observed all the expected imide bands at 1779 and 1721 cm^{-1} (asymmetric and symmetrical C=O stretching), 1354 cm^{-1} (C—N stretching), 1088 and 742 cm^{-1} (imide ring deformation). Figure 3 shows the high-resolution ^{1}H-NMR spectrum of PI derived from AAPT and 6FDA, in which the absorption peaks at 7.5–8.3 ppm are assigned to the aromatic protons in polymer backbone. No absorption was detected in the range of >8.3 ppm, indicating that the concentration of amide group (—C(O)NH—) in polymer chains was lower than the detection limit of ^{1}H-NMR (<5%). In other
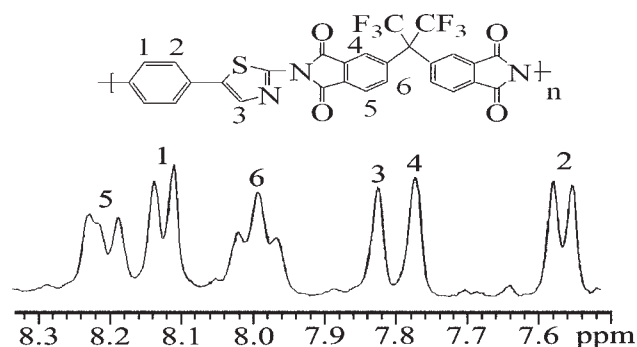

Scheme 2 Synthesis of the polyimides through one-step polymerization.

Figure 3 ^{1}H-NMR spectra of PI based on AAPT-6FDA (300 MHz, DMSO-d_6).

TABLE I
Inherent Viscosity and Element Analysis of Polyimides

Polymer	Yield (%)	PIη_{linh}[a] (dL/g)	Formula of PI (formula weight)		Elemental analysis (%) of polyimides			Film quality[b]
					C	H	N	
PI-1	97	0.58	$(C_{28}H_{11}N_3O_4F_6S)_n$ (599.46)$_n$	Calcd.	56.10	1.85	7.01	C, F, & T
				Found	55.98	1.80	7.03	
PI-2	98	0.69	$(C_{25}H_{11}N_3O_5S)_n$ (465.39)$_n$	Calcd.	64.52	2.38	9.03	C, F, & T
				Found	64.46	2.28	8.99	
PI-3	98	0.49	$(C_{26}H_{11}N_3O_5S)_n$ (477.40)$_n$	Calcd.	65.41	2.32	8.80	C, F, & T
				Found	65.23	2.29	8.76	
PI-4	95	0.36	$(C_{19}H_7N_3O_4S)_n$ (373.29)$_n$	Calcd.	61.13	1.89	11.26	—
				Found	60.94	1.92	11.20	

[a] Inherent viscosity (η) determined on 0.5% solutions in a solvent (NMP) at 30°C.
[b] C: clear; F: flexible; T: tough; —, brittle.

words, the polyimide possesses an imidization degree of >95%. According to the data from Table I, the resulting polyimides were of high yields (95–98%), and the inherent viscosity values of these polyimides were in the range of 0.36–0.69 dL/g, which indicated formation of high molar masses.[19] This was consistent with the fact that tough and flexible films could be obtained by coating and solvent evaporation of polymer solutions. However, the polyimides film based on AAPT-PMDA (PI-4) was brittle because of the rigidity structure of the polymer chains. The elemental analysis data of the resulting polyimides also agreed well with the calculated values. The above results demonstrated that the diamine monomer AAPT polymerized well to form soluble polyimides via one-step synthetic method.

Solubility of the resulting polyimides

The solubilities of the resultant polyimides in several organic solvents at 3.0% (30 mg of the polymer solu-

TABLE II
Soubility Data of the Polyimides

Polyimide	Solvent[a]				
	NMP	DMAc	DMF	DMSO	m-Cresol
PI-1	+ +	+ +	+ +	+	+ +
PI-2	+ +	+ +	+	+	+ +
PI-3	+ +	+	− −	+	+
PI-4	+	+ −	− −	+ −	+
PI-5[b]	+	+	+	+	+
PI-6	− −	− −	− −	− −	+ −
PI-7	− −	− −	− −	− −	− −

Qualitative solubility was determined at 3.0% (w/v); + +, soluble at room temperature; +, soluble on heating; + −, Partially soluble; and − −, insoluble even on heating.
[a] NMP, N-methy-2-pyrrolidone; DMAc, N,N-dimethylacetamide; DMF, N,N-dimethylformamide; DMSO, dimethyl sulfoxide.
[b] PI-5-polyimide based on BAPP and 6FDA; PI-6-polyimide based on BAPP and ODPA; PI-7-polyimide based on BAPP and BTDA.

