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Design and synthesis of unsymmetric phosphinated diamines for high- T_g , transparent polyimides

Hou Chien Chang^a, Sheng Lung Chang^a, Ching Hsuan Lin^{a,*}, Sinn Wen Chen^{b,**}

^a Department of Chemical Engineering, National Chung Hsing University, Taichung, Taiwan ^b Department of Chemical Engineering, National Tsing Hua University, Hsinchu, Taiwan

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ABSTRACT

Two phosphinated diamines, 1-(4-aminophenyl)-1-(3-t-butyl-4-aminophenyl) -1- (6-oxido-6H -dibenz <c,e> <1,2> oxaphosphorin-6-yl)ethane (1) and 1-(4-aminophenyl) -1-(3-methxoy-4-aminophenyl)-1- (6-oxido-6H -dibenz <c,e> <1,2> oxaphosphorin-6-yl)ethane (2), were prepared via a facile, one-pot reaction of DOPO, 4-aminoacetophenone and 2-tertbutylaniline or 2-anisidine in the presence of p-toluenesulfonic acid. Based on diamines (1–2), a series of unsymmetric polyimides (3–4) were prepared in NMP/xylene by high-temperature solution polymerization. Transparency polyimides 3–4 with flexibility, organo-solubility, high-T_g values (310–384 °C), and moderate thermal properties (T_d 5 wt%, nitrogen: 461–477 °C; air, 456–474 °C) can be achieved. We found that the transparency of polyimide films is related with the orientation of the biphenylene phosphinate pendant, and the orientation is influenced by the bulkiness of the ortho-substituted substituent.

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1. Introduction

Aromatic polyimides (PIs) are well-known as high performance material because of their excellent thermal and mechanical properties [1-3]. They are widely applied in electronics and aerospace industries [4,5]. Despite their outstanding properties, most PIs are typically vellow to amber in color because of the conjugation of the polymer chain and the formation of intermolecular/intramolecular charge transfer complex (CTC) [6]. This feature limits their application in optics such as flexible solar radiation protectors and orientation films in liquid crystal display devices [7-10]. Studies have reported that the incorporation of bulky pendants can reduce the CTC effect. For example, Swager et al. prepared triptycene PIs based on 2,6-diaminotriptycene. The resulting PIs exhibit high transparency and extremely low dielectric constants due to the increased free volume resulting from the triptycene structure [11]. Triptycene polyetherimides (PEIs) based on triptycene-containing dietheranhydride [12] and dietheramine [13] have been reported by Zhang et al, and Hsiao et al, respectively. Ando et al. [14,15], Harris et al. [16,17], Yang et al. [18-20], Shu et al. [21,22], Kim et al. [23,24] and Liaw et al. [25] prepared transparent fluorinated PI based on bulky trifluoromethyl pendants. Connell et al. prepared bulky diphenylphosphine oxide-containing, space environmentally stable PIs, in which low color is preferred for low solar absorptivity [26,27]. Another benefit of bulky groups is that they improve the solubility of PIs [28–36].

In our previous work, we reported a facile approach for preparing phosphinated diamines [37]. A series of PIs with high-T_g and good flame retardancy were prepared. Although they exhibited a bulky phosphinate pendant, the solubilities of the resulting PIs were not good enough due to the rigid polymer chains. In the second paper of this series [38], we introduced the unsymmetric concept to enhance the solubility. Unsymmetric diamines with ortho-dimethyl or diethyl substitution were designed, and the corresponding PIs exhibited high-Tg characteristics and good organo-solubility. Although a bulky phosphinate and two alkyl pendants were present to reduce the well-staking of the PI chains, the resulting PIs were even darker than the reference PI, [37], in which no alkyl groups were present. X-ray single crystal diffractogram showed the unusual orientation of the phosphinate pendant [38]. Instead of being distant from the dialkyl groups to reduce the steric and electronic repulsion, the phosphinate inclined toward the diethyl groups. It was speculated that the unusual orientation was resulted from the intramolecular interaction between electron-deficient phosphorus and electron-donating dialkyl groups. Moreover, the intramolecular interaction was probably responsible for the darker colors of the resulting PIs.

We thought that if the dimethyl or diethyl substitution were replaced by a bulkier group, the phosphinate pendant might incline





^{*} Corresponding author.

