Facile Synthesis of High-Performance Poly(pyrrolone imide)s from an Unsymmetric Phosphinated Triamine

Ching Hsuan Lin,[1] Chen Ming Li,[1] Chin Kuang Hsu,[1] Hou Chien Chang,[1] Tzong Yuan Juang[2]
[1]Department of Chemical Engineering, National Chung Hsing University, Taichung, Taiwan
[2]Department of Applied Chemistry, National Chiayi University, Chiayi, Taiwan
Correspondence to: C. H. Lin (E-mail: linch@dragon.nchu.edu.tw) or H. C. Chang (E-mail: hchang@dragon.nchu.edu.tw)

Received 4 January 2013; accepted 7 March 2013; published online 2 April 2013
DOI: 10.1002/pola.26666

ABSTRACT: High-performance and flexible poly(pyrrolone imide)s (PPyIs) were firstly prepared by the reaction of dianhydrides with an unsymmetric phosphinated triamine, 1-(3,4-diaminophenyl)-1-(4-aminophenyl)-1-(6-oxido-6H -dibenz <c,e> <1,2> oxaphosphorin-6-yl)ethane (1), which was prepared by a facile, one-pot procedure from the reaction DOPO, 4-aminoacetophenone in excess *o*-phenylenediamine in the presence of *p*-toluenesulfonic acid. Thermal properties of the resulting PPyIs were evaluated and compared with those of phosphinated polyimides with a similar structure. All of the prepared PPyIs films are tough and creasable. They display higher T_g (374–412 °C), lower coefficient of thermal expansion (34–46 ppm/°C), and better thermal stability (T_d 5 wt %: 456–477 °C, 800 °C char yield: 59–63%) than analogous phosphinated polyimides. © 2013 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2013**, *51*, 2709–2715

KEYWORDS: functionalization of polymers; polyimides; thermal properties; toughness

INTRODUCTION Polypyrrolones (PPys) are one of the most important semiladder heteroaromatic polymers. They were first synthesized by the reaction of dianhydride and aromatic tetraamine in 1965.[1] The reaction involves the formation of poly(amide amino acid), followed by thermal cyclization. Because of the multiaromatic structure of imide and imidazole, PPys exhibit excellent properties such as high-glass transition temperature, high-temperature stability, chemical resistance, and good fluid separation properties.[2] Xuesong and Fengcai[3] compared the gas transport properties of PPys and polyimides with a structure similarity, and found that PPys exhibit higher permeability and selectivity than analogous polyimides do. The much higher rigidity of the backbone of PPys inhibits chain packing, which results in increased permeability, while the suppression of chain segmental motion in the PPys leads to greater selectivity. However, commercially available tetraamines are generally limited to 1,2,4,5-tetraaminobenzene, 3,3′,4,4′-tetraamine biphenyl, and 3,3′,4,4′-tetraamine diphenyl ether, restricting the development of PPys. Therefore, preparation of new tetraamine is crucial in the development of PPys. Koros and Walker[4] prepared bisphenol-based tetraamines using a three-step procedure that included nitration of bisphenols, nucleophilic exchange, and reduction. Through this approach, tetraamines, 3,3′,4,4′-tetraamine biphenyl isopropylidene and 3,3′,4,4′-tetraamine biphenyl hexafluoroisopropylidene were successfully prepared from bisphenol A and hexafluoro bisphenol A, respectively. Vora et al.[5] prepared 3,3′,4,4′-tetraamine biphenyl hexafluoroisopropylidene by a different strategy using aminophenol hexafluoropropane as the starting material. PPy based on hexafluoroisopropylidene-bisphthalic anhydride (6FDA) and 3,3′,4,4′-tetraamine hexafluoroisophenylene biphenyl showed attractive transport properties, high permeability and good selectivity. Another limitation for the development of PPys is their poor solubility in organic solvents. PPys resulting from ester-,[6] amide-,[7] and ether-containing dianhydrides[8] with aromatic tetraamines have been developed to improve their solubility and flexibility. Zhang and coworkers[9] prepared tetraamines with flexible ether linkages by a two-step procedure from bisphenols using nucleophilic substitution of bisphenol with 5-chloro-2-nitroaniline, followed by a reduction in the nitro groups. Organo-soluble poly(bis(benzimidazobenzisoquinolinones)) are prepared from the diether tetraamines and bis(naphthalic anhydrides). Yang and coworkers[10] prepared pyridine-bridge tetraamines with a bulky pendant to improve the solubility of the PPys. Previously, we also prepared organo-soluble phosphinated polyimides from asymmetric diamine with excellent mechanism, high-T_g and flame-retardant properties.[11]

Additional Supporting Information may be found in the online version of this article.

