

Synthesis and Characterization of Unsymmetrical Benzonitrile-Containing Polyimides: Viscosity-Lowering Effect and Dielectric Properties

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Received 14 July 2013; accepted 27 August 2013; published online 24 September 2013

DOI: 10.1002/pola.26927

ABSTRACT: A new unsymmetrical diamine, 2-(3-aminophenoxy)-6-(4-aminophenoxy)benzonitrile (3,4-APBN), is synthesized via two consecutive S_NAr reactions and the temperature-dependent reactivity of the fluorides in 2,6-difluorobenzonitrile, whose first S_NAr reaction occurs at 70 °C and second, at 100 °C, allowing timing control of reaction sequence and circumventing the transesterification side reaction. Thus, a series of polyimides (PIs) is prepared from the polymerization of 3,4-APBN with five common dianhydrides (6FDA, DSDA, OPDA, BTDA, and PMDA). For comparison, a second series is also prepared from two symmetrical diamines ([2,6-bis(3-aminophenoxy)benzonitrile (3,3-APBN) and 2,6-bis(4-aminophenoxy)benzonitrile (4,4-APBN)] and 6FDA or PMDA. The processability of the poly(amic acids) (PAAs), for the first series is greatly improved since their solution viscosities are much lower than PAAs based on symmetrical

diamines. Besides having high glass-transition temperatures (249–332 °C), and thermal stability [5% weight loss in the range of 505–542 °C (air) and 512–546 °C (nitrogen)], these PIs form tough, transparent and flexible films that have a tensile-strength range of 82.1–121.3 MPa, elongations-at-break of 5.33–9.81%, and tensile moduli of 2.11–2.97 GPa. Their film dielectric constants are 3.08–3.62 at 10 kHz, moderately higher than that (2.92) of analogous PI (CP2) without nitrile groups. Overall, we found that the reduction of structural symmetry in repeat units can improve the polymer processability as well as increasing their dielectric constants. © 2013 Wiley Periodicals, Inc. *J. Polym. Sci., Part A: Polym. Chem.* **2013**, *51*, 4998–5011

KEYWORDS: benzonitrile; dielectric properties; polyimides; transesterification; unsymmetrical diamine; viscosity

INTRODUCTION Polyimides (PI) represent one of the most important classes of specialty polymers. This is a direct result of the excellent combination of their physical and mechanical properties as well as outstanding thermal stability. In addition, their monomers are readily available, and are cheaper than many other high temperature polymers. As a result, PIs have found many applications in high performance films and fibers, coatings, and adhesives for a wide range of applications in, just naming a few, microelectronics, optoelectronics, aerospace structures, nonlinear optical devices, light-wave guiding materials, and liquid crystal displays.^{1–6} However, it is well known that fully imidized, linear PIs possess extended rigid and planar, aromatic structures are inherently insoluble in common solvents.^{7–10} As an approach to circumventing this problem, the incorporation of unsymmetrical repeat units into PIs have been recently used to improve

their solubility and processability.^{11–17} For example, the introduction of an unsymmetrical trifluoromethyl group into the polymer chain has resulted in soluble PIs without compromising the properties via the reduction in solubility-impeding inter-chain interactions.^{18–23} Aromatic poly(etherimides) derived from an unsymmetrical indane-based diamine have been evaluated for gas permeation properties.^{24,25} Unsymmetrical diamines containing thiazole ring,^{26,27} triaryl imidazole pendant group,²⁸ diphenylpyridyl pendant group,²⁹ naphthalene unit,³⁰ and phthalazinone moiety,³¹ have been designed for the syntheses of their respective PIs. In other cases, the PIs derived from unsymmetrical dianhydrides have also been prepared for the similar reasons.^{32,33} However, most of these unsymmetrical diamines and dianhydrides are not practical for large scale production because of the high cost inevitably incurred from their multistep

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syntheses. Apart from enhancing solubility to improve processibility, the reduction or elimination of structural symmetry could also have significantly influenced certain polymer properties that are important for specific applications, and such effect was rarely called out.

PIs derived from symmetrical diamines containing benzonitrile units have been studied for the piezoelectric and other dielectric applications due to the high polarity and thermal stability of the nitrile groups.^{34–37} The pendant nitrile groups promote the adhesion of the polymers to many substrates, possibly through the polar and hydrogen bonding interactions with the surface groups that are commonly containing oxygen or OH.³⁸ Polymers with high dielectric constants and low loss are in growing demand for further miniaturization of microelectronic systems.³⁹ Kakimoto et al. have showed that attaching benzonitrile pendants on certain benzophenone-based PI would significantly enhance their dielectric constants.⁴⁰ Hybrid films based on nitrile-containing PIs/inorganic particles (pyrite ash, barium and titanium oxides) have been prepared and their nanoactuation performance has been investigated.⁴¹ The piezoelectric performance of PIs containing one and two nitrile groups per repeat unit has recently been reported. The PIs containing two nitrile groups per repeat unit with higher polarity have shown higher value of remnant polarization than the ones containing only one CN per repeat unit. However, their values are still low in comparison with common piezoelectric polymers such as PVDF.³⁶ Two PIs have been prepared from an unsymmetrical benzonitrile-containing diamine, but their dielectric properties were not reported.⁴²

In this article, an unsymmetrical benzonitrile-containing diamine was synthesized via a convenient one-pot reaction and utilized in PI synthesis. As an effort to probe the structural factors at the molecular level to balance the need for high dielectric constant, low dielectric loss, and thermal stability in high performance capacitors for aerospace applications, two structurally related series of PIs containing benzonitriles have been synthesized. The effect of the unsymmetrical structure on the solution viscosity of poly(amic acid) (PAA) precursors and PIs as well as the dielectric properties of the PI films and have been studied in conjunction with the thermal, UV-vis and morphological properties of the PIs.

EXPERIMENTAL

Materials

2,6-Dichlorobenzonitrile (DCBN) and 2,6-difluorobenzonitrile (DFBN) were obtained from Aldrich Chemical Co. The aromatic tetracarboxylic dianhydrides used in this work: pyromellitic dianhydride (PMDA), 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA), 4,4'-benzophenonetetracarboxylic dianhydride (BTDA), 4,4'-oxydiphthalic dianhydride (ODPA), 3,3',4,4'-diphenylsulfone tetracarboxylic dianhydride (DSDA) and 2,2'-bis(3,4-dicarboxyphenyl)-1,1,1,3,3,3-hexafluoropropane dianhydride (6FDA), were obtained from commercial sources and purified by sublimation. All other reagents and solvents were purchased from Aldrich Chemical Co. and used as received.

Instrumentation

Transmittance Infrared (IR) spectra were recorded on a Nicolet Nexus 470 F-T spectrophotometer. Attenuated Total Reflection IR (ATR-IR) was measured on a Bruker Alpha-R spectrometer. Proton and carbon nuclear magnetic resonance spectra were measured at 300 MHz on a Bruker AVANCE 300 spectrometer. Differential scanning calorimetry (DSC) analysis was performed in nitrogen (heating rate of 10 °C/min) using a Perkin-Elmer DSC 7 Thermal Analyzer. Thermogravimetric analysis (TGA) was conducted in either nitrogen (N₂) or air atmosphere at a heating rate of 10 °C/min using a TA Hi-Res TGA 2950 thermogravimetric analyzer. Dynamic mechanical analysis (DMA) was conducted under a nitrogen atmosphere with a heating rate of 4 °C/min on a TA Instruments DMA Q800. UV-vis spectra of polymer thin films and solutions were measured at 300–800 nm on a Varian Cary-5000 UV-vis-NIR Spectrophotometer. Intrinsic viscosities were determined with Cannon-Ubbelohde No. 75 viscometers. Flow times were recorded in *N*-methyl-2-pyrrolidone (NMP) solution and polymer concentrations were approximately 0.5–0.10 g/dL at 30.0 ± 0.1 °C. Lithium bromide (1.0 wt %) was added to the solution to suppress polyelectrolyte effect. Viscosity of concentrated PAA solution (20 wt % in DMAc) was measured with LVDV-I Prime C Brookfield Digital Viscometer. Gel permeation chromatography (GPC) was carried out on an Agilent 1100 Series instrument equipped with refractive index and light scattering detectors. Tetrahydrofuran (THF) was used as the eluting solvent. Polystyrene standards were used in molecular weight determination. Gas chromatography/mass spectroscopy (GC/MS) was performed using a Varian 1200 Series instrument. Melting Points were obtained from a Buchi Melting Point Apparatus B-545 (at heating rate of 2 °C/min). Tensile strength and moduli of the PI films were determined using a Tinius Olsen H10K-S Benchtop Testing Machine with a cross-head separation speed of 1 mm/min. Wide Angle X-ray diffraction (WAXD) experiments were carried out on a Statton box camera at 53 mm sample to image plate distances in transmission mode using CuK_α generated by a Rigaku Ultrax18 system.

Dielectric Impedance Spectroscopy

Dielectric impedance experiments were performed over broad-band frequency (10⁻¹ to 10⁶ Hz) and temperature (–40 to 150 °C) ranges. Disk-like specimens, formed from cast thin films, featuring thicknesses of 40 μm, were gold-sputtered to form electrodes 10 mm in diameter and sandwiched between gold-plated brass electrodes, prior to insertion in a Novocontrol ZGS Alpha sample cell, connected to a Novocontrol Quatro Cryosystem for temperature stabilization. Broad temperature cycles were undertaken to eliminate thermal hysteresis and water contributions.

Synthesis of Unsymmetrical Diamine via Two-Pot Route 2-Chloro-6-(3-aminophenoxy)benzonitrile (3a)

Into a 500-mL three-necked round-bottomed flask (RFB) equipped with a magnetic stirrer, a Dean-Stark trap/condenser/nitrogen adaptor, a thermometer/adaptor, and a ground-joint glass stopper, 3-aminophenol (5.46 g, 50.0 mmol), potassium carbonate (8.28 g, 60.0 mmol), *N*-methyl-

2-pyrrolidinone (NMP, 100 mL) and toluene (50 mL) were charged. The reaction mixture was heated to reflux under nitrogen in an oil bath, and water was removed by azeotropic distillation with toluene (100–110 °C). After complete dehydration, the remaining toluene was distilled off until the flask temperature reached 120 °C. The reaction mixture was allowed to cool to 100 °C, 2,6-DCBN (8.60 g, 50.0 mmol) was quickly added and the mixture stirred at 120 °C for 24 h under nitrogen atmosphere. The mixture was allowed to cool to room temperature and filtered. The filtrate was poured into water. The white solid was extracted with CH₂Cl₂ and the organic layer was separated. It was washed with water three times and dried over sodium sulfate. After concentrating the extract on a rotavap, the crude liquid was passed through a short column (basic alumina; ethyl acetate/hexane 40:60 used as the eluent). Upon stripping off the solvent from the filtrate, a light yellow liquid was obtained, which solidified as white crystals.