ble in 1 mL of the solvent) were summarized in Table II. It is likely that the good solubility resulted from both the noncoplanar unit and polarizability of nitrogen atom in thiazole ring in the polyimide structure. The solubility varies depending upon the dianhydride used. PI based on AAPT-6FDA and AAPT-ODPA possesses the better solubility because of the presence of the trifluoromethyl and the flexible ether groups. As expected, PI based on AAPT-PMDA has poor solubility, possibly due to the rigid structure of the polymer chains. Moreover, polyimides derived from symmetrical diamine have straight chains, with strong interactions between the chains, thus promoting chain packing, which leads to lower solubility than polyimides with unsymmetrical diamine moieties. In comparison with the polyimides with symmetrical structure based on 4,4′-Bis(4-amino-phenoxy) biphenyl (BAPP) recently reported, polyimides based on AAPT showed superior solubility.[20]

X-Ray diffraction of the polyimides

The crystallinity of the polyimides was examined by wideangle X-ray diffraction analysis with graphite monochromatized CuKα radiation, 2θ ranging from 0° to 50°, using the polyimide powder obtained as
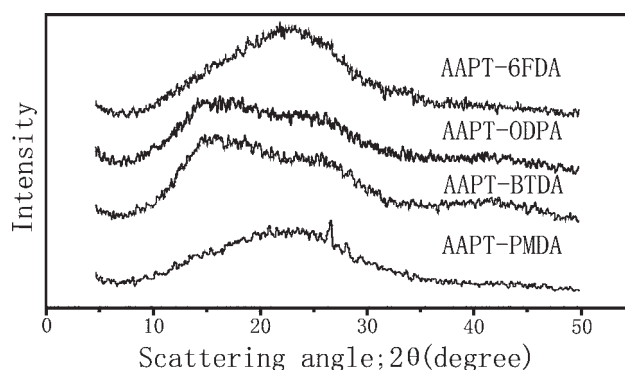

Figure 4 Wide-angle X-ray diffraction curves of the polyimides.

TABLE III
Mechanical and Dielectric Properties of the Polyimides

Polyimide	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation at breakage (%)	Dielectric constant (dry)[a]		Water absorption (%)
				10 MHz	20 MHz	
PI-1	108	2.33	11	3.12	3.05	0.31
PI-2	122	2.62	18	3.25	3.20	0.43
PI-3	94	2.06	5	3.38	3.34	0.38

[a] Measured by Agilent 4291B at room temperature (dry dielectric constant).

samples. The results were shown in Figure 4. The X-ray diffraction curves of these polyimides showed a set of wider diffraction peaks; these should be a reason that could obtain transparent films from these polyimides. The X-ray diffraction curve of the polyimide based on AAPT-PMDA exhibits two peaks around 25°. This might be interpreted as regions of crystallinity. PIs based on AAPT-6FDA, AAPT-ODPA, and AAPT-BTDA appear amorphous, as expected, because the presence of flexible groups induces looser chain packing.

Mechanical and electrical Properties

All of the polyimides could be processed into clear, flexible, and tough films, except the polyimide based on AAPT-PMDA because of the rigidity structure of the polymer chains. These films were subjected to tensile tests. Table III shows the mechanical properties of the polyimides, including the tensile strength, tensile modulus as well as elongation at breakage. The polyimide films had tensile strength of 94–122 MPa, elongations at breakage of 5–18%, and tensile moduli of 2.06–2.62 GPa, which indicated strong and tough materials.

The dielectric constant values of the polyimides are also presented in Table III. In this study, all polyimide samples were prepared with the same curing process. Although the thickness of the polyimide films are different, the dielectric constants of the polyimide films thicker than 1 μm do not vary with the thickness.[21,22] Obviously, the dielectric constants for each sample are quite different, and strongly depend on the chemical structure. This value may be affected by decreasing the molecular packing efficiency of their chemical structures. A low molecular packing order can lead to a decrease in the number of polar group in a unit volume. In other words, fewer polarizable groups in unit volume may lead to a lower dielectric constant for polyimide films.[22]

Polyimides based on AAPT have lower dielectric constants (3.12–3.38 at 10 MHz) compared with conventional polyimides such as PMDA/ODA polyimide film (3.44 at 10 MHz). The dielectric constant values are in increasing order for our samples: PI-1<PI-2<PI-3. PI-1 has the lowest dielectric constant

could be attributed to the presence of the bulky CF_3 groups, which could cause the variation in hydrophobicity, free volume, and total polarizability.[23] PI-2 has lower dielectric constant than PI-3 due to larger polarity of BTDA than ODPA. This can be explained by the existence of carbonyl groups in the PI-3 structure, which cause an increase in the dipole number density. For each polyimide, the dielectric constant reduced followed the increment of the frequency. This behavior could be attributed to the dependence of the polarization mechanisms.[24,25]