Incorporating imide linkage into PPys is a strategy to enhance the solubility and toughness without sacrificing too much in the thermal properties. Bell prepared poly(pyrrolone imides)s (PPyIs) for potential use in aerospace by copolymerizing tetraamine/diamine and dianhydride to increase the toughness of PPys.[12] Yang coworkers prepared thermosetting PMR type PPyIs by copolymerizing tetraamine/diamine, diester of diphthalic acid, and monoester of dicarboxylic acid.[13] Burns and Koros prepared PPyIs by copolymerizing tetraamine/diamine and dianhydride to control the permeability and selectivity.[14] Generally, PPyIs are prepared by the copolymerization of diamine and tetraamine with dianhydrides. To the best of our knowledge, PPyIs based on an unsymmetric triamine have not been reported. Herein, with our continuing effort to prepare high-performance polymers, an aromatic triamine, 1-(3,4-diaminophenyl)-1-(4-aminophenyl)-1-(6-oxido-6H-dibenz <c,e> <1,2> oxaphosphorin-6-yl)ethane **(1)** was prepared. Based on the polycondensation of triamine **(1)** and dianhydrides, a series of poly(pyrrolone imide)s (PPyIs) **(2a–2d)** were prepared. We found that all the prepared PPyI films are tough and creasable, and display better thermal properties than analogous polyimides. Herein, the detailed synthesis and characterization of the triamine **(1)** are reported. The thermal properties of PPyIs are also reported and compared with those of analogous polyimides.[15]

EXPERIMENTAL

Materials

9,10-Dihydro-oxa-10-phosphaphenanthrene-10-oxide (DOPO, TCI), 4-aminoacetophenone (from Acros), *o*-phenylenediamine (from Acros), and *p*-toluenesulfonic acid monohydrate (*p*-TSA, from SHOWA) were used as received. Pyromellitic dianhydride (PMDA, from Acros) was dried at 170 °C overnight before use. 3,3′,4,4′-Benzophenonetetracarboxylic dianhydride (BTDA, from Acros), 4,4′-oxydiphthalic anhydride (ODPA, from Chriskev), and 3,3′,4,4′-biphenyltetracarboxylic dianhydride (BPDA, from Chriskev) were recrystallized from acetic anhydride. *N*,*N*-dimethylacetamide (DMAc) was purchased from TEDIA and purified by distillation under reduced pressure over calcium hydride (from Acros) and stored over molecular sieves. The other solvents used are commercial products (HPLC grade) and used without further purification.

