

## New Polytriazoleimides with High Thermal and Chemical Stabilities

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A series of novel polytriazoleimides were prepared from various aromatic dianhydrides and a new kind of 1,2,3-triazole-containing aromatic diamine synthesized by the Cu (I)-catalyzed 1,3-dipolar cycloaddition reaction in DMAc, and characterized by FT-IR, <sup>1</sup>H-NMR, XRD, DSC and TGA techniques. The results show the polytriazoleimides are soluble in most of strong polar solvents and have inherent viscosity values of 0.51-0.62 dL/g(DMAc). The polytriazoleimide films exhibit a tensile strength of 62.3-104.5 MPa and an elongation at breakage of 4.0-8.1%, a glass transition temperature ( $T_g$ ) of 257-275 °C, a decomposition temperature (at 5% weight loss) of 350-401 °C in N<sub>2</sub> atmosphere, and a dielectric constant of 2.47-3.01 at 10 MHz, which depend on the structure of the polymers. The polytriazoleimides perform good resistance to acid and alkali solution.

**Key Words :** Polytriazoleimide, 1,2,3-Triazole-containing diamine, Dielectric properties, Chemical resistance, High performance film

### Introduction

Aromatic polyimides (PIs) have high thermal stability, chemical resistance, electrical characteristics, toughness, and dimensional stability. Therefore, they have gained much interest in many applications, such as insulating layers for semiconductor devices, microelectromechanical systems or substrates for flexible printed circuits, particularly owing to their relatively low dielectric constant.<sup>1,2</sup> However, most of aromatic PIs are difficult to be processed because they are insoluble in most organic solvents and do not melt or soften below their decomposition temperatures, and thus their applications are restricted. The increasing demands of applications have stimulated extensive researches on soluble PIs. Typical approaches include the introduction of flexible or kinked linkages,<sup>3,4</sup> bulky substituents,<sup>5-7</sup> noncoplanar structures,<sup>8,9</sup> and spiro-skeletons<sup>10,11</sup> into a polyimide backbone.

A low dielectric constant is one of the most attractive properties of polyimide materials for microelectronics applications. In order to achieve a polymer structure with a low dielectric constant, repeating units of the polymer with low polarity and low polarizability are needed. Dielectric constant of polyimides can be lowered by incorporation of segments which minimize polarizability, by substitution with voluminous groups that lead to increased free volume and thus lowering atomic and dipolar polarizability, or by incorporation of fluorine atoms that increase hydrophobicity and decrease total polarizability.<sup>12,13</sup> Recently, Swager et al. reported a new low dielectric constant ( $k$ ) material using the ring-opening olefin metathesis polymerization of a polymer with triptycene unit.<sup>14</sup> Tsuchiya also reported a new low material with low  $k$  value by oxidative coupling polymerization of a polymer with naphthylene unit.<sup>15</sup> Kakimoto *et al.*

reported a new PIs with low  $k$  value containing POSS in main chain.<sup>16</sup>

Recently, we have successfully synthesized two series of polyimides containing 1,2,3-triazole in main chain, and they possess good solubility in organic solvents, mechanical property, as well as adhesive property.<sup>17</sup> However, because of the existence of methylene group between triazole ring and benzene ring, the glass transition temperatures of these polyimides are quite low. In order to improve the heat resistance of triazole-containing polyimides, a new series of polyimides were synthesized with triazole rings which were connected with benzene rings directly in main chains.

In this work, a new kind of heteroaromatic diamine with 1,2,3-triazole unit was successfully synthesized by the copper-catalyzed cycloaddition of azide-alkyne (CuAAC), and further novel polytriazoleimides were prepared by the polycondensation of the diamine with various commercially available aromatic tetracarboxylic dianhydrides. Meanwhile, the composition, structure, and properties of the resulting polytriazoleimides were characterized by FT-IR, <sup>1</sup>H-NMR, elemental analysis, DSC, TGA and wide-angle X-ray diffraction (WXR). Solubility, thermal property, mechanical property, dielectric property and chemical stability were systemically investigated as well.

### Experimental

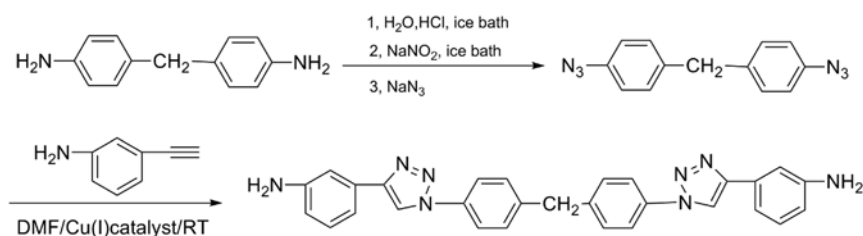
**Materials.** Bis(4-azidophenyl)methane (APM) was synthesized according to the previously reported literature.<sup>18</sup> 2,2-Bis[4-(3,4-dicarboxyphenoxy) phenyl] propane dianhydride (BPADA), 4,4'-oxydiphthalic anhydride (ODPA), and 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) were used as purchased from Shanghai Research Institute of Synthetic Resin. 4,4'-(Hexafluoroisopropylidene)

diphthalic anhydride (6FDA) was used as purchased from Aldrich. 3-Amino-phenylethyne (APE), *N,N*-dimethylacetamide (DMAc), tetrahydrofuran (THF), dimethylformide (DMF), *N*-methyl-2-pyrrolidinone (NMP), sodium ascorbate, sodium hydroxide, hydrochloric acid and  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (analytical reagent grade) were purchased and used as received from Shanghai No.1 Reagent Company.