Yield: 8.9 g (73%), m.p. 68.7–69.1 °C. Anal. Calcd. for C₁₃H₉ClN₂O: C, 63.81%; H, 3.71%; N, 11.45%. Found: C, 63.99%; H, 3.81%; N, 13.46%. FTIR (KBr, cm⁻¹): 3468, 3378 (NH₂), 2234 (nitrile). Mass spectrum (m/e): 244, 246 (M⁺). ¹H NMR (DMSO-d₆, δ in ppm): 5.40 (s, 2H, NH₂), 6.27–6.29 (d, 1H, Ar-H), 6.33 (s, 1H, Ar-H), 6.48–6.50 (d, 1H, Ar-H), 6.91–6.94 (d, 1H, Ar-H), 7.08–7.12 (t, 1H, Ar-H), 7.40–7.42 (d, 1H, Ar-H), and 7.63–7.67 (t, 1H, Ar-H).

2-Chloro-6-(4-aminophenoxy)benzonitrile (3b)

Into a 500-mL three-necked RBF equipped with magnetic stir bar, Dean-Stark trap/nitrogen inlet, a thermometer/adaptor, and a glass stopper were placed 4-aminophenol (2.73 g, 25.0 mmol), potassium carbonate (4.15 g, 30.0 mmol), 50 mL NMP and 10 mL toluene. Water was removed by azeotropic distillation by refluxing the mixture with stirring at 150 °C. After complete dehydration, the remaining toluene was removed by heating to 160 °C. The mixture was allowed to cool to 100 °C and 2,6-DCBN (4.30 g, 25.0 mmol) was added. It was heated at 120 °C for 24 h under nitrogen atmosphere with 98% conversion as indicated by previous GC testing. The mixture was allowed to cool to room temperature and filtered. The filtrate was poured into water. The white precipitate was collected by filtration and air dried. It was then recrystallized from ethanol/water (40/60) mixed solvents to afford white crystals.

Yield: 10.5 g (86%), m.p. 122.2–122.8 °C. Anal. Calcd. for C₁₃H₉ClN₂O: C, 63.81%; H, 3.71%; N, 11.45%. Found: C, 63.74%; H, 3.84%; N, 11.57%. FTIR (KBr, cm⁻¹): 3418, 3349 (NH₂), 2234 (C≡N). Mass spectrum (m/e): 244, 246 (M⁺). ¹H NMR (DMSO-d₆, δ in ppm): 5.16 (s, 2H, NH₂), 6.62–6.64 (d, 2H, Ar-H), 6.69–6.72 (d, 1H, Ar-H), 6.87–6.89 (d, 2H, Ar-H), 7.29–7.31 (d, 1H, Ar-H), and 7.53–7.58 (t, 1H, Ar-H).

Attempted Synthesis of 2-(3-Aminophenoxy)-6-(4-aminophenoxy)benzonitrile (3,4-APBN; 5) from 2-Chloro-6-(3-aminophenoxy)benzonitrile (3a)

Into a 250-mL three-necked round-bottomed flask equipped with a magnetic stirrer, a Dean-Stark trap/condenser/nitrogen adaptor, a thermometer/adaptor, and a ground-joint

glass stopper, 4-aminophenol (2.18 g, 20.0 mmol), potassium carbonate (2.76 g, 20.0 mmol), NMP (50 mL) and toluene (10 mL) were charged and water was removed by azeotropic distillation with toluene by refluxing the mixture in an oil bath at 120–130 °C with stirring and under nitrogen atmosphere. After complete dehydration, the remaining toluene was distilled off until the flask temperature reached 160 °C. The reaction mixture was allowed to cool to 130 °C, compound **3a** (4.88 g, 20.0 mmol) was added, and the mixture was stirred again at 160 °C for 24 h under nitrogen atmosphere. Then, the mixture was allowed to cool to room temperature and filtered. The filtrate was poured into water and the precipitated solid was collected by filtration and dried. The crude product was recrystallized from toluene/heptanes to afford 3.64 g (57%) of yellow crystals, m.p. 153–156 °C.

Anal. Calcd. for C₁₉H₁₅N₃O₂: C, 71.91%; H, 4.76%; N, 13.24%. Found: C, 72.08%; H, 4.75%; N, 13.33%. FTIR (KBr, cm⁻¹): 3400, 3326 (NH₂), 2226 (nitrile). Mass spectrum (m/e): 317 (M⁺). ¹H NMR (DMSO-d₆, δ in ppm): 5.17 (s, 2H, NH₂), 5.38 (s, 2H, NH₂), 6.25–6.34 (m, 2H, Ar-H), 6.38–6.66 (m, 5H, Ar-H), 6.85–6.91 (m, 2H, Ar-H), 7.01–7.11 (m, 1H, Ar-H), and 7.36–7.55 (m, 1H, Ar-H); see Figure 1.

Attempted Synthesis of 2-(3-Aminophenoxy)-6-(4-aminophenoxy)benzonitrile (3,4-APBN; 5) from 2-Chloro-6-(4-aminophenoxy)benzonitrile (3b)

Into a 250-mL three-necked round-bottomed flask equipped with a magnetic stirrer, a Dean-Stark trap/condenser/nitrogen adaptor, a thermometer/adaptor, and a ground-joint glass stopper, 3-aminophenol (2.18 g, 20.0 mmol), potassium carbonate (2.76 g, 20.0 mmol), NMP (50 mL), and toluene (10 mL) were charged and water was removed by azeotropic distillation with toluene by refluxing the mixture in an oil bath at 150 °C with stirring and under nitrogen atmosphere. After complete dehydration, the remaining toluene was distilled off until the flask temperature reached 160 °C. The reaction mixture was allowed to cool to 100 °C, compound **3b** (4.88 g, 20.0 mmol) was added, and the mixture was stirred again at 140 °C for 24 h under nitrogen atmosphere. Then, the mixture was allowed to cool to room temperature and filtered. The filtrate was poured into water and the precipitated solid was collected by filtration and dried. The crude product was recrystallized from toluene/heptanes to afford 4.35 g (68%) of yellow crystals, m.p. 153–156 °C.

2-Fluoro-6-(3-aminophenoxy)benzonitrile (6a)

Into a 500-mL three-necked flask equipped with a magnetic stirrer and two adaptors for nitrogen inlet/outlet, 3-aminophenol (8.74 g, 80.0 mmol), 2,6-DFBN (11.13 g, 80.0 mmol), potassium carbonate (13.24 g, 96.0 mmol) and NMP (150 mL) were charged. The resulting mixture was stirred under nitrogen atmosphere at 70 °C for 48 h. The mixture was allowed to cool to room temperature and poured into water. The white precipitated solid was collected by filtration, washed with water and dried. The crude product was recrystallized from toluene/heptanes (1:2) to afford 13.6g (74.5%) of white crystals, m.p. 79.8–82.6 °C.

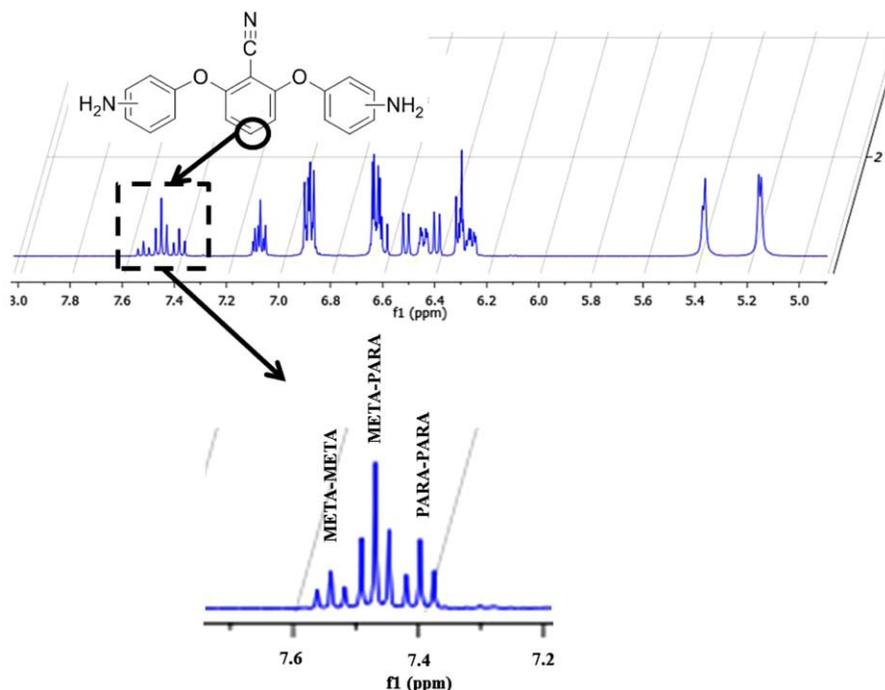


FIGURE 1 ^1H NMR spectrum of isomeric mixture of the APBN diamines. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Anal. Calcd. for $\text{C}_{13}\text{H}_9\text{FN}_2\text{O}$: C, 68.42%; H, 3.98%; N, 12.27%. Found: C, 68.48%; H, 4.07%; N, 12.31%. FTIR (KBr, cm^{-1}): 3435, 3369 (NH_2), 3132, 3077, 2232 (nitrile). Mass spectrum (m/e): 228 (M^+). ^1H NMR (DMSO- d_6 , δ in ppm): 5.39 (s, 2H, NH_2), 6.27–6.29 (d, 1H, Ar-H), 6.32 (s, 1H, Ar-H), 6.47–6.49 (d, 1H, Ar-H), 6.77–6.79 (d, 1H, Ar-H), 7.08–7.11 (t, 1H, Ar-H), 7.18–7.22 (t, 1H, Ar-H) and 7.66–7.72 (q, 1H, Ar-H). ^{13}C NMR (DMSO- d_6 , δ in ppm): 92.01, 92.19, 104.56, 106.37, 109.64, 109.83, 110.83, 111.15, 112.86, 130.41, 136.27, 136.38, 150.86, 155.20, 160.32, 161.81, 164.35.