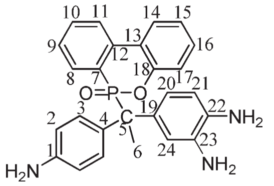
Characterization

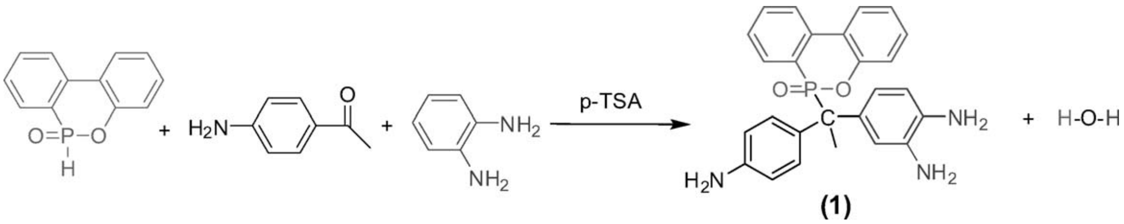
NMR measurements were performed using a Varian Inova 600 NMR in DMSO-d_6, and the chemical shift was calibrated by setting the chemical shift of DMSO-d_6 at 2.49 ppm. The assignment of individual peak of **(1)** is assisted by the correlations shown in the ^{1}H-^{1}H COSY and ^{1}H-^{13}C HETCOR NMR spectra. IR Spectra were obtained in the standard wavenumber range of 500–3650 cm^{-1} by Perkin-Elmer RX1 infrared spectrophotometer. Differential scanning calorimeter (DSC) scans were obtained by a Perkin-Elmer DSC 7 in a nitrogen atmosphere at a heating rate of 20 °C/min. Dynamic mechanical analysis (DMA) was performed with a Perkin–Elmer Pyris Diamond DMA with a sample size of $5.0 \times 1.0 \times 0.2$ cm^3. The storage modulus E' and tan δ were determined as the sample was subjected to a temperature scan mode at a programmed heating rate of 5 °C/min at a frequency of 1 Hz. The test was performed by a bending mode with amplitude of 5 μm. Thermal mechanical analysis (TMA) was performed by a SII TMA/SS6100 at a heating rate of 5 °C/min. Thermal gravimetric analysis (TGA) was performed with a Perkin-Elmer Pyris1 at a heating rate of 20 °C/min in an atmosphere of nitrogen or air. The flame retardancy of polyimides was performed by a UL-94VTM vertical thin test. In that test, an 8″ × 2″ sample was wrapped around a 1/2″ mandrel, and then taped on one end. The mandrel was removed, leaving a cone-shaped sample that was relatively rigid. The two flame applications took 3 s each for the UL-94 VTM vertical thin film. After the first ignition, the flame was removed and the time for the polymer to self-extinguish (t_1) was recorded. Cotton ignition was noted if polymer dripping occurred during the test. After cooling, the second ignition was performed on the same sample and the self-extinguishing time (t_2) and dripping characteristics were recorded. If t_1 plus t_2 was less than 10 s without any dripping, the polymer was considered to be a VTM-0 material. If t_1 plust$_2$ was in the range of 10–30 s without any dripping, the polymer was considered to be a VTM-1 material.

Synthesis of (1)

DOPO 5.00 g (21.7 mmol), 4-aminoacetophenone 2.94 g (21.7 mmol), *p*-TSA 0.20 g (4 wt % based on the weight of DOPO), and *o*-phenylenediamine 11.70 g (108.5 mmol, fivefold equivalents) were introduced into a 250-mL round bottom glass flask equipped with a nitrogen inlet and a magnetic stirrer. The mixture was stirred at 130 °C for 24 h. The precipitate was filtered and washed with ethanol. Purple powder (71% yield) 1-(3,4-diaminophenyl)-1-(4-aminophenyl)-1-(6-oxido-6H -dibenz <c,e> <1,2> oxaphosphorin-6-yl)ethane **(1)** with a sharp melting point at 238 °C (by DSC) was obtained. Elem. Anal. for $C_{26}H_{24}N_3O_2P$: Calcd. C 70.74%, H 5.48%, N 9.52%; Found C 70.60%, H 5.55%, N 9.46%

^{1}H NMR (ppm, DMSO-d_6), $\delta = 1.45$ (3H, H^{6}), 4.39 (4H, NH$_2$), 5.01 (2H, NH$_2$), 6.37 (2H, H^{2}), 6.41 (2H, H^{21}), 6.62 (1H, H^{20}), 6.69 (1H, H^{24}), 6.92 (2H, H^{3}), 7.00 (1H, H^{11}), 7.19 (1H, H^{15}), 7.22 (1H, H^{17}), 7.37 (1H, H^{16}), 7.63 (1H, H^{9}), 8.01 (1H, H^{14}), 8.08 (1H, H^{8}). ^{13}C NMR (ppm, DMSO-d_6), $\delta = 24.21$ (C^{14}), 51.83 (C^{13}), 112.95 (C^{22}), 113.84 (C^{17}), 114.87 (C^{20}), 117.51 (C^{16}), 119.15 (C^{8}), 121.08 (C^{11}), 123.22 (C^{10}), 123.33 (C^{1}), 123.84 (C^{6}), 125.34 (C^{5}), 125.65 (C^{12}), 127.57 (C^{3}), 130.32 (C^{23}), 130.52 (C^{7}), 132.05 (C^{4}), 132.10 (C^{15}), 132.97 (C^{2}), 133.51 (C^{24}), 134.51 (C^{18}), 135.86 (C^{19}), 147.38 (C^{21}), 150.78 (C^{9}).





SCHEME 1 Synthesis of triamine (**1**).