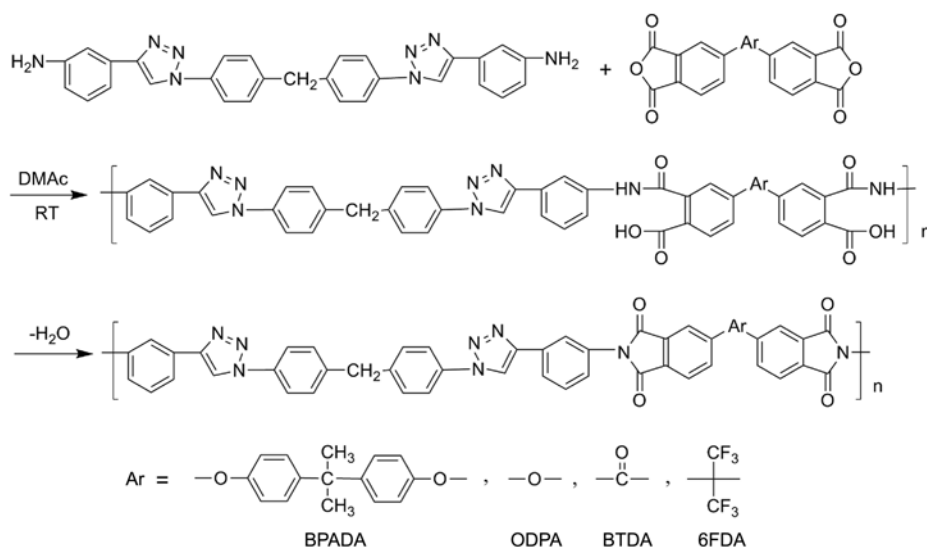
**Measurements.** Fourier transform infrared (FT-IR) spectra were determined by a Thermo Nicolet 5700 spectrometer (KBr disks).  $^1\text{H-NMR}$  spectra were recorded on a Bruker AVANCE 500 spectrometer. The inherent viscosities of polymers were measured with an Ubbelohde viscometer at 30 °C. Qualitative solubility was determined with 10 mg of polymer in 1 mL of solvent at room temperature after 24 h. Gel permeation chromatograph (GPC) analysis was carried out on a Waters 1515 Chromatograph by using DMF as an eluent at 60 °C with a flow rate of 1.0 mL/min. Elemental analyses were conducted with the Elementar Analysensysteme GmbH vario EL III. Differential scanning calorimeter (DSC) analyses were performed with a UniversalV2.3 TA Instruments Q2000 modulated system at a heating rate of 20 °C/min under flowing nitrogen. Thermogravimetric analysis (TGA) was performed on a METTLER TGA/SDTA 851 analyzer at a heating rate of 10 °C/min in nitrogen from 100 °C to 800 °C. The mechanical properties were measured on a ZWICK ZO 10/TN25 universal testing machine with  $120 \times 10 \times 0.06 \text{ mm}^3$  specimens in accordance with the national standard of China GB1040-79 at a drawing rate of

50 mm/min. Wide-angle X-ray diffraction measurements were performed at room temperature on a D/MAX 2550 VB/PC X-ray diffractometer with nickel-filtered  $\text{Cu K}\alpha$  radiation (wavelength  $\lambda = 0.15418 \text{ nm}$ ) at 40 kV and 30 mA with  $2\theta$  ranging from 10° to 60°. The dielectric constants were determined on a CONCEBT 40 instrument with 50-80  $\mu\text{m}$  thickness specimens within at frequencies of 1 and 10 MHz at room temperature. Resistance to chemical reagents of PTAI specimens ( $120 \times 10 \times 0.06 \text{ mm}^3$ ) was measured by immersing in 10 wt % HCl and NaOH solution for 168 h at room temperature in accordance with the standard ASTM D 543-06, and the weight, thickness and tensile strength were measured before and after the test.

**Synthesis of 3,3'-(1,1'-(4,4'-Methylenebis(4,1-phenylene))bis(1*H*-1,2,3-triazole-4,1-diyl))diamine (MPBTA).** The synthetic route of triazole-containing diamine is shown in Scheme 1. To a 250 mL round bottom flask, 5.00 g (0.02 mol) bis(4-azidophenyl)methane (APM), 4.68 g (0.04 mol) 3-amino-phenylethyne and 50 mL DMF were added with magnetic stirring at room temperature. The solution formed in a few minutes. Then 0.396 g (0.04 mol) sodium ascorbate, 0.25 g (0.02 mol)  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  were added into the flask. The solution was stirred for 24 h and poured into 500 mL of water to precipitate out gray solids. The solids were filtrated, washed three times with deionized water and further with acetone, and finally dried at 50 °C for 24 h in a vacuum oven. Yield: 90%, pale gray solid. Melting point: 225-227 °C. FT-IR (neat,  $\text{cm}^{-1}$ ): 3418, 3329 (N-H stretch), 3127