^{**} Corresponding author.

E-mail address: linch@nchu.edu.tw (C.H. Lin).

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Scheme 1. Synthesis of diamines (1-2).

toward the unsbustituted 4-aminophenyl linkage due to the larger steric and electronic repulsion. This would reduce the intramolecular interaction and therefore lighten the color of the PI films. In the third part of this series, we prepared two phosphinated diamines, 1-(4-aminophenyl) -1-(3-t-butyl-4-aminophenyl)-1-(6oxido-6H -dibenz <c,e> <1,2> oxaphosphorin-6-yl)ethane (1) and 1-(4-aminophenyl) -1-(3-methxoy-4-aminophenyl)- 1-(6oxido-6H -dibenz <c,e> <1,2> oxaphosphorin-6-yl)ethane (2), for PIs with low color characteristics. The X-ray single crystal diffractions of diamines (1–2) showed that the orientation of the phosphinate pendant, as thought, was inclined toward the unsubstitued 4-amino phenyl linkage, and the color of the resulting PI films was clearly reduced. The detailed synthesis and the structureproperty relationship are reported in this work.

2. Experimental

2.1. Materials

9,10-Dihydro-oxa-10-phosphaphenanthrene-10-oxide (DOPO, TCI), 4-aminoacetophenone (Acros), 2-tertbutylaniline (Acros), 2anisidine (Acros), p-toluenesulfonic acid monohydrate (p-TSA, Showa) were used as received. Pyromellitic dianhydride (PMDA, Acros) was dried at 170 °C overnight before use. 3,3',4,4'-Benzophenonetetracarboxylic dianhydride (BTDA, Acros), 4,4'-oxydiphthalic anhydride (ODPA, Chriskev), 3,3',4,4'biphenyltetracarboxylic dianhydride (BPDA, Chriskev), and 2,2bis(3,4-dicarboxyphenyl)hexafluoropropane.dianhydride (6FDA, Chriskev) were recrystallized from acetic anhydride. The solvents used are commercial products (HPLC grade) and were used without further purification.

2.2. 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 as 2.49 ppm. IR Spectra were obtained in the standard wavenumber range of $400-4000 \text{ cm}^{-1}$ by a Perkin–Elmer RX1 infrared spectrophotometer. High-resolution mass (HRMS) measurements were performed by a Finnigan/ Thermo Quest MAT 95XL mass spectrometer by fast atom bombardment. Elemental analysis was performed on an Elementar Vario EL III. Wide-angle X-ray diffraction measurements were performed at room temperature by an MAC Science DMAX2000 Xray diffractometer with monochromatic Cu Ka radiation ($\lambda = 1.5418$ Å, operating at 40 kV and 30 mA). The scanning rate was conducted at 3°/min over a range of $2\theta = 5-40^{\circ}$. 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 0.002 cm. The storage modulus E' and tan δ were determined as the sample was subjected to the temperature scan mode at a programmed heating rate of 5 °C/min at a frequency of 1 Hz. The test was performed by tension mode with an amplitude of 25 µm. Thermo mechanical analysis (TMA) was performed by a SII TMA/SS6100 at a heating rate of 5 °C/min. Thermal gravimetric analysis (TGA) was performed by a Perkin–Elmer TGA 7 at a heating rate of 20 °C/min in a nitrogen atmosphere from 105 °C to 800 °C.



Scheme 2. Synthesis of PIs 3-4.

Gel permeation chromatography (GPC) was carried out on a Perkin–Elmer series 200a with an RI detector using THF as the eluent at 60 $^{\circ}$ C with a flow rate of 1.0 mL/min. The data were calibrated with polystyrene standards.