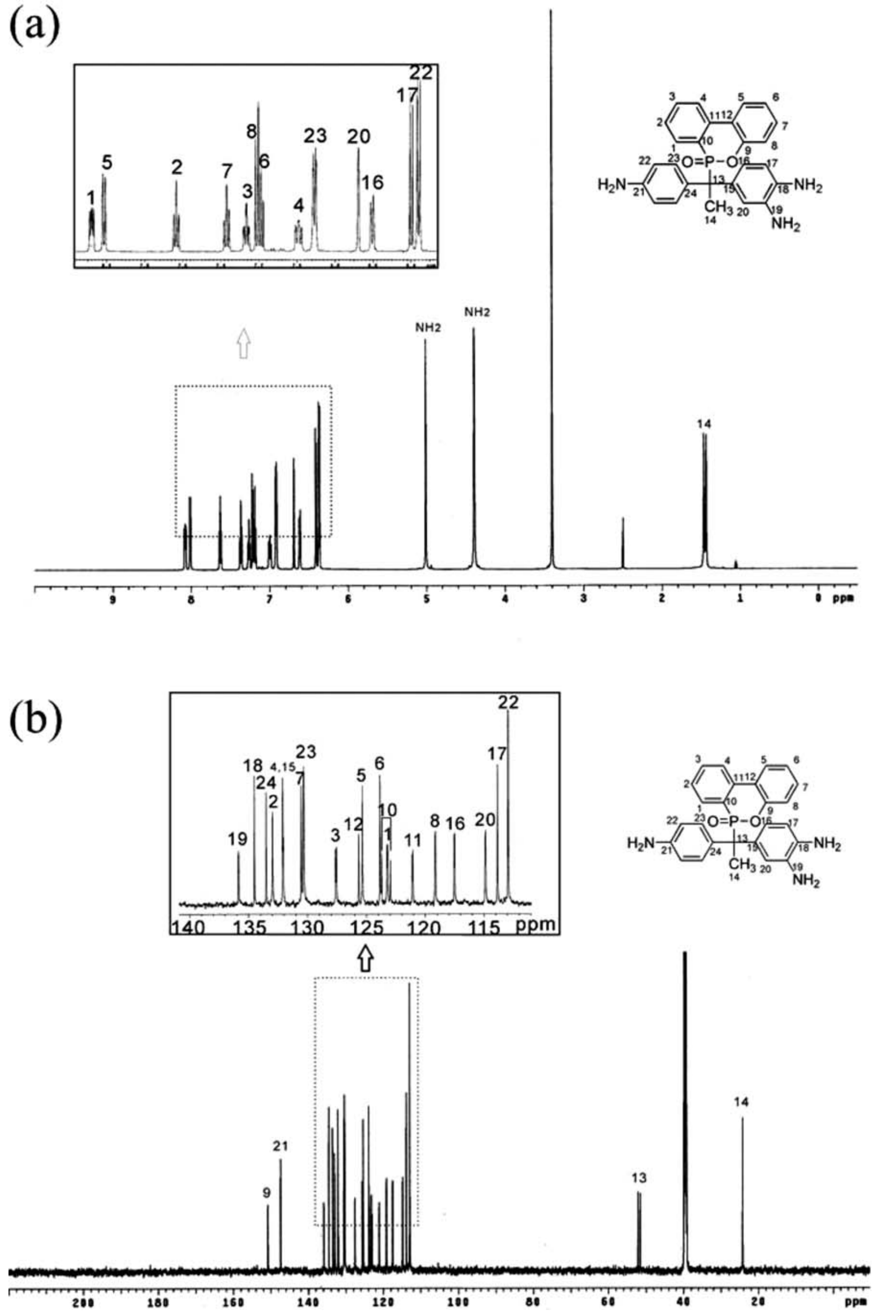
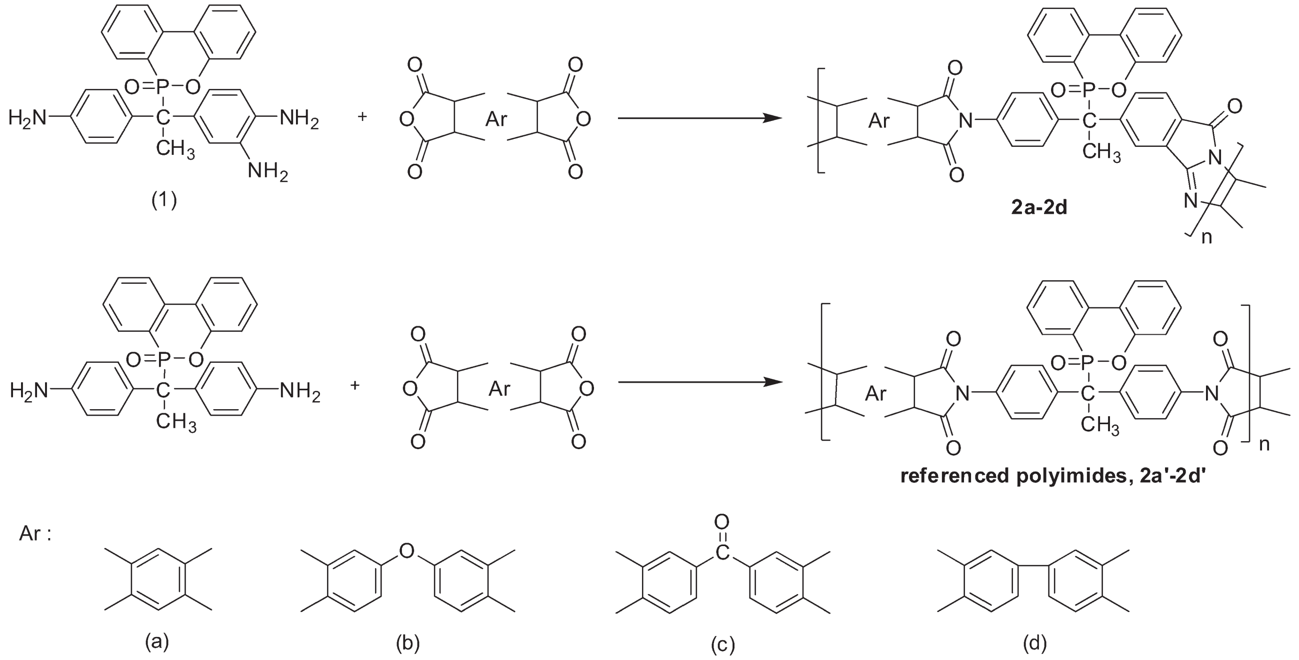