**Scheme 1.** Synthesis of the 1,2,3-triazole-containing diamine.



**Scheme 2.** Synthesis route of the polytriazoleimides.

(triazole-H stretch).  $^1\text{H-NMR}$  (500 MHz,  $\text{DMSO-}d_6$ , ppm)  $\delta$  9.02 (s, 2H, triazole-H), 7.56-7.98 (s, 8H,  $-\text{C}_6\text{H}_4$ ), 6.52-7.25 (m, 8H,  $-\text{C}_6\text{H}_4$ ), 5.25 (s, 4H,  $-\text{NH}_2$ ), 4.16 (s, 2H,  $-\text{CH}_2$ ). Elemental. Calcd. for  $\text{C}_{28}\text{H}_{24}\text{N}_8$ : C 71.88%, H 4.99%, N 23.13%. Found: C 71.56%, H 5.08%, N 23.36%

**Synthesis of Polytriazoleimides.** The synthetic route for polytriazoleimides (PTAIs) is shown in Scheme 2. A series of PTAIs were prepared by polycondensation of diamine MPBTA with various dianhydrides BPADA, ODPA, BTDA, and 6FDA, which were designated as PTAI-1~PTAI-4 subsequently.

To a 50 mL three-necked flask, 2.60 g (5.0 mmol) of BPADA was added gradually to a stirred solution of 2.42 g (5.0 mmol) of MPBTA in 15 mL of DMAc. The mixture was stirred at room temperature for 12 h under nitrogen atmosphere, forming a viscous solution of poly(amic acid) (PAA). The inherent viscosity of the poly(amic acid) in DMAc is 0.72 dL/g, measured at a concentration of 0.50 dL/g at 30 °C. Other poly(amic acid)s derived from diamine and other dianhydrides were prepared in the same procedure described as above.

The PAA was converted into PTAI by either chemical or thermal imidization. The chemical imidization was conducted by adding 6 mL of a mixture of 1.531 g acetic anhydride and 1.515 g triethylamine (molar ratio 1:1) into the above-mentioned poly(amic acid) solution with stirring at room temperature for 1 h, and then heating at 80 °C for 4 h. After cooling, the homogeneous PTAI solution was subsequently poured into 300 mL of ethanol to produce a solid polymer precipitate, which was removed by filtration, washed thoroughly with hot ethanol, and finally dried at 100 °C under vacuum for 24 h. The obtained PTAIs were named with a suffix -ci as PTAI-(1~4)-ci. As for the thermal imidization, the PAA solution was cast uniformly on a glass plate with a glass rod, followed by thermal curing with a programmed procedure (80 °C/2 h, 120 °C/1 h, 150 °C/1 h, 180 °C/1 h, 220 °C/1 h, 250 °C/1 h, 280 °C/1 h) to produce a fully imidized PTAI film. The various PTAI films were designated with a suffix notation -ti as PTAI-(1~4)-ti.

## Result and Discussion

**Synthesis of the Diamine.** The diamine, MPBTA containing 1,2,3-triazole ring, is synthesized by 1,3-dipolar cycloaddition with the stoichiometric molar ratios 1:2 of diazide and 3-amino-phenylethyne in DMF. The cycloaddition is carried out in the presence of the Cu (I) catalyst at room temperature. In the synthesis progress, the solution is colorless after the catalyst is added, and becomes green 10 min later with heat release. The color change is related to the formation of Cu (I) catalyst. The color of the solution turned to be dark brown 2 h later and kept unchanged until the reaction was completed. It indicates that the reaction degree is quite high after 2 h and the rate of the click reaction is very fast in the presence of Cu (I) catalyst.

Figure 1 shows FT-IR spectra of the 1,2,3-triazole-containing diamine. The FT-IR spectra of the MPBTA exhibit

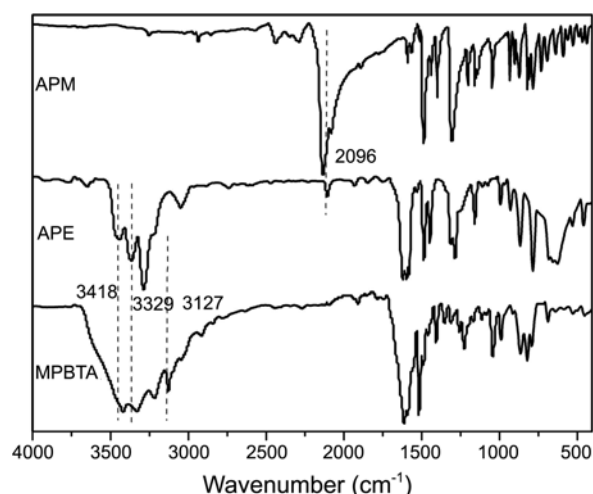


Figure 1. FT-IR spectra of MPBTA.

characteristic absorptions of the amino group at 3418 and 3329  $\text{cm}^{-1}$ . Absorption peaks of  $\text{C}\equiv\text{C-H}$  (3290  $\text{cm}^{-1}$ ),  $\text{C}\equiv\text{C}$  (2100  $\text{cm}^{-1}$ ) and  $-\text{N}_3$  (2096  $\text{cm}^{-1}$ ) for 3-amino phenylethyne (APE) and bis(4-azidophenyl)methane (APM) disappear in the spectrum, while a new peak at 3127  $\text{cm}^{-1}$  occurs for the characteristic absorptions of 1,2,3-triazole ring. It indicates that the reaction between the azide and propargyl groups have taken place and 1,2,3-triazole ring have formed. Figure 2 shows the  $^1\text{H-NMR}$  spectra of the diamine. The assignment of peaks is shown in Figure 2. The peak at 5.05 ppm is associated with the resonances of the amino group, and the peak at 9.12 ppm with the resonances of 1,2,3-triazole ring. The integrate value of various peaks corresponds with the structure of MPBTA. The analysis results of the FT-IR spectra and  $^1\text{H-NMR}$  spectra all demonstrate that the diamine derived from bis(4-azidophenyl)methane and 3-amino phenylethyne has been successfully synthesized.