2.3. Synthesis of (1)

DOPO 4.80 g (22.21 mmol), 4-aminoacetophenone 3.0 g (22.21 mol), 2-tertbutylaniline 9.94 g (66.63 mmol), and p-TSA 0.192 g (4 wt% based on DOPO) were introduced into a 100-mL round-bottom glass flask equipped with a nitrogen inlet and a magnetic stirrer. The reaction mixture was stirred at 90 °C for 12 h. After that, the precipitate was filtered and recrystallized from methanol, and then dried in a vacuum oven at 120 °C for 8 h. Light

white crystal (62% yield) with a melting point of 248 °C (DSC) was obtained. The synthetic equation of diamine **(1)** is shown in Scheme 1. HR-MS(FAB+) m/z : Calcd. for C₃₀H₃₁N₂O₂P 482.2123; Anal., 483.2213 for C₃₀H₃₂N₂O₂P. ¹H-NMR (DMSO-*d*₆), δ = 1.20(9H,(CH₃)₃), 1.58(6H,H²²), 4.63(2H,NH₂), 5.23(2H,NH₂), 6.35 (1H,H¹⁶), 6.43(2H,H²³), 6.73(1H,H¹⁵), 7.04(2H,H²²), 7.07(1H,H⁴), 7.14(2H,H⁶, H²⁰), 7.22(1H,H⁷), 7.34(1H,H¹⁶), 7.34(2H,H³, H⁸), 7.65(1H,H²), 7.93(1H,H⁵), 8.04(1H,H¹). ¹³C-NMR (DMSO-*d*₆), δ = 24.39 (CH₃), 29.09 ((CH₃)₃), 33.95 (C¹⁹), 51.32 (C¹³), 51.93 (C¹³), 113.08 (C²³), 116.13 (C¹⁶), 118.81 (C⁴), 120.95 (C¹¹), 122.69 (C¹⁰), 123.23 (C¹), 123.43 (C¹⁰), 123.66 (C⁶), 125.28 (C⁵), 126.18 (C²⁰), 126.53 (C¹²), 17.04 (C¹⁵), 127.61 (C⁸), 129.40 (C¹⁴), 129.97 (C²²), 130.43 (C³), 130.74 (C²¹), 131.83 (C⁷), 132.97 (C²), 135.93 (C¹⁸), 144.15 (C¹⁷), 147.27 (C²⁴), 150.72 (C⁹). The single crystal data is shown as



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Table	1

PIs	GPC Data ^a		Solubility data ^c						
	$M_n^{\ b}$ (×10 ⁴)	M_w (×10 ⁴)	NMP	DMAc	DMSO	m-cresol	CHCl ₃	CH ₂ Cl ₂	THF
3a	_	_	+	+	+h	+h	+h	+	±
3b	4.7	8.3	+	+	+	+	+	+	+
3c	-	-	+	+	+	+	+	+	±
3d	_	-	+	+	+h	+	+	+	±
3e	4.6	7.9	+	+	+	+	+	+	+
4a	_	-	+h	±	±	+h	±	±	_
4b	-	_	+	+	±	+	+	+	±
4c	-	-	+	+	+h	+	+	+	_
4d	-	-	+h	+	±	+h	+	±	_
4e	6.6	9.0	+	+	+	+	+	+	+

^a Relative to polystyrene standard, using THF as eluent.

^b M_n: number-average molecular weight, M_w: weight-average molecular weight.

^c Solubility was tested with a 5 mg sample in 0.5 g of solvent at room temperature. +, soluble; +h, soluble on heating; ±, partially soluble on heating; -, insoluble on heating.

follows: $C_{30}H_{31}N_2O_2P$, $0.51 \times 0.45 \times 0.11 \text{ mm}^3$, monoclinic with a = 9.1227(8) Å, b = 9.4038(9) Å, c = 15.6412(15) Å, α = 80.957(2), β = 76.915(2), γ = 74.222(2) with Dc = 1.281 mg/m³ for Z = 2, V = 1251.2(2) Å [3], T = 297(2) K, λ = 0.71073 Å, *F*(000) = 512, final *R* indices: *R*1 = 0.0464, WR2 = 0.1293.