2-Fluoro-6-(4-aminophenoxy)benzonitrile (**6b**)

Compound **6b** was synthesized from 4-aminophenol (8.74 g, 80.0 mmol), 2,6-DFBN (11.13 g, 80.0 mmol), potassium carbonate (13.24 g, 96.0 mmol) and NMP (150 mL) according to the same procedure as **6a** to afford 14.6 g (80%) of white crystals, m.p. 156.3–156.6 °C.

Anal. Calcd. for $\text{C}_{13}\text{H}_9\text{FN}_2\text{O}$: C, 68.42%; H, 3.98%; N, 12.27%. Found: C, 68.52%; H, 4.11%; N, 12.23%. FTIR (KBr, cm^{-1}): 3490, 3396 (NH_2), 3100, 3062, 2232 (nitrile). Mass spectrum (m/e): 228 (M^+). ^1H NMR (DMSO- d_6 , δ in ppm): 5.18 (s, 2H, NH_2), 6.57–6.59 (d, 1H, Ar-H), 6.61–6.65 (d, 2H, Ar-H), 6.87–6.91 (d, 2H, Ar-H), 7.09–7.12 (t, 1H, Ar-H), and 7.60–7.65 (q, 1H, Ar-H). ^{13}C NMR (DMSO- d_6 , δ in ppm): 90.77, 90.95, 108.79, 108.98, 111.05, 111.08, 111.56, 114.79, 121.28, 136.30, 136.40, 143.42, 146.94, 161.93, 162.04, 162.08, 164.47.

Synthesis of 2-(3-Aminophenoxy)-6-(4-aminophenoxy)benzonitrile (**4a**, **3,4-APBN**) from 2-Fluoro-6-(4-aminophenoxy)benzonitrile

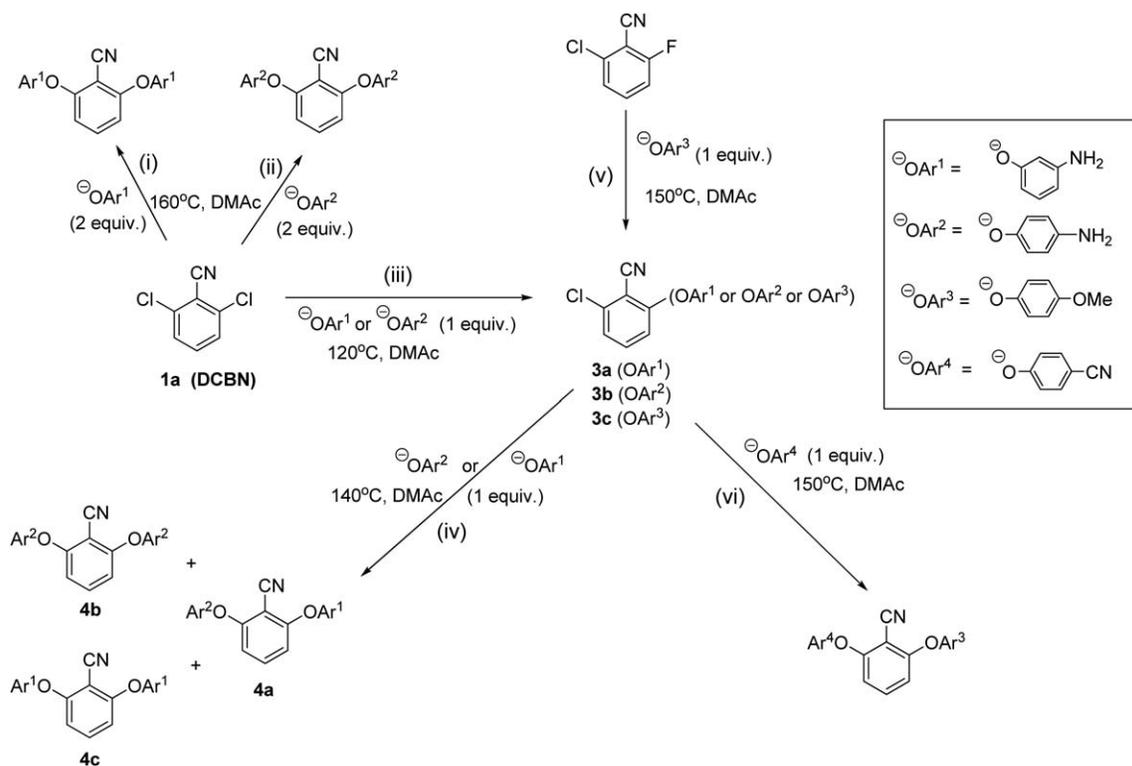
Into a 250-mL three-necked flask equipped with nitrogen inlet, magnetic stir bar, and condenser, 3-aminophenol

(3.44 g, 31.5 mmol), 2-fluoro-6-(4-aminophenoxy)benzonitrile (2.28 g, 10 mmol), potassium carbonate (4.98 g, 36.0 mmol), and 75 mL of anhydrous NMP were charged and the resulting mixture was stirred at 100 °C for 48 h. The mixture was allowed to cool to room temperature and filtered. The filtrate was poured into water to precipitate a white crude product. The white solid was collected by filtration, washed with water and dried. The crude product was recrystallized from ethanol to afford 8.0 g (84%) of white crystals, m.p. 160.8–161.8 °C.

Anal. Calcd for $\text{C}_{19}\text{H}_{15}\text{N}_3\text{O}_2$: C, 71.91%, H, 4.76%, N, 13.24%. Anal Found: C, 72.12%, H, 4.78%, N, 12.90%. FTIR: 3422, 3400, 3322 (NH_2), 2227 (nitrile). Mass spectrum (m/e): 228 (M^+). ^1H NMR (DMSO- d_6 , δ in ppm): 5.15 (s, 2H, NH_2), 5.35 (s, 2H, NH_2), 6.24–6.27 (d, 1H, Ar-H), 6.29–6.30 (t, 1H, Ar-H), 6.38–6.41 (d, 1H, Ar-H), 6.43–6.45 (d, 1H, Ar-H), 6.50–6.52 (d, 1H, Ar-H), 6.62–6.64 (d, 2H, Ar-H), 6.88–6.90 (d, 2H, Ar-H), 7.05–7.09 (t, 1H, Ar-H), and 7.43–7.48 (t, 1H, Ar-H). ^{13}C NMR (DMSO- d_6 , δ in ppm): 92.93, 104.50, 106.39, 108.61, 109.75, 110.79, 113.38, 114.78, 121.31, 130.35, 135.35, 143.65, 146.68, 150.78, 155.60, 160.55, 162.28.

Synthesis of Unsymmetrical Diamine via One-Pot Route 2-(3-Aminophenoxy)-6-(4-aminophenoxy)benzonitrile (**4a**, **3,4-APBN**), Route 1

Into a 250-mL three-necked flask equipped with a magnetic stirrer, a nitrogen inlet and outlet, 4-aminophenol (1.39 g, 10.0 mmol), 2,6-DFBN (1.09 g, 10.0 mmol), potassium carbonate (1.66 g, 912.0 mmol) and NMP (50 mL) were charged and the mixture was stirred under nitrogen atmosphere at 70 °C for 48 h. After GC-MS spectra indicated the



SCHEME 1 Temperature-controlled sequential displacement of *O*-nitrile-activated halide by a phenolate nucleophile with appropriate basicity.

reaction was completed, 3-aminophenol (1.42 g, 13.0 mmol) and potassium carbonate (1.66 g, 12.0 mmol) were added and the mixture was heated at 100 °C for 48 h. The mixture was allowed to cool to room temperature and filtered. The filtrate was poured into water. The white solid was obtained by filtration. It was recrystallized from ethanol to afford 1.96 g (61.8%) of white crystals, m.p. 161.7–161.8 °C. The identity and purity product were confirmed by GC-MS, IR and NMR spectra.

2-(3-Aminophenoxy)-6-(4-aminophenoxy)benzonitrile (4a, 3,4-APBN), Route 2

3,4-APBN was synthesized according to the same procedure as Route 1 with following modification: 3-aminophenol was used in the first step and 4-aminophenol was used in the second step to afford 2.04 g (64.2%) of white crystals after recrystallization from ethanol, m.p. 161.0–161.8 °C. The pure product was confirmed by GC-MS, IR and NMR spectra.

2,6-Bis(3-aminophenoxy)benzonitrile (4b, 3,3-APBN) and 2,6-Bis(4-aminophenoxy)benzonitrile (4c, 4,4-APBN)

Syntheses of compounds **4b** and **4c** were conducted according to the procedures described in reference.³⁸

General Procedure for PI Synthesis (8a-8i and 9)

Into a 50-mL one-necked, round-bottomed flask equipped with a magnetic stir-bar, nitrogen inlet, DMAc (10 mL) and diamine (3.50 mmol) was charged. After diamine was dissolved in DMAc, dianhydride (3.50 mmol) was added. The light yellow solution was agitated at room temperature for

24 h to afford a viscous PAA (**7**). The resulting mixture was diluted with DMAc (4 mL). For the thermally imidized polymer film samples, the PAA/DMAc solution was poured into glass dishes, followed by vacuum evaporation of DMAc at 50 °C for 12 h. The films were further heat-treatment at 100 °C/2 h; 150 °C/2 h; 175 °C/1 h, 200 °C/1 h, and 250 °C/1 h under N₂ to afford light yellow PI films. For the fiber samples, a chemical imidization was used instead. Thus, pyridine and acetic anhydride were added to the PAA. It was agitated at room temperature for 24 h and poured into ethanol to afford a fibrous precipitates, which were collected by filtration. The fibers were soxhlet-extracted with ethanol to remove the residual DMAc and dried in a vacuum-oven at 150 °C for 24 h. The ATR-IR spectra (films) exhibited absorptions at 2230–2232 (CN), 1777–1785, and 1714–1720 cm⁻¹ (imide).