FIGURE 1 (a) ^{1}H and (b)^{13}C NMR spectra of triamine (**1**).



SCHEME 2 Synthesis of PPyIs **2** and referenced polyimides **2′**.

Preparation of PPyIs

PPyIs were prepared by reacting **(1)** with an equal mole of dianhydrides (a–d). The synthesis of PPyIs is exemplified by specific synthesis of **2b** from the condensation of **(1)** and ODPA. The other PPyIs were similarly prepared. **(1)** 0.4415 g (1.000 mmol), two drops of isoquinoline, and m-cresol 15 mL were added into a 100-mL three-neck round-bottom flask equipped with a magnetic stirrer and nitrogen inlet. After **(1)** had dissolved completely, ODPA 0.3102 g (1.000 mmole) was quickly added and the mixture was reacted at reflux temperature for 12 h. The viscous solution was then cast on glass using an automatic film applicator, and dried at 80 °C overnight and imidized at 100 °C (1 h), 200 °C (1 h) and 300 °C (1 h), respectively.

RESULTS AND DISCUSSION

Synthesis of (1)

In this work, triamine **(1)** was facilely prepared by the reaction of DOPO, 4-aminoacetophenone and *o*-phenylenediamine using *p*-TSAS as the catalyst (Scheme 1). The excess o-phenylenediamine (fivefold equivalent) plays the roles of both a reactant and the reaction medium. The only byproduct is water, so the atom efficiency of this reaction is relatively high.

