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Synthesis and characterization of polyimides with low dielectric constants from aromatic dianhydrides and aromatic diamine containing phenylene ether unit

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Abstract

New aromatic polyimides (PIs) having the lowest dielectric constant in nonfluorinated PIs have been developed from aromatic dianhydrides and an aromatic diamine containing phenylene ether units. The diamine monomer was prepared from 4-bromophenyl ether in five steps. Polycondensations were performed in 1-methyl-2-pyrrolidinone at room temperature for 18 h, giving poly(amic acid)s (PAAs) with inherent viscosities up to 0.53 dl/g. PAAs were converted to corresponding poly(imide)s (PIs) by thermal treatment at 300 °C. New PIs showed good thermal stability (5% weight loss around 450 °C) and the low dielectric constant (2.74).

Keywords: Polyimide; Phenylene ether; Dielectric constant

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1. Introduction

Polyimides (PIs) are used as protection and insulation materials in microelectronics, because they possess good thermal and mechanical stability, solution processability, and low dielectric constants (ε) [1]. In microelectronic device circuit, the propagation velocity of the signal is inversely proportional to the square of ε of the propagation medium. Therefore, materials with the low ε are required for faster signal propagation in microelectronic devices without cross-talk in new multilevel high-density and high-speed electronic circuits.

Recently, Goto et al. [2,3] reported low ε and thermally stable PI with fluorene structure, which has the lowest ε in the nonfluorinated PIs. Introducing aromatic bulky fluorene moieties into PI structure is effective to lower the ε with keeping its superior thermal stability due to decreasing both the density of the polymer and the imide group concentration per repeating units [4]. It is of interest to develop another connecting unit between imide groups to produce PIs with low ε.

Poly(2,6-dimethyl-1,4-phenylene ether) (PPE), a typical engineering plastic, is well known as a low ε material ($\varepsilon = 2.5$) [5–7]. PPE is prepared by oxidative coupling polymerization of 2,6-dimethylphenol with a copper-amine catalyst, which is an atom-economical polymerization because the side product is only water. These findings prompted the development of new nonfluorinated PIs with the very low ε by introducing phenylene ether units in the main chains.

This report describes the synthesis and properties of novel nonfluorinated PIs with the very low ε from aromatic dianhydrides and an aromatic diamine containing phenylene ether units.

2. Experimental section

2.1. Materials

1-methyl-2-pyrrolidinone (NMP), *N*,*N*-dimethylformamide (DMF) were purified by the usual manner, and stored under an atmosphere of N_2. Pyromellitic dianhydride (PMDA) (**1a**) and 4,4′-oxydiphthalic anhydride (ODPA)

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(**1b**) were purified by recrystallization from acetic anhydride and dried at 150 °C under vacuum before use. Other reagents and solvents were used as received.

2.2. Measurements

The infrared spectroscopy (IR) was taken with a Horiba FT-210 spectrophotometer. The ^{1}H nuclear magnetic resonance (NMR) spectra were recorded on a Bruker GPX300 (300 MHz) spectrometer. Thermogravimetry (TG) and differential scanning calorimetry (DSC) were performed on a Seiko TG/DTA 6300 and DSC 6200, respectively. Refractive indices of PI films formed on quartz substrates were measured at a wavelength of 1.320 μm at room temperature with a Metricon model PC-2000 prism coupler. Using linearly polarized laser with parallel (TE: transverse electric) and perpendicular (TM: transverse magnetic) polarization to the film plane, the in-plane (n_{TE}) and out-of-plane (n_{TM}) refractive indices and the film thickness of the samples were determined. The ε at 1.0 MHz frequency was calculated from the equation as follows: $\varepsilon = 1.10 n_{\mathrm{AV}}^2$, where n_{AV} is average refractive index (i.e. $n_{\mathrm{AV}} = (2n_{\mathrm{TE}} + n_{\mathrm{TM}})/3$).