RESULTS AND DISCUSSION

Monomer Synthesis

While both 2,6-DCBN (**1a**) and 2,6-DFBN (**1b**) have been utilized as co-monomers with bis(phenolate) monomers in the synthesis of benzonitrile-containing poly(arylene-ether)s, the polymer-forming conditions are such that both halo-substituents are generally assumed to have comparable reactivity above certain temperature, leading to various ether-nitrile polymers.⁴³ During the preparation of the known, symmetrical diamino monomers namely 3,3-APBN and 4,4-APBN,³⁸ using the potassium salts of 3-aminophenol (**2a**) or 4-aminophenol (**2b**) as a nucleophile [Scheme 1, reactions

(i) and (ii)], we found that two halo groups on the same phenyl ring of either DCBN or DFBN had shown different but exploitable rates in the aromatic nucleophilic substitution (S_NAr) reaction. Specifically, as observed by GC-MS monitoring of a reaction mixture of 4-DCBN and aminophenol/ K_2CO_3 (Supporting Information Figure 1), the reactivity of second halide toward the same nucleophile was apparently mitigated, and therefore, heating at a higher temperature was required for the second aromatic displacement reaction to occur. Thus, this substantial temperature difference (~ 20 – 40 °C) in the leaving-group activation by the ortho-nitrile has allowed the isolation of the mono-substituted products, i.e., 2-chloro-6-(3-aminophenoxy)benzotrile (**3a**) and its fluoro-analog, in good yields. Therefore, this sufficiently broad difference in reactivity presents an opportunity to regioselectively synthesize various unsymmetrical diamines, and in particular, 3,4-APBN. We note that this rationale is also supported by several reported examples of 2-chloro-aryloxy-benzonitriles⁴⁴ or 2-fluoro-6-aryloxy-benzonitriles⁴⁵ isolated from the respective reaction of 2,6-dichloro- or 2,6-DFBN with an appropriate aryloxy anion in DMF.

However, in our initial effort to further validate such two-step synthesis [Scheme 1, (i) and (iv)] of 3,4-APBN (**4a**), we used DCBN (**1a**) as the starting material to react with 3-aminophenolate (or 4-aminophenolate) at 120 °C and isolated the chloro-aryloxy intermediate **3a** (or **3b**) before its use in the second aromatic displacement reaction at 160 °C with 4-aminophenolate as the second nucleophile. To our surprise, the isolated mixture, based on 1H NMR peak area integration (Fig. 1; see also Supporting Information Figure SI-2 for the peak assignments), was actually comprised of 58% 3,4-APBN (**4a**), 13% 3,3-APBN (**4b**), and 29% 4,4-APBN (**4c**), which provided a strong evidence that the transesterification process had occurred at 160 °C. Further, when we conducted a similar experiment in a one-pot fashion that entailed heating an equimolar mixture of DCBN and 4-aminophenol/ K_2CO_3 in NMP at 120 °C and monitoring the reaction progress by GC-MS, we found that only a single product, i.e., the 2-chloro-6-(4-aminophenoxy)benzotrile intermediate (**3b**) was detected and $\sim 98\%$ conversion was observed after 24 h. After the reaction mixture had been allowed to cool to 100 °C, an equimolar amount of 3-aminophenol/ K_2CO_3 was added and the reaction temperature was raised to 140 °C. After 19 h at this temperature, GC-MS detected the presence of 4,4-APBN and 3,3-APBN in addition to 3,4-APBN with the elution times of 18.7, 19.1, and 19.4 min, in that order (Supporting Information Figure SI-1) with 3,4-APBN being the major component.

We attribute the isomeric mixture to the redistribution equilibrium being driven by the occurrence of transesterification (i.e. aryloxy-aryloxy exchange reaction) at relatively high reaction temperatures. The first aromatic displacement reaction occurred quite cleanly at 120 °C to afford the mono-substituted product, 2-chloro-6-(3-aminophenoxy)benzotrile (**3a**) or 2-chloro-6-(4-aminophenoxy)benzotrile (**3b**). However, at ≥ 140 °C, it became apparent that the

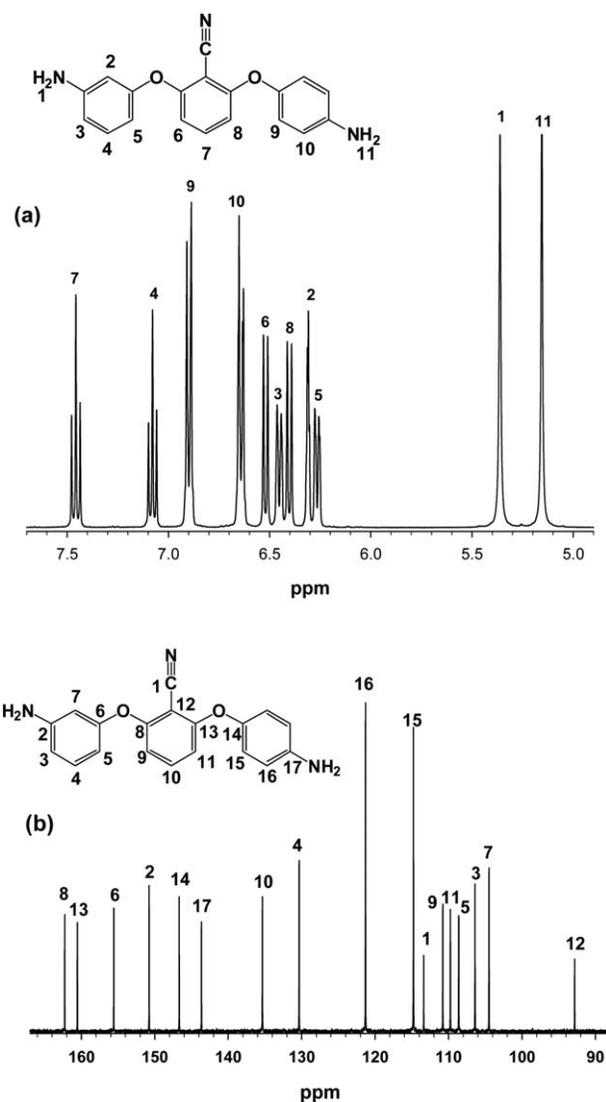
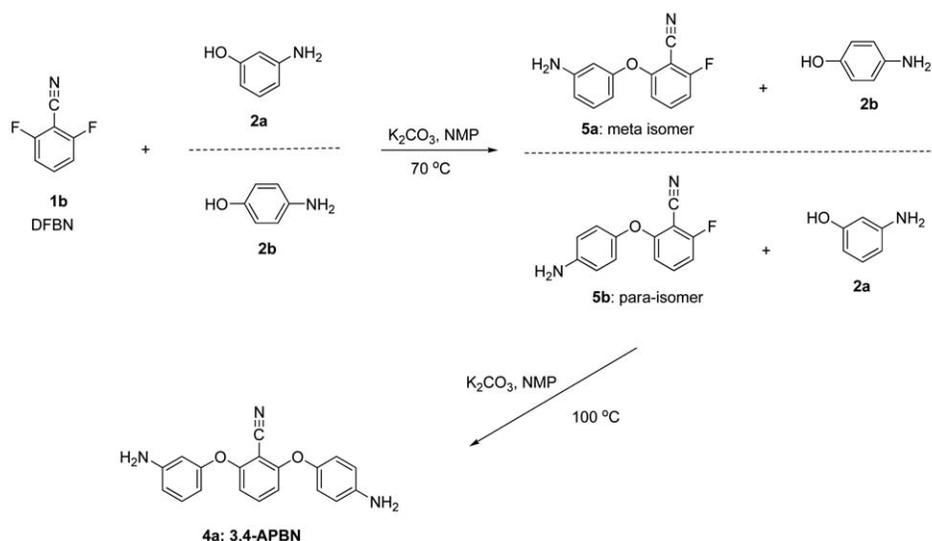


FIGURE 2 NMR spectra of 3,4-APBN: (a) 1H NMR and (b) ^{13}C NMR both in $DMSO-d_6$.

4-aminophenoxy ($pK_a = 9.99$) substituent in **3a** could also act as a leaving group in the presence of 3-aminophenolate (**2b**; $pK_a = 10.43$), and vice versa in the case of **3b** via a dynamic transesterification process, leading eventually to an equilibrium mixture of all three possible isomers. It is noteworthy that Mercer et al.⁴⁶ has reported a successful synthesis of a model compound, 2-(*p*-methoxyphenoxy)-6-(*p*-cyanophenoxy)benzotrile (**3c** in Scheme 2) from a similar two-step reaction (but in the same-pot) of 2-chloro-6-fluorobenzotrile and two different phenolates generated in situ in the presence of potassium carbonate, namely first from 4-methoxyphenol ($pK_a = 10.27$), and then 4-cyanophenol ($pK_a = 7.80$). However, it is noted that 2-chloro-6-fluorobenzotrile which costs more than 2,6-dichloro- and 2,6-DFBN was used as the starting material [see Scheme 1, reactions (v) and (vi)]. On the basis of these results, we hypothesize that to avoid the occurrence of transesterification in a 2-halo-6-aryloxybenzotrile system, the



SCHEME 2 Alternative routes to the unsymmetrical benzonitrile-ether-diamine from 2,6-DFBN.

second phenolate must be much weaker in its basicity (in our estimation, by at least 2 pK_a units) than the first one, and the reaction temperature threshold, being tied closely to the reduced leaving tendency of second halide, should be kept as low as possible ($\ll 150$ °C, and 100–120 °C is optimal from our study).

Our subsequent tactic for the 3,4-APBN synthesis is further based on the fact that fluoride is more reactive than chloride as well as the premise that a much lower reaction temperatures can be used for DFBN (1b) to circumvent the transesterification side reaction (Scheme 2). Indeed, the first S_NAr reaction between DFBN and 4-aminophenol (2a) occurred at 70 °C to cleanly give the isolable, mono-substituted product, 2-fluoro-6-(4-aminophenoxy)benzonitrile (6a). In a subsequent treating 6a with 3-aminophenolate (2b) at 100 °C to afford pure 3,4-APBN (4a) in good yield. Thus, the reaction progress of the mixture of 1b, 3-aminophenolate, and 4-aminophenolate, with the phenolates being introduced at different temperatures, was monitored with the aid of GC-MS (depicted in Supporting Information Figure SI-3). It is clearly shown that in these two separate reactions, neither 3,3- nor 4,4-APBN isomers (4b or 4c) was observed. The unsymmetrical structure of 3,4-APBN was confirmed by the ¹H and ¹³C NMR (Fig. 2) and FTIR (Supporting Information Figure SI-4) spectral analyses as well as the elemental analysis results.