**Synthesis of Polytriazoleimides.** Polytriazoleimides were obtained from 1,2,3-triazole-containing aromatic diamine MPBTA and various aromatic dianhydride by the conventional two-step polymerization method in DMAc. Firstly,

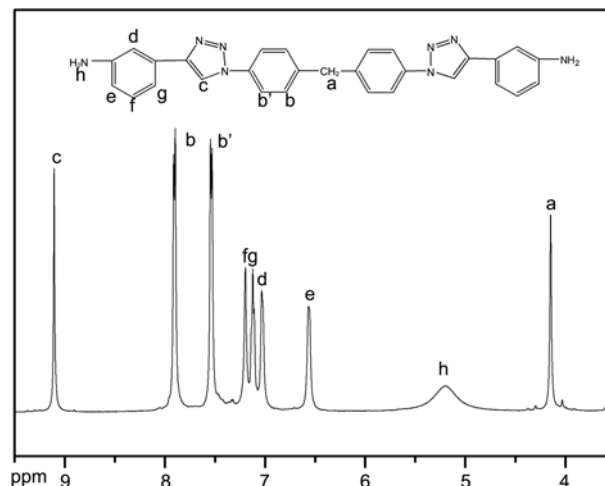


Figure 2.  $^1\text{H-NMR}$  spectra of MPBTA.

**Table 1.** Inherent viscosity and elemental analysis of PTAIs

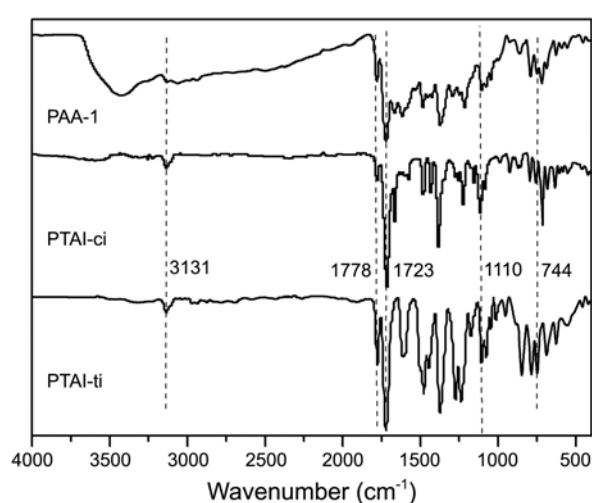
| Polymer | Yield (%) | $\eta_{inh}^a$ (dL/g) | Composition of repeating unit  | Elemental analysis (%) |       |      |       |
|---------|-----------|-----------------------|--|------------------------|-------|------|-------|
|         |           |                       |  | C                      | H     | N    |       |
| PTAI-1  | 95%       | 0.51                  | C <sub>61</sub> H <sub>44</sub> N <sub>8</sub> O <sub>6</sub>                | Calcd.                 | 74.38 | 4.50 | 11.38 |
|         |           |                       |  | Found                  | 74.12 | 4.64 | 11.25 |
| PTAI-2  | 93%       | 0.53                  | C <sub>45</sub> H <sub>30</sub> N <sub>8</sub> O <sub>5</sub>                | Calcd.                 | 71.31 | 3.90 | 14.46 |
|         |           |                       |  | Found                  | 71.18 | 3.96 | 14.40 |
| PTAI-3  | 96%       | 0.54                  | C <sub>47</sub> H <sub>30</sub> N <sub>8</sub> O <sub>5</sub>                | Calcd.                 | 71.75 | 3.84 | 14.24 |
|         |           |                       |  | Found                  | 71.83 | 3.93 | 14.14 |
| PTAI-4  | 97%       | 0.62                  | C <sub>49</sub> H <sub>30</sub> F <sub>6</sub> N <sub>8</sub> O <sub>4</sub> | Calcd.                 | 64.76 | 3.33 | 12.33 |
|         |           |                       |  | Found                  | 64.67 | 3.48 | 12.17 |

<sup>a</sup>Polyimide by chemical imidization. <sup>†</sup>Inherent viscosity ( $\eta$ ) determined on 0.5% polymer solution in DMAc at 30 °C.