*2.3. Synthesis of 4-[2-(1-methoxy-2,6-dimethylphenyl)isopropylidene](2,6-dimethylphenol) (**2**)*

4,4′-Isopropylidenebis(2,6-dimethylphenol) (10.1 g, 35.6 mmol), iodomethane (2.21 ml, 35.6 mmol), potassium carbonate (10.3 g, 74.7 mmol), and acetone (100 ml) were refluxed for 24 h under nitrogen. After cooling this solution to room temperature, the reaction mixture was extracted with dichloromethane, and washed subsequently with 3 M aqueous NaOH solution to remove the starting material. The organic layer was evaporated, and the obtained solid was purified by silica gel column chromatography (toluene). The product was recrystallized from hexane to give a white-plate. The yield was 4.48 g (42%): mp 127–128 °C. IR (KBr): ν 3460 (Ar–OH), 2970, 2870 (C–H), 2827 (–OCH_3), 1600, 1489 (Ar), 1188 (C–O) cm^{-1}. ^{1}H NMR ($CDCl_3$, δ, ppm): 6.84 (s, 2H), 6.82 (s, 2H), 4.48 (s, 1H), 3.70 (s, 3H), 2.23 (s, 3H), 2.20 (s, 3H), 1.59 (s, 3H). Anal. Calcd for $C_{20}H_{26}O_2$: C, 80.50; H, 8.78. Found: C, 80.09; H, 8.53.

*2.4. Synthesis of 4,4′-bis{4-[2-(1-methoxy-2,6-dimethylphenyl)isopropylidene]-(2,6-dimethylphenyl)diphenyl ether (**3**)*

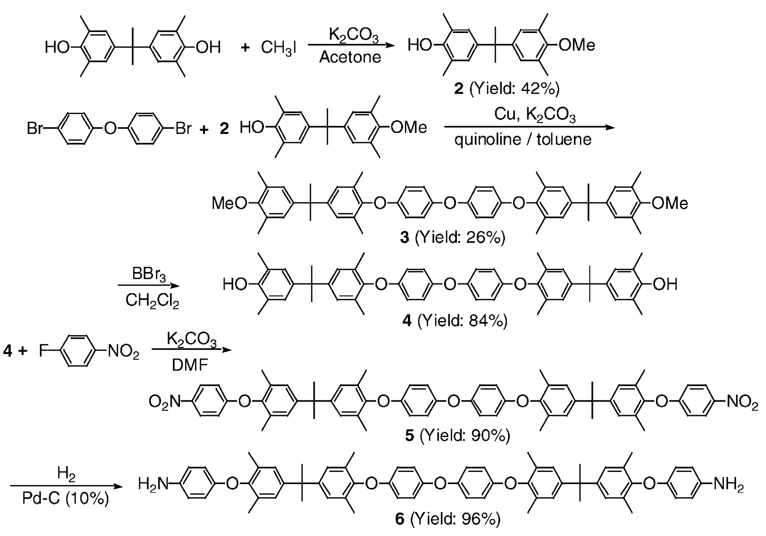
To the solution of compound **2** (5.74 g, 19.2 mmol) in quinoline (50 ml) and toluene (50 ml) was added potassium carbonate (3.32 g, 24.0 mmol), and the mixture was heated at 150 °C for 4 h to remove water with a Dean–Stark apparatus. After the formation of the potassium salt, toluene was removed by heating at 130 °C, and the solution was cooled to room temperature. To this suspension were added copper powder (0.122 g, 1.92 mmol) and 4-bromophenyl ether (3.15 g, 9.61 mmol), and the mixture was heated at 200 °C for 72 h under nitrogen atmosphere. After cooling the solution to room temperature, the reaction mixture was extracted with dichloromethane, and washed subsequently with 1 M aqueous HCl solution. The organic solvents were evaporated, and the residual oil was purified by silica gel column chromatography (toluene) to give oil. The yield was 1.90 g (26%). IR (KBr): ν 2966, 2870 (C–H), 2823 (–OCH_3), 1597, 1489 (Ar), 1196, 1176 (C–O–C) cm^{-1}. ^{1}H NMR ($CDCl_3$, δ, ppm): 6.92 (s, 4H), 6.86 (s, 4H), 6.86 (d, $J = 8.4$ Hz, 4H, ArH), 6.69 (d, $J = 9.3$ Hz, 4H, ArH), 3.71 (s, 6H), 2.25 (s, 12H), 2.08 (s, 12H), 1.62 (s, 12H).