Figure 1 shows the (a) ^{1}H and (b) ^{13}C NMR spectra of **(1)**. In the ^{1}H NMR spectrum, two amino peaks at 5.0 ($C^{21}—NH_2$) and 4.4 ($C^{18}—NH_2$ and $C^{19}—NH_2$) ppm were observed. The resonance between the ortho amino groups upshifted the chemical shift 4.4 ppm. Methyl peaks at around 1.5 ppm were observed**.** The methyl signals were split into two peaks with a coupling constant of 17.4 Hz because of a $^3J_{P\text{-}H}$ coupling. The assignment of Ar-H, assisted by the correlations in the ^{1}H-^{1}H COSY spectrum (Supporting Information Fig. S1), confirms the structure of **(1)**. In the ^{13}C NMR spectrum, due to the P-C ^{1}J coupling, the C^{13} signals were split into two peaks at 51.1 and 51.7 ppm with a coupling constant of 92 Hz. The C^{10} signals were also split into two peaks at 122.6 and 123.4 ppm with a coupling constant of 111.0 Hz for the same reason. The Ar-C peaks, assigned by the correlations in the ^{1}H-^{13}C HETCOR spectrum (Supporting Information Fig. S2), were detailed in Figure 1(b), also confirming the structure of **(1)**. In the ^{31}P NMR spectrum, only one ^{31}P NMR peak at 40.4 ppm was observed, indicating the intactness of the biphenylene phosphinate pendant during preparation.

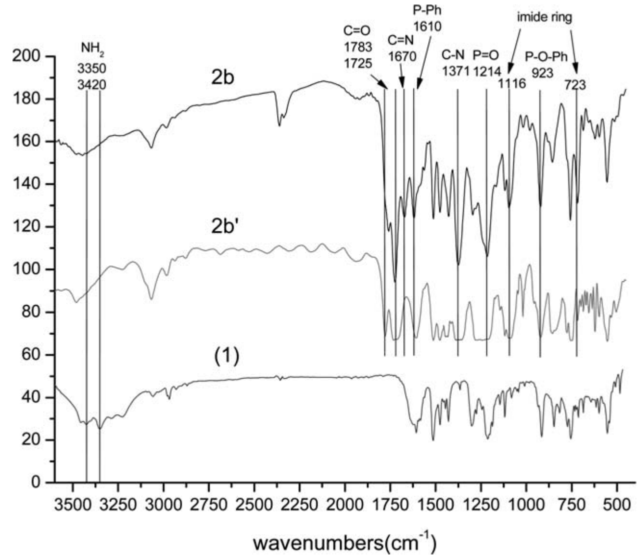


FIGURE 2 IR spectra of **2b**, **2b′**, and (**1**).

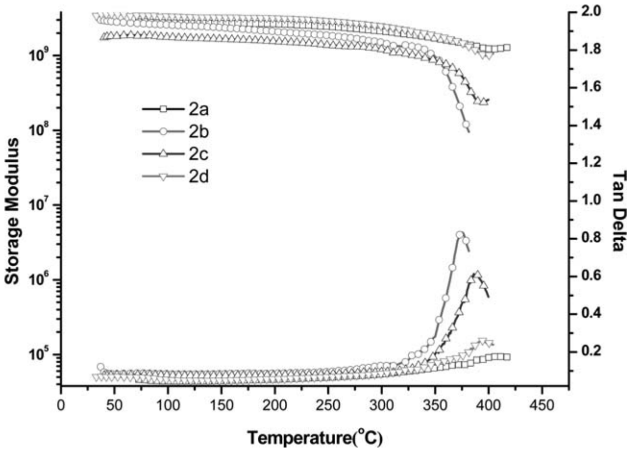


FIGURE 3 DMA thermograms of PPyIs **2**.

Referring to the reaction mechanism reported by Choi and coworker[16] and Kray and Rosser [17] a reaction mechanism was proposed for the preparation of **(1)** in Supporting Information Scheme S1. In Supporting Information Scheme S1, DOPO attacks the carbonyl group of 4-aminobenzophenone via a nucleophilic addition, forming an intermediate with a tertiary hydroxyl group. The tertiary hydroxyl group is then protonated by the acid. Spontaneous dissociation of the protonated hydroxyl group occurs to yield a tertiary carbocation. The o-phenylenediamine then reacts with the resulting carbocation via an electrophilic substitution, yielding **(1)**.

Polymer Synthesis

PPyIs (**2a-2d)** were prepared by reacting **(1)** with various commercially available dianhydrides (**a–d**) in m-cresol through high temperature solution polymerization (Scheme 2). The yield is quantitative. Figure 2 shows the IR spectra of **2b**, the referenced polyimide **2b′**, and **(1)**. The absorptions of C═O asymmetric and symmetric stretches at 1783 and 1725 cm^{-1} were clearly observed for **2b**. The absorptions at 1371 cm^{-1} (C—N Stretch), 1116 and 723 cm^{-1} (imide ring deformation) support the imide structure of **2b**. In particular, a C═N absorption at 1670 cm^{-1}, which is not observed in **2b′**, supports the structure of pyrrolone. As shown in Figure 2, the amino absorptions of **(1)** are located at 3350 and 3420 cm^{-1}. However, no obvious amino absorptions were observed in **2b**, supporting the cyclization of imide and pyrrolone.