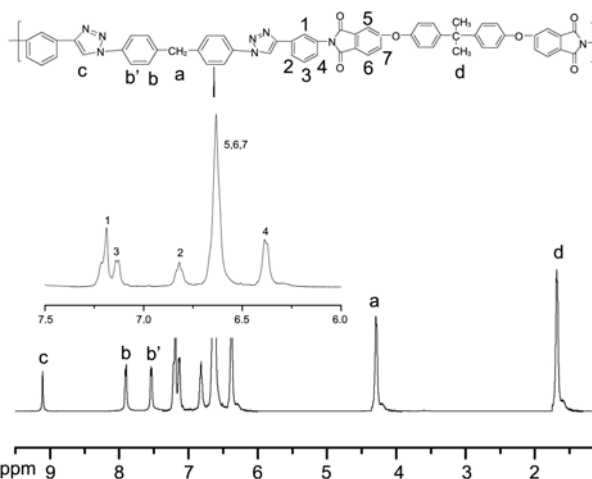
MPBTA reacted with equimolar amounts of BPADA, ODPDA, BTDA, or 6FDA to form poly(amic acid)s (PAAs) at almost 20% solid content in DMAc at room temperature. The reaction mixtures became viscous within 10-15 min, and the polymerization reaction continued for 12 h. Thus poly(amic acid) solution with high viscosity was gotten. This indicates the formation of poly(amic acid)s with high molecular weight. Secondly, the poly(amic acid)s were converted into PTAIs by either the chemical or thermal imidization method.

The experimental data of the isolated PTAIs have been summarized in Table 1. According to the data from Table 1, all PTAIs are produced with high yields (93-97%), and elemental analyses show that elemental compositions found of the repeating unit PTAIs agree with those calculated on the structures as shown in Scheme 2. The inherent viscosities of the chemically cyclized PTAIs are 0.51-0.62 dL/g at 30 °C. The number average molecular weight ( $M_n$ ) of the PTAI-1 was measured and arrives at  $3.05 \times 10^4$  by GPC with  $M_w/M_n$  1.77, while the inherent viscosity of the PTAI-1 is 0.51 dL/g. The results imply that PTAIs with high molecular weights were obtained.

FT-IR spectra of PAA and related PTAI-ci and PTAI-ti based on MPBTA and BPADA are shown in Figure 3. The complete conversion of amic acid to imide is shown by the disappearance of the amic acid bands at 1650-1700  $\text{cm}^{-1}$ , together with the appearance of characteristic imide absorption bands at 1778 (asymmetrical C=O stretch), 1723 (symmetrical C=O stretch), 1375 (C-N stretch), 1113 and 744  $\text{cm}^{-1}$  (imide ring deformation), and no absorption is seen in the range of 3350-3400  $\text{cm}^{-1}$  which are usually present in the spectra of non-cyclized precursor poly(amic acid)s. Comparing with the FT-IR spectra of PTAI obtained either by thermal or by chemical imidization, there exists similar absorption bands for them. These indicate that the conversion from PAA to PTAI is basically complete by using the two kinds of imidization methods. Meanwhile, the characteristic absorption of the 1,2,3-triazole ring at 3131  $\text{cm}^{-1}$  still exists. Figure 4 shows  $^1\text{H-NMR}$  spectrum of PTAI by chemical imidization, in which all the protons in the polymer backbone can be assigned, indicating that complete imidization is really achieved. The characterization by FT-IR,  $^1\text{H-}$



**Figure 3.** FT-IR spectra of PAA and PTAI derived from MPBTA and BPADA.



**Figure 4.**  $^1\text{H-NMR}$  spectra of PTAI-1 from MPBTA and BPADA (chemical imidization).

NMR, and elemental analysis confirms that the PTAIs have the expected chemical structures and complete imidization is achieved.

**Solubility of Polytriazoleimides.** The solubility of these PTAIs was determined by dissolving 10 mg of polymers in 1

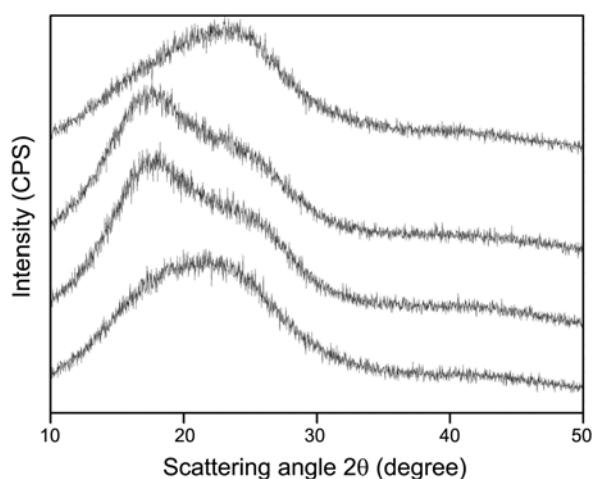
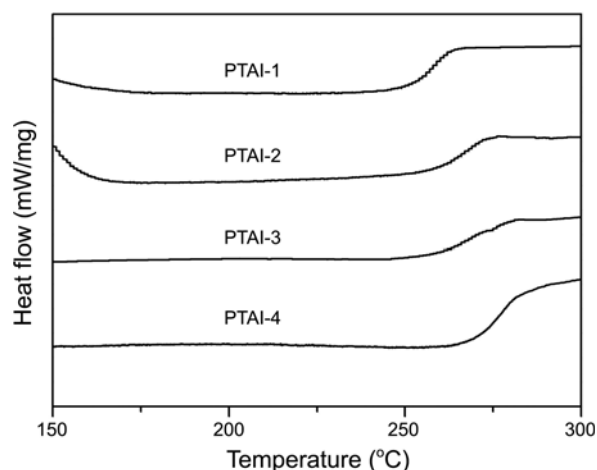
**Table 2.** Solubility of PTAI<sup>a</sup>