As water has a very high dielectric constant, absorption in even small amounts can affect the dielectric constant of polyimide films. Absorbed water in the package has a critical effect on the electrical properties of polyimide films. Water uptake properties of the polyimide films are depicted in Table III. The values are in the range of 0.31–0.43%, and in such order: PI-1<PI-3<PI-2. Because the hexafluoroisopropylide-ne group acts as a hydrophobic hindrance in the polyimide, PI-1 has the smallest value. Moreover, a structurally flexible polymer with bulky chemical groups in its structure shows more water uptake than a linear, rigid polymer.[26] So, PI-2 show higher water uptake values than PI-3 because of the more free volume between the molecules. As the results show in Table III, the low water uptake and the low dielectric constants of these polyimides present potential utility of the material in the microelectronics industry, where a low dielectric constant is desired to prevent crosstalk between conducting paths.

TABLE IV
Data of Thermal Analysis of the Polyimides

Polyimide	T_g (°C)[a]	In N_2[b]		In air[b]		Char yield (%)[c]
		T_5 (°C)	T_{10} (°C)	T_5 (°C)	T_{10} (°C)	
PI-1	281.8	492	526	425	451	56.87
PI-2	276.7	451	481	422	458	55.42
PI-3	301.5	459	487	435	472	58.81
PI-4	346.1	489	519	440	468	59.29

[a] T_g measured by DSC at a scanning rate of 10°C/min in flowing nitrogen.
[b] Temperature at a 5 or 10% weight loss at a 20°C/min heating rate.
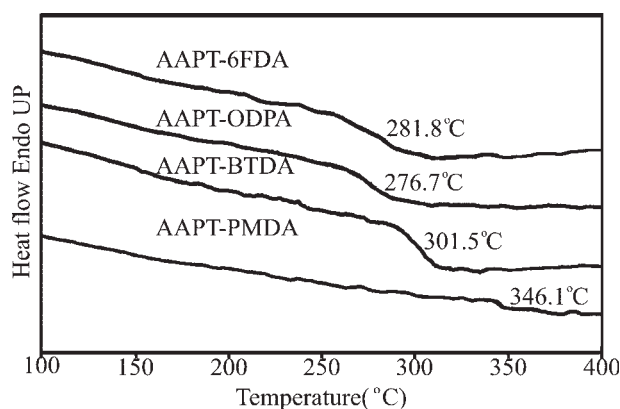[c] Residual weight (%) at 700°C in nitrogen.

Figure 5 DSC thermograms of the polyimides.

Thermal properties of the resulting polyimides

The thermal properties of the polyimides, which were evaluated by DSC and TGA methods, were listed in Table IV. DSC curves of the polyimides are shown in Figure 5. These polyimides were heated to 400°C and then rapidly cooled to induce an amorphous state, and then reheated to find the T_g. The T_g values of PI-1, PI-2, and PI-3 were in the range of 276.7–301.5°C. There is a slight inflection at 346°C in the DSC curve of PI-4 which might be the T_g, but is not clearly distinguished since it is at the noise level. In comparison with commercial polyimide, the T_g values of these polyimides are higher than commercial polyimide, Ultem 1000 (T_g, 217°C), based on bisphenol-A diphthalic anhydride and m-phenylene diamine.[27] However, the T_g values of these polyimides are lower than Kapton films derived from PMDA-ODA (T_g, 390°C).[27]

As we expected, the T_g values of these PIs depended on the structure of the dianhydride component, and decreased with increasing flexibility of the polyimides backbones based on applied the structure of dianhydride. PI obtained from ODPA showed a lower T_g because of the presence of a flexible ether linkage between the phthalimide units. PI derived from PMDA exhibited the highest T_g due to the rigid pyromellitimide unit. Clearly, the difference in T_gs was attributed to the rigidity and packing of the polymer chains. According to Figure 4, some of the resulting polyimdes might exhibit melting peaks from the crystalline morphology in DSC curves. However, no melting peaks were observed in the DSC curves presented in Figure 5, the T_m values represented the crystalline morphology was not obtained from the DSC curves certainly. These probably were that the T_m values of the resulting polyimides were too high to have overstepped measure range of used DSC meter.[28,29]

The TGA curves of polyimides followed the decreasing order of chain flexibility and steric hin-

drance of the dianhydrides. All of the polymers showed higher stabilities in N_2 than in air. It is due to the presence oxidizable thiazole ring in the polymer backbone. Table IV gives the temperature of the 5 and 10% gravimetric loss in nitrogen and in air, respectively, i.e., T_5 and T_{10} values. T_5 and T_{10} of the polyimides reached 451–492°C and 481–526°C in nitrogen, while those of them were in the range 422–440°C and 451–472°C in air, and the amount of residue of all polyimides at 700°C in nitrogen atmosphere was higher than 55.4%, especially, the polyimide derived from AAPT-PMDA had the highest yield up to 59.3%. Obviously, the data from thermal analysis shows that the resulting polyimides have fairly high thermal stability and the thermo-oxidative stability derived from thiazole rings.