2.4. Synthesis of (2)

Diamine (2) was synthesized with a procedure similar to (1) using 2-anisidine as the starting material. White crystal (70% yield) with a melting point of 237 °C (DSC) was obtained. The synthetic equation of diamine (2) is shown in Scheme 1. HR-MS(FAB+) m/z: Calcd. for C₂₇H₂₅N₂O₃P 456.1603; Anal., 457.1691 for C₂₇H₂₆N₂O₃P. ¹H-NMR (DMSO- d_6), $\delta = 1.57(3H, CH_3)$, 3.58(3H,H¹⁹), 4.63(2H,NH₂), 5.04(2H, NH₂), 6.41(2H, H²³), 6.45(1H, H¹⁶), 6.71(1H, H¹⁵), 6.88(1H,H²⁰), 6.99(2H,H²²), 7.12(1H,H⁴), 7.16(1H,H⁶), 7.17(1H,H⁷), 7.33(1H,H⁸), 7.35(1H,H³), 7.65(1H,H²), 7.99(1H,H⁵), 8.07(1H,H¹). ¹³C-NMR (DMSO- d_6), $\delta = 24.26$ (CH₃), 51.44 (C¹³), 51.05 (C¹³), 51.35 (C⁵), 55.0 (C¹⁹), 111.2 (C²⁰), 113.03 (C¹⁶, C²³), 118.93 (C⁴), 120.89 (C¹¹), 121.22 (C^{15}), 122.59 (C^{10}), 123.27 (C^{1}), 123.32 (C^{10}), 123.78 (C^{6}), 125.31 (C^5) , 125.94 (C^{12}) , 127.68 (C^8) , 130.06 (C^{22}) , 130.34 (C^{14}) , 130.51 (C³), 131.85 (C⁷), 133.06 (C²), 135.86 (C²¹), 136.10 (C¹⁷), 145.49 (C²⁴), 147.40 (C¹⁸), 150.64 (C⁹). The Single crystal data is as follows: $C_{27}H_{25}N_2O_3P,~0.32~\times~0.25~\times~0.15~mm^3,$ monoclinic with a = 9.3407(4) Å, b = 9.9427(3) Å, c = 12.8449(5) Å, $\alpha = 78.401(3)$ o, $\beta = 83.937(3)$, $\gamma = 79.619(3)$ o with Dc = 1.322 mg/m³ for Z = 2, V = 1146.46(7) Å [3], T = 297(2) K, $\lambda = 0.71073$ Å, F(000) = 480, final *R* indices: *R*1 = 0.0404, WR2 = 0.1064.



2.5. Preparation of PIs

Pls syntheses are exemplified by the synthesis of **3a** from the condensation of **(1)** and PMDA. To a 50-mL round-bottom flask equipped with a magnetic stirrer, a Dean–Stark trap with condenser, a nitrogen inlet. **(1)** 1.4477 g (3 mmol), PMDA 0.6544 g (3 mmol) and NMP 8.5 g were added. After the monomer had dissolved completely, xylene 5 g was added. The reaction was carried out at reflux temperature for 12 h. Then, the viscous Pls solution was casted on glass by an automatic film applicator, and dried at 80 °C overnight and 100 °C (1 h), 200 °C (2 h), respectively. The other Pls **(3b–3d, 4a–4d)** were similarly prepared. The synthetic equation of Pls **3–4** is shown in Scheme 2.

3. Results and discussion

3.1. Synthesis of (**1**–**2**)

Unsymmetric diamine **(1-2)** with the t-butyl/methoxy substituent were prepared by a one-pot reaction of DOPO, 4-aminoacetophenone in excess 2-tertbutylaniline (or 2-anisidine) using p-TSA as the catalyst (Scheme 1).

The excess 2-tertbutylaniline (or 2-anisidine) played the roles of both reactant and reaction medium. Initially, a similar reaction condition (130 °C for 24 h) [37,38] was applied to prepare unsymmetric diamines **(1–2).** However, judging from the NMR spectra, complicated products were obtained. It is speculated the t-



Fig. 2. WXRD diffraction of PIs 3.



Fig. 3. Picture of PI 3a, 4a, and ref PI.

butyl/methoxy and amine group are both para-directed substituents. Electrophilic substitution might occur at two position sites, resulting in complicated products at high temperatures. After changing to a mild reaction condition (90 °C, 12 h), diamines (1–2) were successfully synthesized. Therefore, the reaction temperature is crucial for the electrophilic substitution of compounds with two electron-donating groups.