Operationally more convenient, the preparation of 3,4-APBN was also conducted in a “one-pot” fashion by effecting the tandem S_NAr reactions, via sequentially adding 4-aminophenol (or 3-aminophenol) to DFBN at 70 °C (in the presence of K₂CO₃) and 3-aminophenol (or 4-aminophenol) at 100 °C. It is critical to keep the reaction ≤ 120 °C, above which, transesterification would occur, resulting in the formation of three isomers (4a–c). Finally, two symmetrical diamines, namely, 3,3-APBN and 4,4-APBN were prepared by treating DCBN with 3-aminophenol and 4-aminophenol, respectively (see Supporting Information Figures SI-2, SI-4,

and SI-5 for NMR, FTIR spectra, and “ball-stick” molecular structures of the diamines 4a–c, in that order).³⁸ All the intermediates and diamines were also confirmed by elemental analysis, which were in good agreement with the calculated values.

Synthesis of PIs

The polymerization of the diamines 4 with the dianhydrides (6) was conducted in DMAc at room temperature for 24 h to afford PAAs (7), which were subsequently imidized by either thermal or chemical route to afford the PIs (8) as shown in Scheme 3. The unsymmetrical diamine (4a) was polymerized with the dianhydrides includes 6FDA (6a), OPDA (6b), DSDA (6c), BTDA (6d), and PMDA (6e). Two symmetrical diamines (4b–c) were also polymerized with 6FDA (6a) and PMDA (6e) for comparison purposes. The films prepared from thermal imidization are tough and creasable; they were used for the evaluation of mechanical, electrical, thermal and

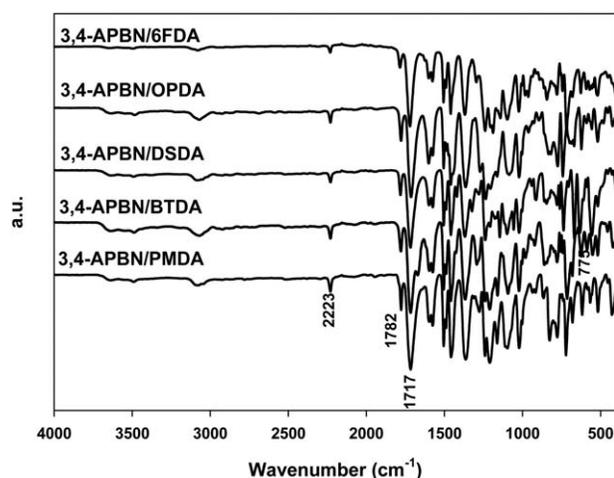


FIGURE 3 FTIR spectra of the PIs containing the 3,4-di(aminophenoxy)benzonitrile moiety.

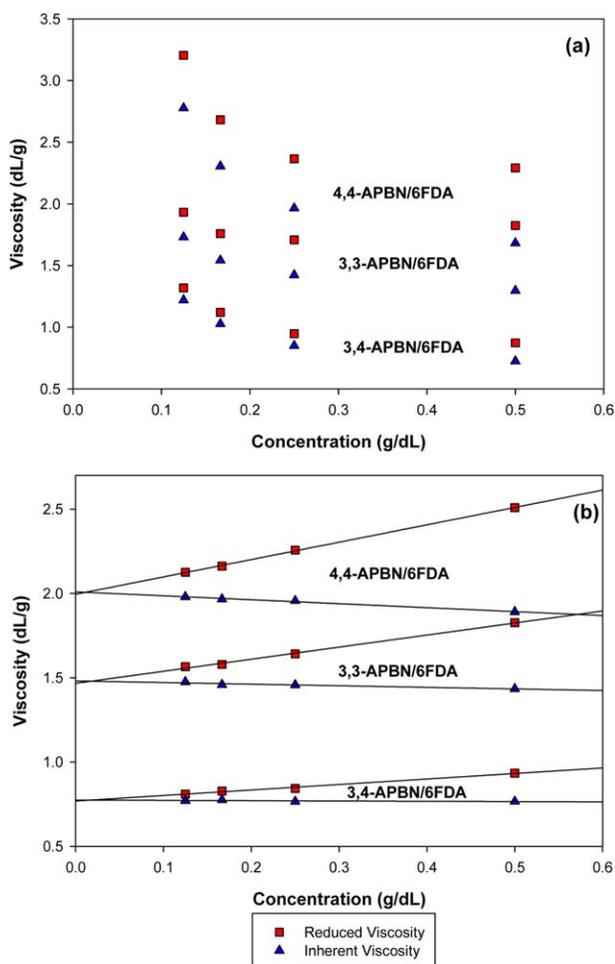


FIGURE 4 Inherent viscosity and reduced viscosity plots of the PAAs derived from 6FDA and the isomeric APBN diamines: data taken in NMP (a) without 1 wt % LiBr; (b) with 1 wt % LiBr. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

morphological properties. The chemical imidization in solution was performed using a mixture of acetic anhydride and pyridine as a dehydrating agent/catalyst system. The precipitated, fibrous PI samples were first soxhlet-extracted with denatured ethanol and oven-dried before they were in the characterization of their solubility, molecular weights and solution-viscosity property. Their repeat-unit structures were verified by ATR-IR spectroscopy, which confirmed the expected absorptions due to the nitrile around 2230–2232 cm^{-1} and the symmetrical and asymmetrical stretches due to the imide-carbonyls around 1777–1785 and 1714–1720 cm^{-1} , respectively (Fig. 3). The elemental analysis data of the resulting PIs also agreed well with the calculated values (Table 1).

Solution Properties

The solubilities of the PIs (**8**) were evaluated in several organic solvents at 2.0% (w/v) (Table 2). Three 6FDA-based PIs (**8a**, **f**, and **h**) showed the best solubility in all the solvents except ethanol since the flexible 6FDA units and tri-

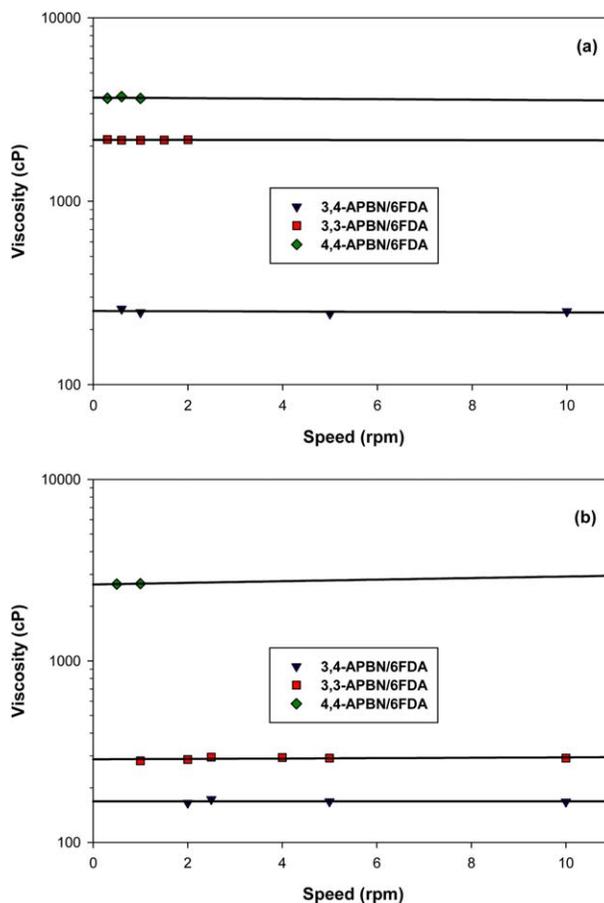
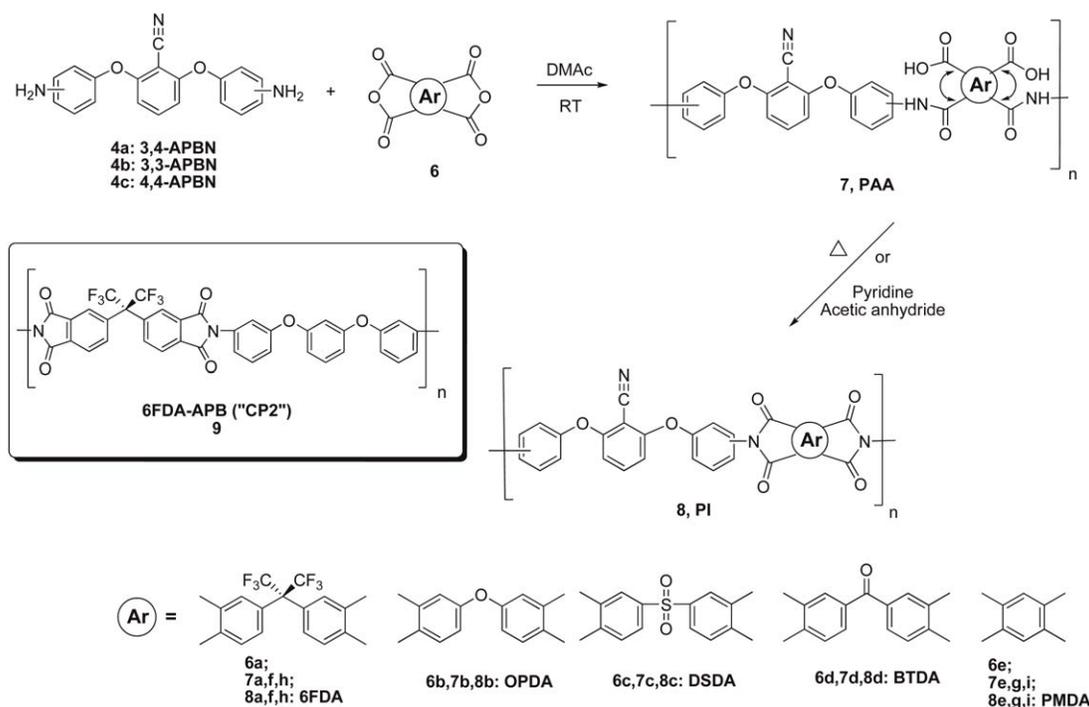


FIGURE 5 Viscosity versus stirring speed plots of the PAAs and PIs derived from 6FDA and the isomeric APBN diamines: (a) concentrated PAA solution (20 wt %) and (b) concentrated PI solution (20 wt %). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

fluoromethyl groups disrupt the polymer-chain packing and inter-chain charge-transfer complexation in more stiff PIs. In fact, the 6FDA-based PIs could even dissolve in chloroform. On the other hand, the most rigid PMDA-based PIs (**8e**, **g**, and **i**) are not soluble in any solvents tested. The OPDA-, DSDA- and BTDA-based PIs (**8b**, **c**, and **d**) showed intermediate solubility. Therefore, the PI solubility is mainly determined by structures and geometry of the dianhydrides (6FDA > OPDA > DSDA > BTDA > PMDA).