*2.5. Synthesis of 4,4′-{2-[oxybis(1-phenoxy-2,6-dimethylphenyl)isopropylidene](2,6-dimethylphenol)} (**4**)*

A solution of **3** (1.90 g, 2.49 mmol) in dry dichloromethane (15 ml) was cooled to −78 °C. BBr_3 (9.97 ml, 9.97 mmol in dichloromethane) was added and the reaction mixture was allowed to warm to room temperature for 2 h. The brown solution was cooled on ice and deionized water was slowly added. The organic layer was separated and the aqueous phase is extracted with 20 ml of dichloromethane twice. The combined organic layers were washed once with 50 ml of water, and dried with $MgSO_4$ and concentrated. The crude material was purified by silica gel column chromatography (dichloromethane/*n*-hexane = 4/1), to give a solid. The yield was 1.53 g (84%): mp 97–99 °C. IR (KBr): ν 3568 (Ar–OH), 2966, 2870 (C–H), 1604, 1489 (Ar), 1196, 1176 (C–O–C) cm^{-1}. ^{1}H NMR ($CDCl_3$, δ, ppm): 6.92 (s, 4H), 6.85 (s, 4H), 6.86 (d, $J = 9.0$ Hz, 4H, ArH), 6.69 (d, $J = 9.0$ Hz, 4H, ArH), 4.50 (s, 2H), 2.22 (s, 12H), 2.07 (s, 12H), 1.62 (s, 12H). Anal. Calcd for $C_{50}H_{54}O_5$: C, 81.71; H, 7.41. Found: C, 81.42; H, 7.23.

*2.6. Synthesis of 4,4′-{{4-[2(4-nitrophenoxy)-2,6-dimethylphenyl]}isopropylidene}(2,6-dimethylphenoxy) diphenyl ether (**5**)*

A mixture of **4** (1.50 g, 2.04 mmol), 4-fluoro-1-nitrobenzene (0.47 ml, 4.47 mmol), potassium carbonate (0.618 g, 4.47 mmol), and dry DMF (30 ml) was refluxed for 14 h under nitrogen. The reaction mixture was allowed to cool to room temperature, and the mixture was then poured into water. The precipitate was collected by filtration and purified by silica gel chromatography (toluene) to give a solid. The yield was 1.80 g (yield 90%): mp 126–129 °C. IR (KBr): ν 2966, 2870 (C–H), 1589, 1489 (Ar), 1520, 1342 (NO_2), 1241, 1196, 1169 (C–O–C) cm^{-1}. ^{1}H NMR ($CDCl_3$, δ, ppm): 8.22 (d, $J = 9.6$ Hz, 4H, ArH), 7.02 (s, 4H), 6.98 (s, 4H), 6.91 (d, $J = 8.7$ Hz, 4H, ArH), 6.89 (d, $J = 9.0$ Hz, 4H, ArH), 6.74 (d, $J = 9.0$ Hz, 4H, ArH), 2.14 (s, 12H), 2.10 (s, 12H), 1.71 (s, 12H). Anal. Calcd for $C_{62}H_{60}N_2O_9$: C, 76.21; H, 6.19; N, 2.87. Found: C, 75.66; H, 6.16; N, 3.00.



Scheme 1. Synthesis of compound **6**.

2.7. Synthesis of 4,4′-{2-[oxybis(1-phenoxy-2,6-dimethylphenyl)isopropylidene](2,6-dimethylphenoxy)}aniline (*6*)

Diamine **6** was synthesized by the catalytic reduction of dinitro compound **5**. A mixture of **5** (1.76 g, 1.80 mmol) and 0.078 g of 10% palladium on carbon in 20 ml (*N*,*N*-dimethylacetamide (DMAc)/ethanol = 3/1) was stirred at 20 °C under hydrogen for 16 h. The solution was filtered to remove Pd–C, and the filtrate was poured into water. The precipitate was collected by filtration. The yield was 1.58 g (yield 96%): mp 123–126 °C. IR (KBr): ν 3444, 3367 (NH_2), 2966, 2870 (C–H), 1608, 1504 (Ar), 1227, 1200, 1176 (C–O–C) cm^{-1}. ^1H NMR ($CDCl_3$, δ, ppm): 6.93 (s, 4H), 6.92 (s, 4H), 6.87 (d, $J = 8.7$ Hz, 4H, ArH), 6.70 (d, $J = 8.7$ Hz, 4H, ArH), 6.59 (s, 8H), 3.41 (s, 4H, NH_2), 2.00 (s, 24H), 1.66 (s, 12H). Anal. Calcd for $C_{62}H_{64}N_2O_5$: C, 81.19; H, 7.03; N, 3.05. Found: C, 79.97; H, 6.94; N, 3.42.