| Polytri-azoleimides    | Monomers    | Solvent |     |      |     |      |
|------------------------|-------------|---------|-----|------|-----|------|
|                        |             | THF     | NMP | DMAc | DMF | DMSO |
| PTAI-1-ti <sup>b</sup> | MPBTA-BPADA | -       | -   | -    | -   | -    |
| PTAI-2-ti <sup>b</sup> | MPBTA-ODPA  | -       | -   | -    | -   | -    |
| PTAI-3-ti <sup>b</sup> | MPBTA-BTDA  | -       | -   | -    | -   | -    |
| PTAI-4-ti <sup>b</sup> | MPBTA-6FDA  | -       | -   | -    | -   | -    |
| PTAI-1-ci <sup>c</sup> | MPBTA-BPADA | -       | +   | +    | +   | +    |
| PTAI-2-ci <sup>c</sup> | MPBTA-ODPA  | -       | +   | +    | +   | +    |
| PTAI-3-ci <sup>c</sup> | MPBTA-BTDA  | -       | +   | +    | +   | +    |
| PTAI-4-ci <sup>c</sup> | MPBTA-6FDA  | -       | +   | +    | +   | +    |

(+): soluble at room temperature; (-): insoluble even on heating. <sup>a</sup>Qualitative solubility was determined with 10 mg of polymer in 1 mL of solvent at room temperature. <sup>b</sup>Thermal imidization polyimide. <sup>c</sup>Chemical imidization polyimide.

mL of solvent, and the results are summarized in Table 2. PTAI-(1~4)-ti series obtained *via* thermal imidization are insoluble in all test solvents, while PTAI-(1~4)-ci series prepared *via* chemical imidization have much better solubility. The result also indicates that the polymer containing 1,2,3-triazole rings and imide units is dissolved readily in organic polar solvents at room temperature. The good solubility of these PTAs can be attributed to the presence of trifluoromethyl, flexible aryl ether linkages, and the high polarity 1,2,3-triazole ring along the polymer backbone, which increase the free volume allowing for the small solvent molecules to penetrate more easily among the polymer chains. Comparing with solubility of PTAs obtained by chemical imidization, the poor solubility of PTAs obtained by thermal imidization is possibly due to the presence of partial intermolecular crosslinking at the thermal imidization stage.<sup>19,20</sup>

**Morphology of Polytriazoleimides.** Figure 5 shows wide-angle X-ray diffraction curves of PTAs derived from MPBTA and BPADA, ODPA, BTDA and 6FDA and obtained by thermal imidization. The X-ray diffraction curves of the PTAI-ti show a wide diffraction peak. PTAI-ci also demonstrates the similar results. These evidences indicate that the polymers (PTAI-1~PTAI-4) are amorphous. It is a reason

**Figure 5.** Wide-angle-X-ray diffraction diagram of the PTAI-ti.**Figure 6.** DSC thermograms of PTAs prepared by thermal imidization.

that these PTAs have a good film forming ability.

**Thermal Properties of Polytriazoleimides.** The thermal properties of PTAs were determined with DSC and TGA. Figure 6 shows the DSC curves of the PTAs prepared by thermal imidization. The analysis data of the PTAs are listed in Table 3. The values of the glass transition temperature ( $T_g$ ) of the PTAs are located in the range of 257-275 °C, which depend on the chemical structure of aromatic dianhydride component. The glass transition temperatures ( $T_g$ s) of the resulting PTAs are higher than previously reported PTAs whose main chains exist methylene group between the triazole ring and benzene ring ( $T_g$ , 208-262 °C).<sup>17</sup>

The PTAI-1 derived from MPBTA and BPADA exhibits lowest  $T_g$  because of the presence of the relative flexible groups in polymer chain. On the other hand, the PTAI-2 derived from MPBTA and ODPA and PTAI-3 derived from MPBTA and BTDA, which have a similar chemical structure, show higher  $T_g$  due to the effect of the rigid polymer backbone. The  $T_g$ s of the resulting PTAs are higher than that of commercial polyimide Ultem 1000 ( $T_g$ , 217 °C) based on bisphenol-A diphthalic anhydride and *m*-phenylene diamine and lower than that of Kapton films derived from PMDA and ODA ( $T_g$ , 390 °C).<sup>21</sup>

Figure 7 shows the TGA curves of the PTAs prepared by thermal imidization. The PTAs have high initial decomposition temperatures. As shown in Table 3, the temperatures at 5% weight losses of the thermal imidization PTAs reach

**Table 3.** Thermal Properties of PTAs

| Polymer <sup>a</sup> | $T_g^b$ (°C) | $T_{d5}^c$ (°C) | $Y_r^c$ (%) |
|----------------------|--------------|-----------------|-------------|
| PTAI-1               | 257          | 350             | 63.3        |
| PTAI-2               | 267          | 359             | 66.8        |
| PTAI-3               | 265          | 357             | 68.4        |
| PTAI-4               | 275          | 401             | 61.1        |

<sup>a</sup>Measured samples were obtained by thermal imidization. <sup>b</sup> $T_g$  was measured by DSC at a heating rate of 20 °C/min in N<sub>2</sub>. <sup>c</sup> $T_{d5}$ , temperature at a 5% weight loss. Residual yield (%) at 800 °C in N<sub>2</sub>.