Since the 6FDA-based PIs are soluble in THF, their molecular weights were measured in THF using polystyrene standards. Polymer **8h** exhibited the highest molecular weights with average M_n of 66,300 Da. while the molecular weight of polymer **8a** is the lowest one with average M_n of 41,400 Da. Their intrinsic viscosities are in the range of 0.73 and 1.75 dL/g (Table 3).

The PAA solutions prepared from 3,4-APBN showed much lower viscosity values than those from 3,3-APBN and 4,4-APBN. Both the dilute and concentrated solutions of three 6FDA-based PAA were further investigated.



SCHEME 3 Synthesis of benzonitrile-containing PIs via PAA intermediates. In the inset, the polymer structure for CP2, labeled as PI 9 in Table 5 is shown. Other members of 6FDA-APBN series are labeled as PIs 8a, 8f, and 8h in Table 1.

Inherent and reduced viscosities were measured in 0.5–0.10 g/dL dilute NMP solution at 30 °C. All the solutions showed polyelectrolyte effect without addition of LiBr [Fig. 4(a)]. The polyelectrolyte effects were suppressed with addition of 1 wt % LiBr [Fig. 4(b)]. However, with or without the presence of LiBr, the PAA of 3,4-APBN/6FDA invariably exhibited the lowest viscosity. Its intrinsic viscosity was 0.76 dL/g. The intrinsic viscosities (with suppressed polyelectrolyte effect) were much higher the symmetrical analogs: almost double for 3,3-APBN/6FDA PAA (1.48 dL/g) and triple for 4,4-APBN/6FDA PAA (2.0 dL/g).

The viscosities of PAA and chemically imidized PI concentrated solutions (20 wt % in DMAc) were measured using a Brookfield Viscometer (Fig. 5). While the viscosity of 3,4-

APBN/6FDA PAA was only 250 cP at 30 °C, it increased almost 9 folds (~2200 cP) for 3,3-APBN/6FDA PAA and 15-folds (3700 cP) for 4,4-APBN/6FDA PAA [Fig. 5(a)]. The ultralow viscosity of 3,4-APBN/6FDA PAA is attributed to the diamine unsymmetrical structure (Supporting Information Figure SI-5). For the 3,4-APBN-6FDA polymer, there are three possible structural arrangements: head-to-head, head-to-tail and tail-to-tail (Supporting Information Figure SI-6). These different arrangements make the PAA chains difficult to pack closely, which dramatically reduces the interaction among polymer chains thus PAA viscosity. The viscosity of three 6FDA-based PIs at 20 wt % concentration was also measured using a Brookfield Viscometer as shown in Figure 5(b). Similar trend was also observed for the chemically imidized PI samples: 4,4-APBN/6FDA PI (2650 cP at 30 °C) > 3,3-

TABLE 1 Elemental Analysis of PIs

PI No.	Diamine	Dianhydride	Theoretical (%)			Elemental Analysis (%)		
			C	H	N	C	H	N
8a	3,4-APBN, 4a	6FDA, 7a	62.90	2.36	5.79	62.91	2.53	5.90
8b	3,4-APBN, 4a	OPDA, 7b	71.07	2.90	7.10	70.90	3.33	7.19
8c	3,4-APBN, 4a	DSDA, 7c	65.73	2.68	6.57	65.38	2.89	6.79
8d	3,4-APBN, 4a	BTDA, 7d	71.64	2.84	6.96	71.32	2.94	7.18
8e	3,4-APBN, 4a	PMDA, 7e	69.74	2.62	8.41	69.67	2.74	8.50
8f	3,3-APBN, 4b	6FDA, 7a	62.90	2.36	5.79	63.26	2.67	5.88
8g	3,3-APBN, 4b	PMDA, 7e	69.74	2.62	8.41	69.82	2.81	8.58
8h	4,4-APBN, 4c	6FDA, 7a	62.90	2.36	5.79	63.04	2.58	5.83
8i	4,4-APBN, 4c	PMDA, 7e	69.74	2.62	8.41	69.55	2.79	8.62

TABLE 2 Solubility of PIs

PI No.	Ethanol	CH ₂ Cl ₂	CHCl ₃	Acetone	THF	DMSO	DMAc	NMP	<i>m</i> -Cresol
8a	–	+	+	+	+	+	+	+	+
8b	–	+	PS	–	–	+	+	+	+
8c	–	–	–	–	PS	+	+	+	+
8d	–	–	–	–	–	PS	PS	+	+
8e	–	–	–	–	–	–	–	–	–
8f	–	+	+	+	+	+	+	+	+
8g	–	–	–	–	–	–	–	–	–
8h	–	+	+	+	+	+	+	+	+
8i	–	–	–	–	–	–	–	–	–

+, Soluble; –, insoluble; PS, partly soluble.

APBN/6FDA PI (291 cP) > 3,4-APBN/6FDA PI (162 cP). All the PAA solutions, because of their interchain hydrogen bonding, are more viscous than the corresponding PIs. The low viscosity of 3,4-APBN-based PAAs is able to improve the PI processibility and significantly reduce the amount of used solvents. Such processing advantage is parallel to that reported for high-temperature polymer-matrix composite fabrication as illustrated by the work of Chuang *et al.*³³ that very low-melt viscosity reactive imide oligomers (5–20 P at 260–280 °C) could be formulated from three different unsymmetrical dianhydrides with diamines and terminated with the 4-phenylethynylphthalic anhydride endcapper.⁴⁷

Thermal and Mechanical Properties

The glass transition temperatures (T_g s) were measured on both DSC and DMA instruments. The PMDA-based PIs are too rigid for their T_g s to be detected by DSC method (Table 4; see also Table 1 for the diamine/dianhydride compositions for the PI designations below). Therefore, DMA results were used for the following discussion. The polymer chain rigidity imposes a direct effect on their T_g s. For three 6FDA-based PIs, **8f** containing totally bent *meta,meta* or 3,3-units displays the lowest T_g (249 °C, DSC) while **8h** containing rigid *para,para* or 4,4-units has the highest value (292 °C). The T_g (279 °C) of semi-rigid **8a** is higher than that of **8f**, but lower than **8h**. Three PMDA-based PIs displayed the

TABLE 3 Molecular Weights and Viscosity of PIs

PI No.	$[\eta]$ (dL g ⁻¹) ^a	$M_n \times 10^{-3}$ (Da) ^b	$M_w \times 10^{-3}$ (Da) ^b	PDI ^b
8a	0.78	41.4	81.5	1.98
8b	0.98	– ^c	– ^c	– ^c
8c	0.73	– ^c	– ^c	– ^c
8d	1.22	– ^c	– ^c	– ^c
8f	0.99	45.1	87.2	1.93
8h	1.75	66.3	126	1.91

^a Intrinsic viscosity ($[\eta]$) determined in NMP solutions at 30 °C.

^b Molecular weights and molecular distributions (PDI) measured by size-exclusion liquid chromatography in THF.

^c Insoluble in THF.

highest T_g s among all the PIs here, and showed the same trend as the 6FDA-based PIs, that is, PI **8i** containing rigid 4,4-units has the highest value (332 °C), followed by **8e** and then **8g** (321 and 294 °C).

Table 4 also gives the temperatures of the 5 wt % gravimetric loss in nitrogen and in air. Their 5% weight losses are in the range of 505–542 °C and 512–546 °C in air and nitrogen, respectively. The amount of residue of all PIs at 850 °C in nitrogen atmosphere was higher than 48%, especially, the PI derived from PMDA and DSDA with the highest char yields. Obviously, the data from thermal analysis showed that the resulting PIs had fairly high thermal stability and the thermo-oxidative stability.

These films were subjected to tensile testing. Table 4 shows the mechanical properties of the PIs, including the tensile strength, tensile modulus, and elongation at break. The PI films possess tensile strength of 82–121 MPa, an elongation at break of 5.3–9.8% and a tensile modulus of 2–3 GPa, indicative of their being made of strong and tough materials. The mechanical properties of the PIs **8a** and **8e** containing unsymmetrical units are comparable with **8f–i** containing symmetrical units, implying that the unsymmetrical

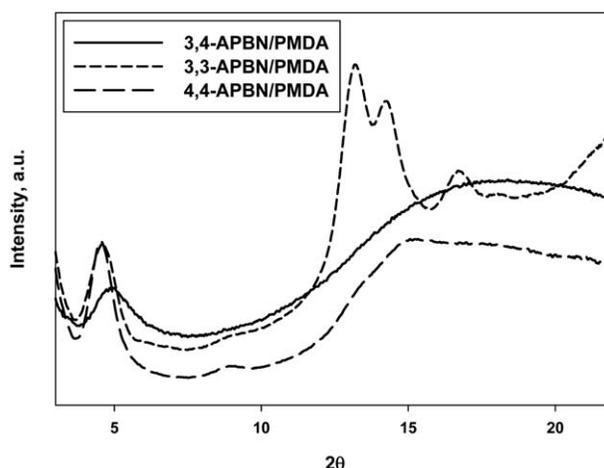


FIGURE 6 Wide-angle X-ray diffraction patterns of PMDA-based PIs.