2.8. Poly(amic acid)s (PAAs) (*7*)

A flame-dried 20 ml flask was charged with **6** (0.672 g, 0.732 mmol) and NMP (2.7 ml) under nitrogen. PMDA **1a** (0.160 g, 0.732 mmol) was added to this solution at 20 °C in one portion. The solution was stirred at this temperature for 18 h under nitrogen. The polymer was obtained quantitatively. The inherent viscosity of the resulting polymer was 0.38 dl/g, measured at a concentration of 0.5 g/dl in NMP at 30 °C. IR (KBr): ν 1724 (C=O, carboxylic acid), 1674 (C=O, amide) cm^{-1}. Anal. Calcd for $C_{72}H_{66}N_2O_{11}\cdot 2.17H_2O$: C, 73.64; H, 6.24; N, 2.39. Found: C, 73.63; H, 5.91; N, 2.58.

2.9. PIs (*8*)

The PI film was prepared by casting the solution of PAA **7a** on a silicon wafer at room temperature and then by

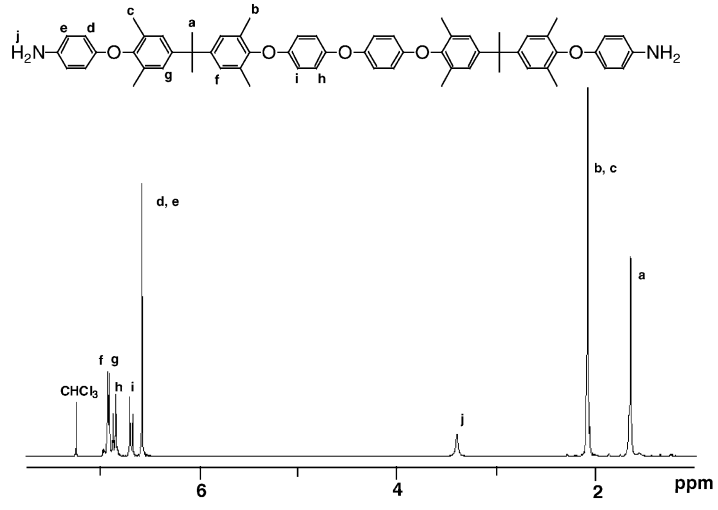


Fig. 1. ^1H NMR spectrum of **6** in $CDCl_3$ at 25 °C.

Table 1
Synthesis of poly(amic acid)[a]

Dianhydride	Diamine	Solvent	Polymer	Inherent viscosity (dl/g)[b]
1a	**6**	NMP	**7a**	0.38
1b	**6**	NMP	**7b**	0.53

[a] Polymerization was carried out with each monomer in NMP at room temperature for 18 h under nitrogen.

[b] Measured at a concentration of 0.5 g/dl in NMP at 30 °C.

heating at 70 °C for 1 h, 160 °C for 1 h, 250 °C for 0.5 h, and 300 °C for 1 h under nitrogen atmosphere. IR (KBr): ν 1778 and 1732 (imide C=O), 1373 (C–N) cm^{-1}. Anal. Calcd for $C_{72}H_{62}N_2O_9$: C, 78.67; H, 5.68; N, 2.55. Found: C, 78.83; H, 5.82; N, 2.65.

3. Results and discussion

3.1. Monomer synthesis

Diamine **6** was designed to decrease the ε with the dilution effect of the polar imide groups by the phenylene ether group (a weight basis based on polymer). Diamine **6** was prepared from 4-bromophenyl ether in five steps as shown in Scheme 1. Reaction of 4,4′-isopropylidenebis(2,6-dimethylphenol) with iodomethane in acetone gave **2**, which was reacted with 4-bromophenyl ether in the presence of Cu(I) in quinoline/toluene to yield **3** [8]. Next, the demethylation of compound **3** with BBr_3 in dichloromethane produced **4**. Then, condensation of **4** with 4-fluoro-1-nitrobenzene in anhydrous DMF in the presence of potassium carbonate afforded **5**, which was hydrogenated to monomer **6**. The structure of **6** was confirmed by IR and ^1H NMR spectroscopy. The IR spectrum of **6** showed characteristic absorptions of amino and ether groups at 3444, 3367 and 1227, 1200, 1176 cm^{-1}, respectively. Elemental analysis also supported the formation of **6**. The ^1H NMR spectrum of **6** is presented in Fig. 1. The inset in Fig. 1 shows the assignment of each resonance. All peaks are well assigned to the expected structure of **6**.