CONCLUSIONS

A novel kind of unsymmetrical diamine with thiazole ring, i.e., 2-amino-5-(aminophenyl)-thiazole (AAPT), was successfully synthesized in high purity and high yields in this work, and the resulting AAPT was employed to react with various aromatic dianhydrides by one-step polyimidation process. The experimental results indicate that the novel polyimides obtained have higher T_g values, excellent thermal and thermo-oxidative stability, as well as good solubility in organic solvents. These polymers also have good mechanical properties with low dielectric constants. These features are desirable for polyimides as potential candidate for microelectronics packaging applications.

References

1. Wilson, D.; Stenzenberger, H. D.; Hergenrother, P. M., Eds. Polyimides; Chapman and Hall: New York; 1990.
2. Ghosh, M. K.; Mittal, K. L., Eds. Polyimides Fundamentals and Applications. Marcel Decker: New York; 1996.
3. Ahn, S. K.; Kim, H. S.; Kim, Y. H.; Kwon, S. K. Macromolecules 2003, 36, 2327.
4. Shao, Y.; Li, Y. F.; Zhao, X.; Wang, X. L.; Ma, T.; Yang, F. C. J Polym Sci Part A: Polym Chem 2006, 44, 6836.
5. Aihara, Y.; Cebe, P. Polym Eng Sci 1994, 34, 1275.
6. Fang, X. Z.; Wang, Z.; Yang, Z. H.; Gao, L. X.; Ding, M. X. Polymer 2003, 44, 2641.
7. Xu, J. W.; Chng, M. L.; Chung, T. S.; He, C. B.; Wang, R. Polymer 2003, 44, 4715.
8. Yang, C. P.; Su, Y. Y. Polymer 2003, 44, 6311.
9. Fang, X. Z.; Yang, Z. H.; Zhang, S. B.; Gao, L. X.; Ding, M. X. Polymer 2004, 45, 2539.
10. Yang, C. P.; Su, Y. Y.; Wu, K. L. J Polym Sci Part A: Polym Chem 2004, 42, 5424.
11. Zhang, M.; Wang, Z.; Gao, L. X.; Ding, M. X. J Polym Sci Part A: Polym Chem 2006, 44, 959.
12. In, I.; Kim, S. Y. Polymer 2006, 47, 547.
13. Liu, S.; Sun, W.; He, B. J.; Shen, Z. Q. Eur Polym J 2004, 40, 2043.
14. Leng, W. N.; Zhou, Y. M.; Xu, Q. H.; Liu, J. Z. Polymer 2001, 42, 9253.

15. Al-Dujaili, A. H.; Atto, A. T.; Al-Kurde, A. M. Eur Polym J 2001, 37, 927.
16. Sek, D.; Wanic, A.; Schab-Balcerzak, E. J Polym Sci Part A: Polym Chem 1995, 33, 547.
17. Mehdipour-Ataei, S.; Arabi, H.; Bahri-Laleh, N. Eur Polym J 2006, 42, 2343.
18. Sek, D.; Pijet, P.; Wanic, A. Polymer 1992, 33, 190.
19. Chen, H.; Yin, J. J Polym Sci Part A: Polym Chem 2003, 41, 2026.
20. Yang, C. P.; Hsiao, S. H.; Hsu, M. F. J Polym Sci Part A: Polym Chem 2002, 40, 524.
21. Liang, T.; Makita, Y.; Kimura, S. Polymer 2001, 42, 4867.
22. Deligoz, H.; Yalcinyuva, O. S.; Yildirim, S. J Appl Polym Sci 2006, 100, 810.

23. Yiang, L. Y.; Ley, C. M.; Wei, K. H. Adv Mater 2002, 14, 426.
24. Muruganand, S.; Narayandasss, S. K.; Mangalaraj, D.; Vijayan, T. M. Polym Int 2001, 50, 1089.
25. Alegaonkar, R. S.; Mandela, A. B.; Sainker, S. R.; Bhoraskar, V. N. Nucl Instr Methods Phys Res B 2002, 194, 281.
26. Lee, C.; Shu, Y.; Han, H. J Polym Sci Part B: Polym Phys 2002, 40, 2190.
27. Takekoshi, T. In Encyclopedia of Chemical Technology, 4th ed.; Kirk-Othmer, Ed.; Wiley: New York, 1996; Vol. 19, p 813.
28. Ratta, V.; Ayamben, A.; McGrath, J. E.; Wilkes, G. L. Polymer 2001, 42, 6173.
29. Liu, X. Q.; Yamanaka, K.; Mitsutoshi, J. K.; Kakimoto, M. A. Chem Mater 2000, 12, 3885.