TABLE 4 Thermal and Mechanical Properties of PIs

PI No.	T_g (DSC, °C) ^a	T_g (DMA, °C) ^b	In Air		In Nitrogen		Modulus (GPa)	Tensile Strength (MPa)	Elongation (%)
			$T_{d5\%}$ ^c (°C)	Char ^d (%)	$T_{d5\%}$ ^c (°C)	Char ^d (%)			
8a	252	279	525	1.08	528	57.9	2.39 ± 0.26	103.7 ± 5.1	7.43 ± 0.90
8b	235	255	530	3.62	534	57.6	2.68 ± 0.37	95.1 ± 8.4	8.36 ± 1.66
8c	254	281	505	2.66	512	48.5	2.44 ± 0.22	82.1 ± 3.4	5.33 ± 0.97
8d	245	267	550	4.05	536	61.8	2.76 ± 0.42	88.6 ± 9.3	5.06 ± 1.45
8e	ND	321	537	0.71	539	61.6	2.11 ± 0.19	121.3 ± 6.2	6.35 ± 0.78
8f	238	249	519	0.26	528	52.3	2.34 ± 0.55	93.7 ± 4.4	6.29 ± 1.57
8g	ND	294	543	1.12	546	59.4	2.69 ± 0.36	115.8 ± 5.6	6.74 ± 0.81
8h	284	292	526	0.63	527	52.2	2.47 ± 0.25	106.2 ± 5.7	9.81 ± 0.46
8i	ND	332	542	1.42	537	59.6	2.97 ± 0.32	119.2 ± 13.5	7.13 ± 0.67

^a T_g measured by DSC at a scanning rate of 10 °C/min in flowing nitrogen.

^b T_g measured by DMA at a scanning rate of 4 °C/min in flowing nitrogen.

^c Temperature at which 5% weight loss occurred on TGA thermogram obtained with a heating rate of 10 °C/min.

^d Residual weight (%) at 850 °C in nitrogen.

structures improve the processing conditions of PAAs and at same time they preserve the rigidity of PI chains and the consequential mechanical properties.

Wide-Angle X-Ray Diffraction (WAXD)

Because of its unsymmetrical nature, 3,4-APBN/PMDA (**8e**) PI is expected to be amorphous and this is further confirmed by its featureless WAXD pattern in Figure 6. WAXD patterns of both 3,3- and 4,4- and APBN/PMDA (**8g** and **8i**) PI indicated that they are semi-crystalline. 3,3-APBN/PMDA WAXD result revealed multiple peaks, indicative of high order (crystallinity) in the lateral direction of the polymer backbone. 4,4-APBN/PMDA sample falls in between 3,3- and 3,4-APBN/PMDA films in terms of relative crystallinity. The long period diffraction peak at 19 Å for 4,4-APBN/PMDA indicates a better ordering along the backbone.

UV-Vis Absorption

It is well known that the PI molecular structures have a direct effect on the film color and transmittance. Colorless PI films have been used in LCD, LED and solar battery panel applications.⁴⁸ The optical properties of the PI thin films were evaluated by UV-vis spectroscopy. The UV-vis spectra of three APBN/6FDA PIs were measured in both films and DMAc solutions (see Fig. 7 and Supporting Information Figure SI-7, respectively). As expected, the film and solution of 3,4-APBN/6FDA are the most transparent since the unsymmetrical structures disrupts the formation of charge-transfer complexes, which are considered the major contributor to high color in PI films, such as Kapton.¹ The optical transparency of 3,3-APBN/6FDA film and solution is only marginally lower than the unsymmetrical one due to the bending structure of 3,3-diamine unit. Since 4,4-APBN/6FDA PI exhibits highly symmetrical repeat units, the color of its film and solution is the darkest. While the 3,4- and 3,3-APBN/6FDA films show about 95 and 93% of transmittance at 400 nm the 4,4-APBN/6FDA one has only 88% transparency (Supporting Information Table SI-2). They show similar trend in other wavelengths.

Dielectric Properties

Dielectric impedance experiments were performed over broad band frequency (10^{-1} to 10^6 Hz) and temperature (−40 to 150 °C) ranges. Dielectric spectra of all the PIs are shown in Figures 8 and 9. Their permittivity (ϵ') and dielectric loss (ϵ'') at 1, 10, and 1 kHz are also listed in Table 5. For comparison purpose, the dielectric properties of APB-6FDA (CP2, **9**), an analog of **8f** containing no nitrile group, was also measured.⁴⁹ 6FDA-based PIs (**8a**, **8f**, and **8h**) showed higher dielectric constants than CP2 (**9**) due to the presence of nitriles as high polarity groups on the polymer backbone. The unsymmetrical polymer **8a** exhibited highest value in the whole frequency range among three 6FDA-based PIs (Fig. 8 and Table 5). Although the differences are small (3.30 for **8a** vs. 3.27 for **8f** and 3.17 for **8h**), they are noticeable. The high permittivity of **8a** could be attributed to its unsymmetrical repeat units, which give the neighboring benzonitrile units higher polarity. For the same argument, 3,3-APBN/PMDA polymer (**8f**) displayed a higher permittivity than 4,4-APBN/PMDA (**8h**) since the latter has more symmetrical structure than the former. The structures of dianhydrides demonstrate some influence on the dielectric properties. For 3,4-APBN series, BTDA PI showed highest dielectric constant (3.62–3.81 at 1–1k Hz) since ketone (benzophenone) groups are easily polarized in the electric field. The permittivity of PMDA PI is second due the high polarity of pyromellitimide units. DSDA PI display a lowest permittivity since the polarity of two sulfone groups is partially cancelled each other. The dielectric loss (ϵ'') of CP2 is very low (0.002–0.003). For the 3,4-APBN PIs, their ϵ'' 's are higher than CP2, which probably arises from the polar nitrile groups. 3,4-APBN/PMDA polymer showed much higher loss at low frequency (Fig. 9). Since its T_g is over 321 °C and the highest imidization temperature is only 300 °C, it may contain small amount of solvent and /or PAA residues which contribute to the higher loss.⁴³

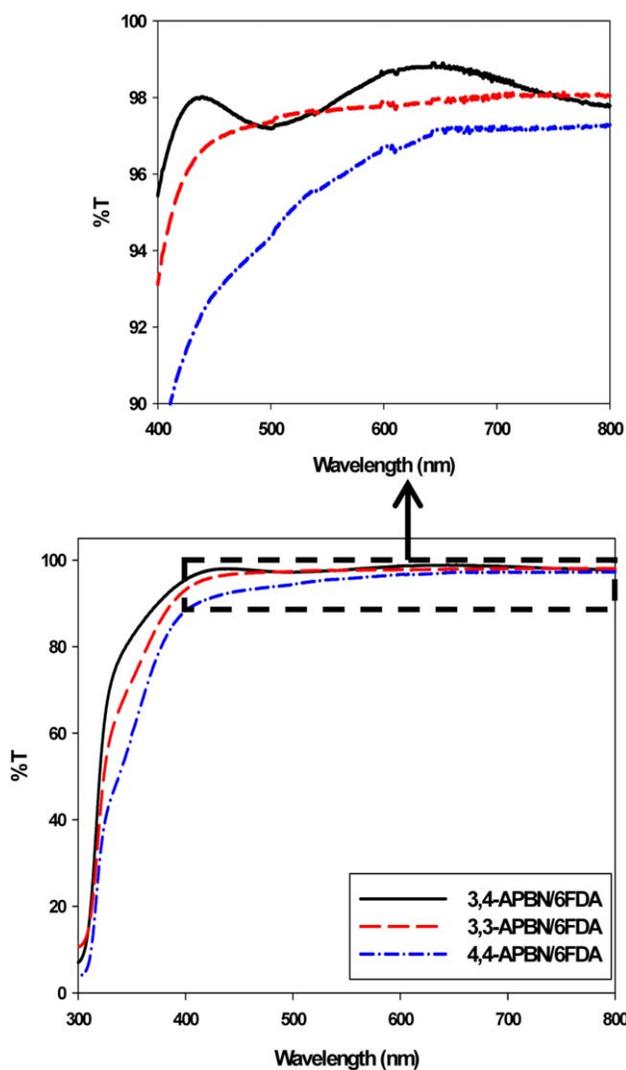


FIGURE 7 UV-vis spectra of APBN-6FDA PI thin films ($\sim 3 \mu\text{m}$). Magnified spectral region (400–800 nm) is depicted in the top spectrum. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

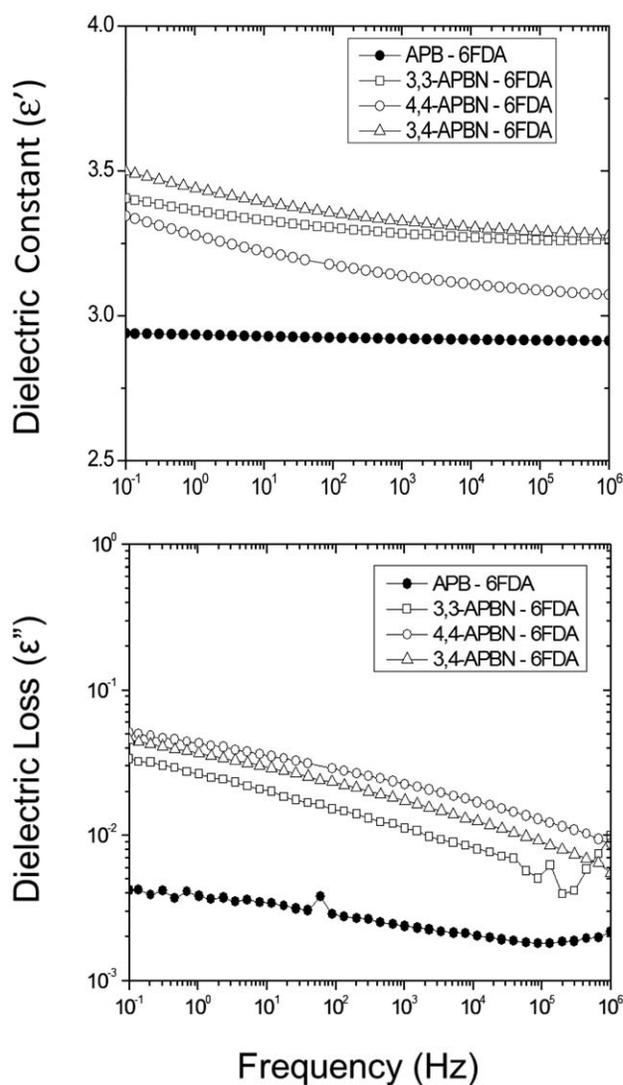


FIGURE 8 Composite plot of the dielectric constants (top) and loss (bottom) of 6FDA-based PIs as a function of scanning frequency at ambient conditions.