Table 2
Thermal properties of polyimides

Polyimide	T_5 (°C)[a]	T_{10} (°C)[b]	T_g (°C)[c]
8a	450	460	261
8b	450	460	230

[a] 5% weight loss temperature measured by TGA at heating rate of 10 °C/min.

[b] 10% weight loss temperature measured by TGA at heating rate of 10 °C/min.

[c] Glass transition temperature measured by DSC at heating rate of 5 °C/min.

3.2. Synthesis of polymers

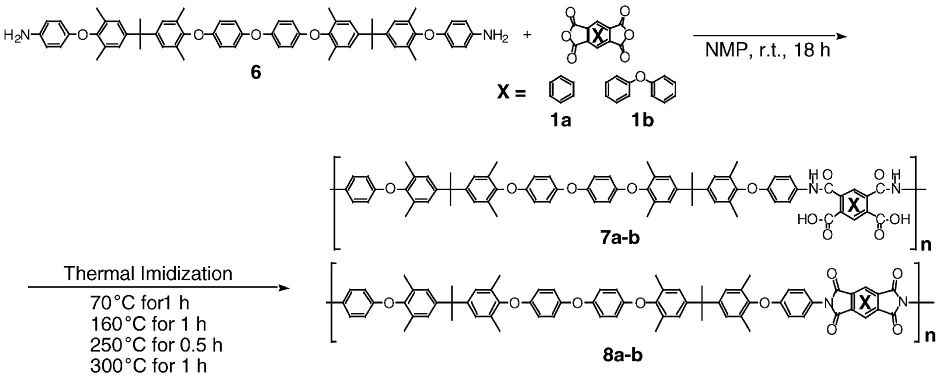
As aromatic dianhydrides, **1a** and **1b** were employed. Polycondensations of diamine **6** with aromatic dianhydrides **1** (**1a**, **1b**) were performed in NMP at room temperature for 18 h. The results are summarized in Table 1. Polymerizations proceeded smoothly, giving PAAs **7a** and **7b** in quantitative yields with high inherent viscosities (Scheme 2).

3.3. Polymer characterization

PAAs **7a–b** were identified as the expected structures by IR spectroscopy. The IR spectra of **7a** showed characteristic amide and carboxylic acid absorptions at 1724 (carboxylic acid, C=O str), 1674 (amide, C=O str), and 1543 cm^{-1} (N–H bending).

A weight loss for **7a** was observed at 100–300 °C. In this range, the weight loss was 3.1 wt%, which is in good agreement with the value (3.2 wt%) calculated from the elimination of water due to the imidization. On the basis of this finding, the thermal conversion of **7a–b** to PIs **8a–b** were performed by successive heating **7a–b** to 300 °C under N_2. The IR spectrum of thermally treated polymer **8a** is shown in Fig. 2, where characteristic imide absorptions at 1778 (asym C=O str), 1732 (sym C=O str), 1373 (C–N str) are observed and the absorptions of amic acid groups have completely disappeared.

Table 2 lists the thermal properties of the PIs evaluated by TG and DSC. The 5% weight loss temperatures (T_{d5}) in



Scheme 2. Synthesis of polyimides **8a–b**.

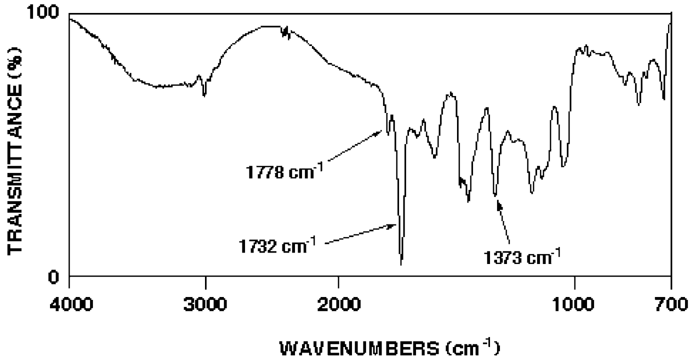
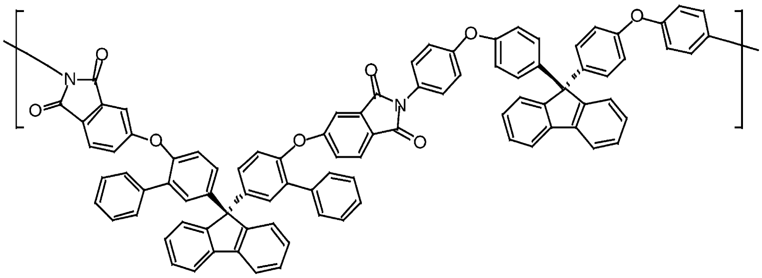