3.2. Characterization of (1–2)

Fig. 1 shows the (a) 1 H-NMR and (b) 13 C-NMR spectra of (1). Two amino signals were observed at 4.63 and 5.23 ppm, confirming the unsymmetric structure of diamine (1). A t-butyl signal at 1.20 ppm and a methyl doublet at 1.58 ppm were observed. The splitting of methyl signal is due to the ${}^{3}J_{P-H}$ coupling, and the coupling constant is 10.2 Hz. The assignment of Ar-H, assisted by the correlations in the ¹H-¹H COSY NMR spectrum (Figure S1), confirms the structure of (1). The signals of aliphatic carbon adjacent to phosphorus (C¹³) were split into two peaks at 51.3 and 51.9 ppm with a coupling constant of 92 Hz due to the P–C 1 coupling. The signals of aromatic carbon adjacent to phosphorus (C^{10}) were also split into two peaks at 122.7 and 123.4 ppm with a coupling constant of 111 Hz for the same reason. The assignment of Ar-C, assisted by the correlations in the ¹H-¹³C HETCOR NMR spectrum (Figure S2), also confirms the structure of (1). Unsymmetric diamine (2) was characterized by ¹H, ¹³C, ¹H-¹H COSY and



Fig. 4. UV-Vis spectra of PI 3a, 4a, and ref PI.

¹H-¹³C HETCOR NMR spectra (Figure S3-S5), and the assignments of each peaks support the structure and purity.

3.3. PI synthesis

PIs **3**–**4** were prepared by reacting **(1–2)** with equal molar dianhydrides **(a–d)** in NMP/xylene by high-temperature solution polymerization (Scheme 2).

Initially, we attempted to prepare PIs **3**–**4** via the standard twostep procedure: polycondensation at a low temperature, followed by high-temperature thermal imidization. However, the viscosity of poly(amic acid) in the first step was not very high. It is speculated that the steric hindrance resulting from the *ortho*-substituted tbutyl/methoxy group reduced the reactivity. Therefore, a hightemperature solution polymerization was applied to overcome the steric hindrance. No precipitate was formed during the polymerizaiton, so PIs with moderate-to-high molecular weight were expected. Table 1 lists the GPC data of the resulting PIs. The number-average molecular weights range from 4.6 to 6.6×10^4 g/ mol, and the weight-average molecular weights range from 7.9 to 9.0×10^4 g/mol, demonstrating moderate-to-high molecular weight.

3.4. Organosolubility and crystallinity

Table 1 also lists the solubility data of PIs **3**–**4**. Except for **4a**, all PIs display good solubility in NMP, DMAc, DMSO, m-cresol and CHCl₃. PIs **3b**, **3e**, and **4e** are even soluble in THF. If one compares the solubility data of PIs **3** with those of PIs **4**, one can find that PIs **3** show better solubility. It is probably because the bulkiness of t-butyl is higher than that of the methoxy group. Fig. 2 shows the wide-angle X-ray diffraction pattern of PIs **3**. All PIs are amorphous. Although polyimides are generally amorphous, the bulky biphenylene phosphinate and unsymmetric linkage, which prevents PI chains from packing well, further enhance the amorphous characteristic of the resulting PIs.

3.5. Film quality and color

Fig. 3 shows a picture of PI 3a, 4a, and ref PI (the structure of ref PI is shown in the Figure). Fig. 4 shows UV–Vis spectra of PIs **3a**, **4a** and ref PI with thickness of 40 μ m. As shown in Figs. 3and 4, PI **3a** shows much lower cutoff wavelength and higher transparency than ref PI.

We speculated that the (1) intramolecular interaction between electron-donating dialkyl and electron-deficiant phosphorus, and (2) the π ... π interaction between phenylene and biphenylene resulted in the dark color of the PI films in previous work [38]. In



Fig. 5. Single crystal diffractograms of (1–2).

this work, the bulky t-butyl group was introduced in diamine (1) to increase the steric and electronic repulsion to prevent the intramolecular interaction. X-ray single crystal diffraction of (1) (Fig. 5) shows the orientation of the phosphinate pendant inclines toward the unsubstitued 4-aminophenyl linkage, which has conformation that is completely different from that of a diethyl substituted diamine [38]. The orientation reduces the π ... π interaction, and PIs with much better transparency are achieved. However, a detailed analysis is required to confirm the speculation.