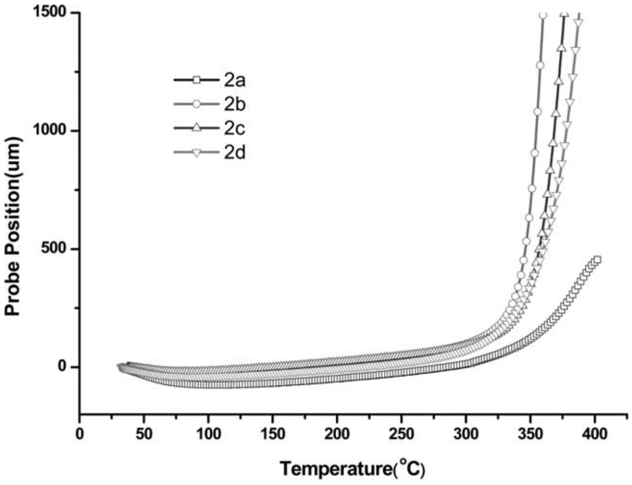


FIGURE 4 TMA curves of PPyIs **2**.

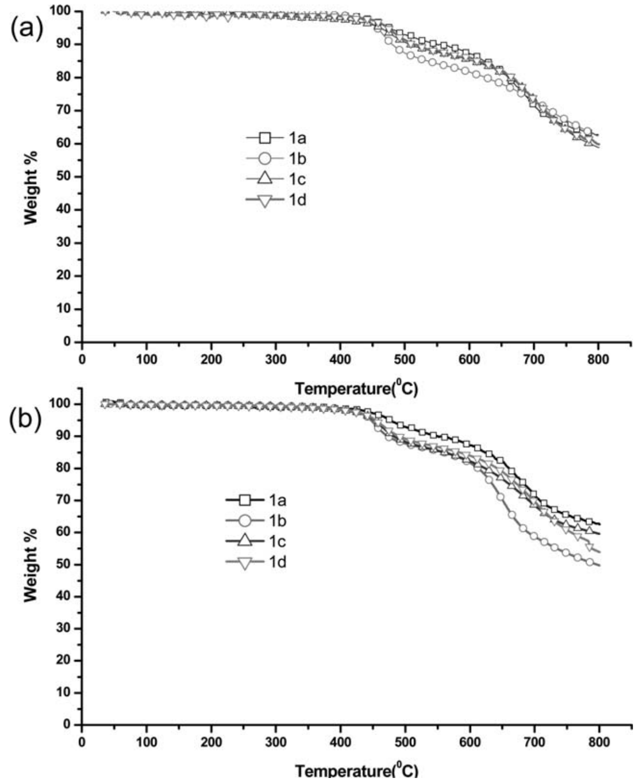


FIGURE 5 TGA thermograms of **2** in the atmosphere of (a) nitrogen and (b) air.

Film Quality and Thermal Properties

As all of the PPyI films are tough and creasable, DMA and TMA were applied to evaluate their thermal mechanical properties and dimensional stability. No GPC data were available since the films are insoluble in THF. However, all the films are tough and creasable, so the molecular weights are thought to be relatively high. Figure 3 shows the DMA thermograms of the PPyIs **2**. The value of T_g obtained from the peak temperature of tan(delta) is as high as 412, 374, 388, and 393 °C for **2a–2d**, respectively. Among the PPyIs, **2a** shows the highest T_g value due to the rigid pyromellitic moieties. In contrast, **2b** displays the lowest T_g value because of the flexible ether linkage. Except for **2a**, the T_g values of PPyIs **2** are 50–60 °C higher than those of analogous polyimides,[15] demonstrating the high-T_g characteristic of the pyrrolone linkage.