Fig. 2. IR spectrum of thermally treated polymer **8a**.



Scheme 3. Structure of fluorene-type polyimide (F–PI).

nitrogen for PIs **8a–b** were observed around 450 °C. The glass transition temperatures (T_g) were observed at 261 °C for PI **8a**. These results show that the thermal stability is lower than that of typical wholly aromatic PIs, whereas it is enough for microelectronics applications.

3.4. Dielectric constant (ε) of PIs

As listed in Table 3, the average refractive indices (n_{AV}) of PIs **8a** and **8b** were determined as 1.5784 and 1.5794, respectively. ε of a material at optical frequencies can be estimated from the refractive index n according to Maxwell's equation, $\varepsilon \fallingdotseq n^2$. The ε value at 1 MHz has been evaluated as $\varepsilon \fallingdotseq 1.10n_{AV}^2$, including an additional contribution of approximately 10% from the infrared absorption [9]. The n_{AV} of 1.5784 and 1.5794 can be translated into dielectric constant of 2.74. These values are lower than the optically estimated ε of conventional PIs (ε = 3.00) [10]. Lower ε values result from the introduction of phenylene ethers unit in diamine part that induces the dilution effect of the polar imide ring per repeating units.

In addition, the in-plane/out-of-plane birefringences (Δn) of PIs **8a** and **8b** were estimated as 0.0042 and 0.0049, respectively. The values of Δn were far lower than conventional aromatic PIs. The negligibly small birefringence implies that these polymers have low anisotropy and the polymer chain is randomly oriented in the film. The absence of birefringence was also reported for alicyclic PIs [11,12].

As described in the Introduction, the fluorene-type PI (**F–PI**) has the lowest ε in the reported nonfluorinated PIs. Table 4 lists the thermal properties and dielectric constants of **8a** and fluorene-type PI (**F–PI**) (Scheme 3). The 5% weight loss temperature of **8a** is lower than that of **F–PI**, and the ε of **8a** is comparable to that of **F–PI**.

Table 3
Refractive indices and birefringence of polyimide films

Polyimide	d (μm)[a]	n_{TE}[b]	n_{TM}[c]	n_{AV}[d]	Δn[e]	ε[f]
8a	6.0	1.5798	1.5756	1.5784	0.0042	2.74
8b	13.8	1.5810	1.5761	1.5794	0.0049	2.74

[a] Film thickness.
[b] In-plane refractive indices.
[c] Out-of plane refractive indices.
[d] Average refractive index; $n_{AV} = (2n_{TE} + n_{TM})/3$.
[e] Birefringence; $\Delta n = n_{TE} - n_{TM}$.
[f] Optically estimated dielectric constant; $\varepsilon = 1.10n_{AV}^2$.

Table 4
Properties of **8a** and **F–PI**

Polyimide	Imide group concentration (wt%)	T_{d5} (°C)	T_g (°C)	ε
8a	12.7	450	261	2.74[a]
F–PI	10.9[b]	525[b]	266[b]	2.77[b]

[a] Optically estimated dielectric constant; $\varepsilon = 1.10 n_{AV}^2$.

[b] Ref. [3].

4. Conclusion

Polycondensations of an aromatic diamine with aromatic tetracarboxylic dianhydrides in NMP at room temperature produced PAAs with inherent viscosities up to 0.53 dl/g. The film of PAAs was converted to transparent film of PIs by thermal treatment at 300 °C. PIs showed good thermal stability with the 5% weight loss temperature around 450 °C, and the lowest dielectric constant ($\varepsilon = 2.74$) among nonfluorinated wholly aromatic PIs.

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