A similar orientation was observed in diamine (2). PI 4a, as shown in Figs. 3and 4, also shows much better transparency than the ref PI. If one compares 3a and 4a, one can find that 3a shows slightly better transparency. Similar results can also be observed for the higher transparencies of 3b and 3e compared to those of 4b and **4e**, respectively (Fig. 6). The higher bulkiness of t-butyl group, which leads to not only less intramolecular but also intermolecular interaction, might be responsible for this phenomenon. In particular, the cutoff wavelengths of **3b** and **3e** are 369 and 362 nm, respectively, which are comparable with those of fluorinated diamine-based PIs with the same dianhydride moiety [39,40].

3.6. Thermal properties

Since PIs **3–4** are flexible and foldable, DMA was applied to evaluate their thermal mechanical properties. Fig. 7 shows the DMA thermograms of PIs **3**, and detailed data are listed in Table 2. T_{gs} obtained from the peak temperature of tan(delta) range from 312 to 384 °C. Generally, T_{g} is correlated with the stiffness and



Fig. 6. UV-Vis spectra of PIs 3b, 3e, 4b and 4e.



Fig. 7. DMA thermograms of PIs 3.

Table 2Thermal and mechanical properties of PIs 3–4.

Sample	Film	E'(GPa) ^a	T _g (°C)	T _g (°C)	Td _{5%} (oC) ^d		Char yield ^e	
	quality		(DMA) ^b	(TMA) ^c	N ₂	air	N ₂	air
3a	Foldable	4.0	384	353	477	460	52	46
3b	Foldable	3.7	312	279	465	458	53	38
3c	Foldable	3.7	322	284	456	456	54	37
3d	Foldable	4.3	343	318	461	462	49	45
3e	Foldable	3.9	328	292	464	457	47	1
4a	Foldable	4.0	391	358	467	466	54	39
4b	Foldable	2.4	293	262	461	460	56	43
4c	Foldable	3.5	310	276	464	456	55	37
4d	Foldable	4.5	332	304	469	474	59	47
4e	Foldable	2.3	310	281	466	469	48	4

 $^a\,$ Measured by DMA; heating rate, 5 $^\circ C/min;$ storage modulus (E') are recorded at 50 $^\circ C.$

^b Measured by DMA; the peak temperature of the Tan δ curve.

^c Measured by TMA; heating rate, 5 °C/min.

^d The 5% decomposition temperature.

^e Residual wt% at 800 °C in nitrogen.



Fig. 8. TMA curves of PIs 3.

conformation of polymer chain. Thus, the highest T_g value of **3a** may be attributed to the rigidity of PMDA moiety. In contrast, the lowest T_g value of **3b** may be due to the flexible ether linkage of OPDA moiety. A similar trend can also be observed in the **4** series.

Fig. 8 shows the TMA curves of the **3** series, and the results are listed in Table 2. T_{gs} of PIs **3** measured by TMA range from 279 to 353 °C, and the trend is the same as that observed in DMA measurement. The thermal stability of PIs **3**–**4** was evaluated by TGA. The 5 wt% degradation temperatures range from 461 to 477 °C in a nitrogen atmosphere and range from 456 to 474 °C in an air atmosphere, demonstrating moderate-to-high thermal properties.

4. Conclusions

Two phosphinated diamines (1-2), designed to reduce the intermolecular interaction, were successfully prepared. PIs based on (1-2) were prepared in NMP/xylene by high-temperature solution polymerization. PIs with an ortho t-butyl or methoxy substitution display much higher transparency and lower cutoff wavelengths than those with ortho-dialkyl substituted PIs [38]. Xray single crystal diffractograms of (1-2) show the orientation of the phosphinate pendant inclines toward the unsubstitued 4aminophenyl linkage, which has conformation with much smaller intramolecular interaction than that of a diethyl substituted diamine [38]. It is thought that the improved transparency of PIs 3-4 is related with the reduced intramolecular interaction. To the best of our knowledge, this is the first study discussing the effect of orientation of a bulky pendant on the transparency of PI films. In addition to good transparency, PIs 3-4 display flexibility, good organo-solubility, high-T_g values, and moderate thermal properties. The combination of these characteristics makes PIs 3-4 attractive for applications in microelectronic and optical devices.

Appendix. Supporting information

Supplementary data related to this article can be found online at doi:10.1016/j.polymer.2012.02.037.

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