Figure 4 shows the TMA curves of PPyIs **2**. The T_g values measured by TMA are in the range of 378–304 °C, which is slightly lower than those measured by DMA. CTE at 100–250 °C are in the range of 34–46 ppm/°C. The CTE values are

TABLE 1 Thermal Properties of PPyIs **(2)** and Ref PI **(2′)**

						$T_{d5\%}$[e]		Char Yield[f]	
Sample Code	Film Quality	E' (GPa)[a]	T_g (°C)[b]	T_g (°C)[c]	CTE[d]	N_2	Air	N_2	Air
2a	creasable	2.82	412	378	34	477	477	63	63
2b	creasable	2.82	374	345	46	456	447	62	50
2c	creasable	1.82	388	355	43	474	452	60	60
2d	creasable	3.58	393	361	38	462	454	59	54
2a′	creasable	4.49	392	388	42	435	448	57	34
2b′	creasable	4.44	318	304	48	439	447	51	21
2c′	creasable	3.39	326	312	50	426	439	55	21
2d′	creasable	4.69	343	330	43	437	439	50	20

[a] Measured by DMA at a heating rate of 5 °C/min; storage modulus (E') are recorded at 50 °C.
[b] Peak temperature of tan(δ) in the DMA thermogram.
[c] Measured by TMA at a heating rate of 5 °C/min.
[d] Coefficient of thermal expansion are recorded from 100 to 250 °C.
[e] Temperature corresponding to 5% weight loss by thermogravimetry at a heating rate of 20 °C/min in the atmosphere of nitrogen or air.
[f] Residual weight % at 800 °C in the atmosphere of nitrogen or air.

smaller than those of the analogous polyimides, displaying the dimensional stability of the pyrrolone linkage is better than that of the imide linkage.

Thermal Stability and Flame Retardancy

The thermal stability of the PPyIs was evaluated by TGA in an atmosphere of (a) nitrogen and (b) air (Fig. 5 and Table 1). The 5 wt % degradation temperatures of the PPyIs **2** range from 477 to 456 °C, which are approximately 30 °C higher than those of **2′**. Therefore, the semiladder structure of pyrrolone that exhibits better rigidity than linear imide[2,3] is thought to be responsible for the enhanced thermal stability. The char yields in a nitrogen atmosphere are in the range of 63–59 wt %, and are 5–10 wt % higher than those of **2′**. As listed in Table 1, the difference in the char yields of **2** in nitrogen and air is smaller than that of **2′**. For example, the difference in the char yield of **2b** is 12 wt %, while the value is 30 wt % for **2b′**. The TGA data demonstrate the better anti-oxidative properties of the pyrrolone linkage. The flame retardancy of the PPyIs was measured by a UL-94VTM vertical thin test (Table 2). The $t_1 + t_2$ value was less than 3 s for the PPyIs. Therefore, they belong to the VTM-0 grade. Experimental data also show that the total burning time of PPyIs is comparable with the analogous phosphinated polyimides **2′**. In contrast, the $t_1 + t_2$ took more than 6 s for Kapton. Although Kapton also belongs to the VTM-0 grade, the shorter total burning time of PPyIs **2** demonstrates the excellent flame retardancy provided by the phosphorus element.

TABLE 2 Data of UL-94 VTM test for **2**, **2′**, and Kapton

Sample Code	First Burning Time (s)	Second Burning Time (s)	Dripping	UL-94 Grade
2a	0.9 (0.7)[a]	0.4 (0.2)	No	VTM-0
2b	1.4 (1.5)	0.3 (0.3)	No	VTM-0
2c	1.3 (1.2)	0.3 (0.3)	No	VTM-0
2d	1.3 (1.0)	0.4 (0.3)	No	VTM-0
Kapton	4.6	1.8	No	VTM-0

[a] The data in the parentheses is the average burning time of polyimide **2′**.

CONCLUSIONS

We have revealed a one-pot process to prepare an unsymmetric triamine **(1)**. Based on **(1)**, a series of phosphinated PPyIs were prepared. Because of the unsymmetric structure of **(1)** that leads to irregular pyrrolone and imide sequence, all the PPyIs are soluble in m-cresol. Tough and creasable films can be obtained even without the presence of flexible linkages in the main chain. The resulting PPyIs display higher glass transition temperature, dimensional stability and thermal stability than the analogous polyimides do. The combination of flexibility, high glass transition temperature, high thermal stability, organosolubility in m-cresol, and excellent flame retardancy makes PPyIs **2** promising high-performance polymers.

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