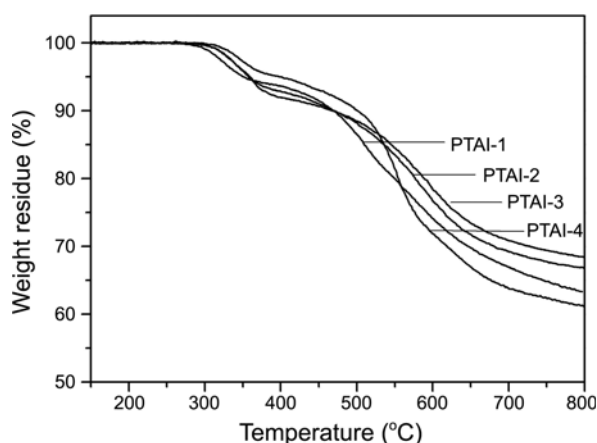


Figure 7. TGA curves of PTAIs prepared by thermal imidization.

350–402 °C. The large loss occurs in the range from 350 to 500 °C for the PTAIs due to the low thermal stability of the triazole structure. In addition, the residual weight at 800 °C for the PTAIs were 61.1–68.4%. The thermal stabilities of PTAIs vary with the structures of the polymers. The higher the chain rigidity is, the better the stability is.

**Mechanical Properties of Polytriazoleimides.** Table 4 summarizes the tensile strength, modulus and elongation of the PTAI films prepared by thermal imidization and chemical imidization. The PTAI-ti films show a tensile strength of 68.4–104.5 MPa, a tensile modulus of 3.28–3.69 GPa, and an elongation at breakage of 4.2–8.1%; while PTAI-ci films show a tensile strength of 62.3–95.4 MPa, a tensile modulus of 3.16–3.46 GPa, and an elongation at breakage of 4.0–6.8%. The mechanical property values of the PTAI-ti films are comparable to those of many commercial polyimides (Ultem 1000: tensile strength, 105 MPa; tensile modulus, 3.0 GPa; elongation at break, 60%. Avimid N: tensile strength, 110 MPa; tensile modulus, 4.13 GPa; elongation at break, 6%).<sup>21</sup> The PTAI-1-ti and PTAI-4-ti films have higher tensile strength and elongation than PTAI-2-ti and PTAI-3-ti films. These probably result from the contribution of isopropyl in BPADA monomer and hexafluoroisopropyl in 6FDA monomer to properties of the PTAIs. The PTAI films prepared by thermal imidization exhibit higher mechanical properties because some crosslinking structures are generated during the heating process of imidization, as compared with PTAIs by the chemical imidization. The crosslinking structures highly reinforce mechanical properties of the polytriazoleimides.

Table 4. Mechanical Properties of PTAIs

| Polymer | Thermal imidization    |               |                | Chemical imidization   |               |                |
|---------|------------------------|---------------|----------------|------------------------|---------------|----------------|
|         | Tensile strength (MPa) | Modulus (GPa) | Elongation (%) | Tensile strength (MPa) | Modulus (GPa) | Elongation (%) |
| PTAI-1  | 95.6 ± 2.1             | 3.47          | 6.7            | 87.7 ± 2.3             | 3.46          | 6.2            |
| PTAI-2  | 68.4 ± 0.8             | 3.28          | 4.2            | 62.3 ± 0.5             | 3.16          | 4.0            |
| PTAI-3  | 72.2 ± 1.1             | 3.43          | 4.9            | 63.1 ± 1.4             | 3.29          | 4.5            |
| PTAI-4  | 104.5 ± 1.9            | 3.69          | 8.1            | 95.4 ± 1.6             | 3.44          | 6.8            |

Table 5. Dielectric properties of the PTAI films

| Polymer <sup>a</sup> | 1 MHz       |                           | 10 MHz      |                            |
|----------------------|-------------|---------------------------|-------------|----------------------------|
|                      | $\epsilon'$ | $\tan \delta \times 10^3$ | $\epsilon'$ | $\tan \delta' \times 10^3$ |
| PTAI-1               | 2.76        | 7.0                       | 2.73        | 7.2                        |
| PTAI-2               | 3.04        | 7.3                       | 3.01        | 7.5                        |
| PTAI-3               | 2.88        | 7.1                       | 2.84        | 7.2                        |
| PTAI-4               | 2.50        | 6.6                       | 2.47        | 6.7                        |

<sup>a</sup> $\epsilon'$ ,  $\tan \delta$ , dielectric constant and dielectric dissipation factor at 1 MHz;  $\epsilon'$ ,  $\tan \delta'$ , dielectric constant and dielectric dissipation factor at 10 MHz; thickness of PTAI films obtained by thermal imidization, 60–80  $\mu\text{m}$ .

**Dielectric Properties of Polytriazoleimides.** The dielectric properties of the PTAI films were measured at 1 and 10 MHz at 25 °C and tabulated in Table 5. The dielectric constants of these PTAIs at 1 and 10 MHz are in the range of 2.50–3.04, and 2.47–3.01, and the dielectric dissipation factor ( $\tan \delta$ ) in the range of  $6.6\text{--}7.3 \times 10^{-3}$ , and  $6.7\text{--}7.5 \times 10^{-3}$ , respectively. The dielectric constant at 1 MHz is higher than that at 10 MHz. This variation is attributed to the frequency dependence of the polarization mechanisms, which depend on the dielectric constant. The dielectric constant values of these films are comparable to Kapton H (3.3 at 10 MHz), and those of many semifluorinated polyimides (6FDA-MPD: 3.0; 6FDA-7FMDA: 2.9; TFDA-*p*-APB: 2.89).<sup>20,22</sup> It indicates that the introduction of polar triazole ring has not increased the dielectric constant of PIs obviously.

The PTAI-4 containing  $-\text{CF}_3$  units has the lowest dielectric constant (at 1 MHz, at 10 MHz) in the series. This fact is due to the presence of  $-(\text{CF}_3)_2$  group which decreases the electronic polarizability owing to strong electron-withdrawing inductive effects.<sup>20</sup> The  $-\text{CF}_3$  groups determine a competition between the increase of interchain interactions (thus a decrease of the free volume) and sterical effects (and consequently increasing the free volume), but there are evidences in literature that prove the increase of free volume in the case of replacement of  $-\text{CH}_3$  groups by  $-\text{CF}_3$ .<sup>24</sup> The increased free volume, which reduces the total number of polarizable atoms in a concerned molar volume, also reduces the interchain interactions.<sup>25</sup> Therefore, polymers which two symmetric  $\text{CF}_3$  groups exhibit lower dielectric constants.

**Chemical Stability of Polytriazoleimides.** Table 6 summarizes the weight and tensile strength changes of the PTAIs. The weight and thickness of the PTAI films increase a little due to the occurrence of the swelling. The PTAI films have the weight change of  $+(0.8\text{--}1.7)\%$ , tensile strength of 53.1–98.4 MPa after HCl solution test, and weight change of

**Table 6.** Resistance of the PTAI films to acid and alkaline solution

| Polymer <sup>a</sup> | HCl solution <sup>b</sup> |                        |                      | NaOH solution <sup>b</sup> |                        |                      |
|----------------------|---------------------------|------------------------|----------------------|----------------------------|------------------------|----------------------|
|                      | $\Delta W/W_0^c$ (%)      | Tensile strength (MPa) | $\Delta S/S_0^d$ (%) | $\Delta W/W_0^c$ (%)       | Tensile strength (MPa) | $\Delta S/S_0^d$ (%) |
| PTAI-1               | +1.1                      | 88.6 ± 0.6             | -7.3                 | +0.5                       | 92.3 ± 0.4             | -3.5                 |
| PTAI-2               | +1.7                      | 53.1 ± 1.2             | -22.4                | +1.3                       | 57.6 ± 0.8             | -15.8                |
| PTAI-3               | +1.4                      | 65.2 ± 0.5             | -9.7                 | +1.2                       | 68.9 ± 0.7             | -4.6                 |
| PTAI-4               | +0.8                      | 98.4 ± 1.2             | -5.8                 | +0.7                       | 101.8 ± 1.7            | -2.6                 |

<sup>a</sup>Measured by thermal imidization PTAs with the dimension of 120 × 10 × 0.06 mm<sup>3</sup>. <sup>b</sup>Immersed in 10 wt % HCl or NaOH solution for 168 h. <sup>c</sup> $W_0$ , initial weight of the specimens;  $\Delta W/W_0$ , the weight change percentage; <sup>d</sup> $S_0$ , initial tensile strength of the specimens;  $\Delta S/S_0$ , the tensile strength change percentage.

+(0.5-1.3)%, tensile strength of 57.5-101.8 MPa after NaOH solution test. The results show that PTAI films have better resistance to alkali than acid. It occurs probably because the 1,2,3-triazole exhibits weak alkaline. The tensile strength change, except PTAI-2, are all below -10%. It is obvious that the PTAI films exhibit good dimensional stability and chemical resistance to acid and alkali solution.

### Conclusion

New processable polytriazoleimides were successfully prepared from a new kind of aromatic diamine containing triazole rings and various dianhydrides by solution polymerization and further chemical or thermal imidization. The results show that the chemical imidization PTAs, with inherent viscosities of 0.51-0.62 dL/g, have good solubility in strong polar solvents and can easily form transparent, tough and flexible films. These PTAs exhibit not only good thermal properties with a glass transition temperature ( $T_g$ ) of 257-275 °C, and a decomposition temperature at 5% weight loss ( $T_{d5}$ ) of 350-401 °C in nitrogen, but also outstanding mechanical properties with a tensile strength of 62.3-104.5 MPa, as well as an elongation at breakage of 4.0-8.1%. The thermal and mechanical properties of PTAs vary with the structure of the polymers. The higher the rigidity of the structure of the polymer is, the better the thermal property is. The certain flexibility of PTAI chains is benefit to the improvement of mechanical properties of the polymer. In addition, the 1,2,3-triazole-containing polyimides have low dielectric constants of 2.50-3.04 at 1 MHz, and 2.47-3.01 at 10 MHz. The PTAI films also exhibit good dimensional stability and chemical stability. Especially, the PTAI prepared from MPBTA and 6FDA exhibits excellent comprehensive properties.

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