TABLE 5 Dielectric Properties of PIs

PI No.	1 Hz		10 Hz		1 kHz		$\Delta\epsilon_{10 \text{ Hz}}^a$
	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	
8a	3.39	0.025	3.33	0.017	3.30	0.013	10.5
8b	3.33	0.022	3.24	0.012	3.14	0.0077	10.0
8c	3.23	0.026	3.17	0.014	3.16	0.010	5.0
8d	3.81	0.024	3.68	0.013	3.62	0.009	13.0
8e	3.64	0.050	3.55	0.025	3.51	0.018	— ^b
8f	3.33	0.02	3.28	0.011	3.27	0.008	8.9
8g	3.53	0.17	3.42	0.019	3.39	0.011	—
8h	3.19	0.033	3.11	0.021	3.08	0.016	7.0
8i	3.49	0.051	3.25	0.028	3.17	0.017	— ^b
9	2.92	0.003	2.92	0.002	2.92	0.002	0.7

^a Permittivity difference before and after T_g .

^b Not determined because polymer T_g exceeds the upper temperature limit of the instrument.

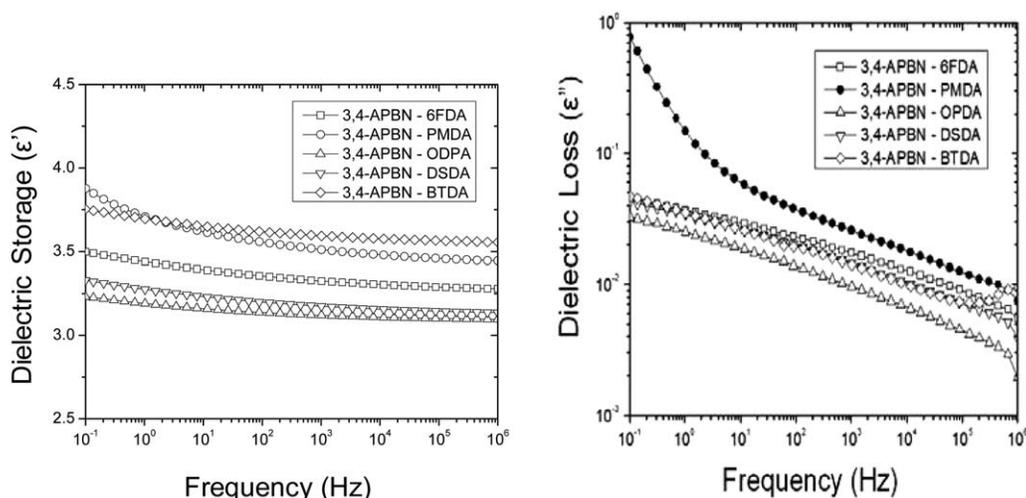


FIGURE 9 Composite plots of the dielectric constants (left) and loss (right) of 3,4-APBN-based PIs as a function of scanning frequency at ambient conditions.

Polarization response ($\Delta\epsilon$) is defined as the dielectric constant changes before and after T_g s. While CP2s polarization response is only 0.7, the 6FDA-APBN-PIs showed a huge increase to 5.0 and 13.0 due to the presence of benzonitrile groups on the backbone (Fig. 10 and Table 5). Apparently, among these structurally isomeric PIs, the repeat-unit asymmetry has resulted in the largest polarization response. Together with the same trend observed at room temperature, it can be speculated that with creative design, the possibility may exist for such effect on polymer permittivity to be amplified at relatively high operation temperatures, e.g. 100–150 °C, which are well above room temperature and below the polymer softening temperatures.

CONCLUSIONS

Having found that the differential susceptibility to aromatic nucleophilic displacement of the fluorides in 2,6-DFBN is chemically exploitable and a way to avoid transesterifica-

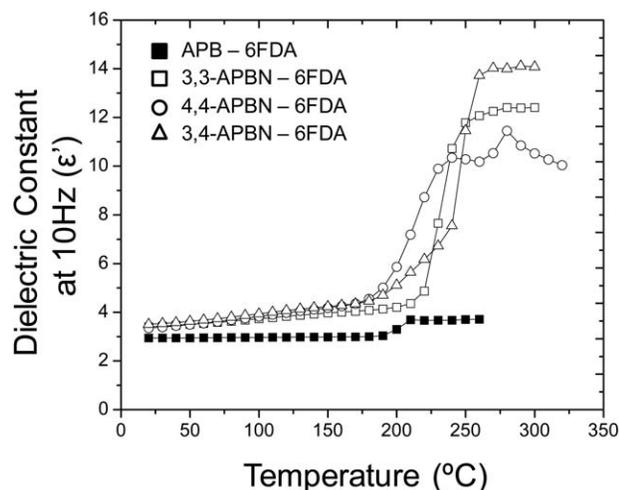


FIGURE 10 Composite plot of the dielectric constants of 6FDA-based PIs at 10 Hz and as a function of temperature.

tion side reaction, we demonstrates that an unsymmetrical diamine could be conveniently prepared by sequentially adding two isomeric (or in a broader scope, structurally different) aminophenols at 70 and 100 °C, respectively. Three synthetic routes have been successfully developed, but the ease of one-pot route would make the monomer synthesis more practical and perhaps, commercially viable. We have prepared a series of new PIs from this unsymmetrical diamine and five dianhydride via thermal and chemical imidization of the respective PAAs. These PIs are soluble in common organic solvents, can form tough and creasable films, and possess T_g well above 200 °C. More importantly, as exemplified by the 6FDA-APBN series, when comparing to the PAA precursors containing symmetrical units, we have found that the processibility of the unsymmetrical PAAs have been greatly improved because of an order-of-magnitude solution-viscosity reduction by the presence of unsymmetrical repeat units, and all three PIs show similar mechanical properties and thermal stability. Therefore, an element of asymmetry at the molecular level must have a cumulative effect on the conformational entropy of the polymer chains that can enhance not only the solubility, but also reduces the hydrodynamic volumes (viscosities) of both the PAA precursor and PI. On the other hand, the repeat-unit asymmetry effect in enhancing the polymer permittivity is relatively small at ambient temperature but significantly larger (>3 times) at ca. 250 °C as the polarization response results of the 6FDA-APBN series have indicated, and provided a starting point toward designing high temperature polymer capacitors.

ACKNOWLEDGEMENTS

This work was completed at Air Force Research Laboratory (AFRL) at Wright Patterson Air Force Base with funding from Materials and Manufacturing Directorate as well as Air Force Office of Scientific Research. The authors are grateful to Marlene Houtz (University of Dayton Research Institute) for TGA and DMA data, Brian Kurish (UES, Inc.) for the assistance of

monomer synthesis and Robert Strong and Hilmar Koerner (UES, Inc.) for WAXD measurements.

REFERENCES AND NOTES

- 1 D. Wilson, H. D. Stenzenberger, P. M. Hergenrother, *Polyimides*; Chapman and Hall: New York, **1990**, pp 1–78.
- 2 P. M. Hergenrother, In *Polyimides and Other High-Temperature Polymers*; M. J. M. Abadie, B. Sillion, Eds.; Elsevier: New York, **1991**, pp 1–18.
- 3 J. P. Critchley, G. J. Knight, W. W. Wright, *Heat Resistant Polymers*; Plenum Press: New York, **1983**, pp 186–258.
- 4 C. E. Sroog, *J. Polym. Sci., Macromol. Rev.* **1976**, *11*, 161.
- 5 S. Z. D. Cheng, F. Li, E. P. Savitski, F. W. Harris, *Trends Polym. Sci.* **1997**, *5*, 51.
- 6 D. H. Wang, M. J. Arlen, J.-B. Baek, R. A. Vaia, L.-S. Tan, *Macromolecules* **2007**, *40*, 6100.
- 7 R. A. Dine-Hart, W. W. Wright, *Macromol. Chem.* **1984**, *143*, 189.
- 8 B. V. Kotov, T. A. Gordina, V. S. Voishchev, O. V. Kolninov, A. N. Pravednikov, *Polym. Sci. USSR* **1977**, *19*, 711.
- 9 M. Fryd, In *Polyimides: Synthesis, Characterization and Applications*; Mittal, K. L., Ed.; Plenum: New York, **1984**; Vol. 1, p 377.
- 10 H. Ishida, S. T. Wellinghoff, E. Baer, J. L. Koenig, *Macromolecules* **1980**, *13*, 826.
- 11 X. Zhu, H. Pan, Y. Liang, X. Jian, *Eur. Polym. J.* **2008**, *44*, 3782.
- 12 C.-L. Chung, W.-F. Lee, C.-H. Lin, S.-H. Hsiao, *J. Polym. Sci. Part A: Polym. Chem.* **2009**, *47*, 1756.
- 13 F. Yang, Y. Li, Q. Bu, S. Zhang, T. Ma, X. Zhao, *J. Polym. Degrad. Stab.* **2010**, *95*, 1950–1958.
- 14 Y. Shao, Y. Li, X. Zhao, T. Ma, C. Gong, F. Yang, *Eur. Polym. J.* **2007**, *43*, 4389–4397.
- 15 Z. X. Li, L. Q. Lin, W. M. Zhang, T. Wu, J. L. Pu, *J. Polym. Sci. Part A: Polym. Chem.* **2006**, *44*, 1291–1298.
- 16 J. Yan, Z. Wang, C. Lv, H. Yang, Z. Shang, L. Gao, M. Ding, *J. Appl. Polym. Sci.* **2008**, *110*, 706–711.
- 17 C. H. Lin, S. L. Chang, L. A. Peng, S. P. Peng, Y. H. Chuang, *Polymer* **2010**, *51*, 3899–3906.
- 18 S. Chung, S. Y. Kim, *Macromolecules* **2000**, *33*, 3190–3193.
- 19 V. Kute, S. Banerjee, *Macromol. Chem. Phys.* **2003**, *204*, 2105–2112.
- 20 H. Choi, I. S. Chung, K. Hong, C. E. Park, S. Y. Kim, *Polymer* **2008**, *49*, 2644–2649.
- 21 F. Yang, Y. Li, T. Ma, Q. Bu, S. Zhang, *J. Fluorine Chem.* **2010**, *131*, 767–775.
- 22 C.-Y. Wang, G. Li, J.-M. Jiang, *Polymer*, **2009**, *50*, 1709–1716.
- 23 Y. Shao, Y.-F. Li, X. Zhao, X.-L. Wang, T. Ma, F.-C. Yang, *J. Polym. Sci. Part A: Polym. Chem.* **2006**, *44*, 6836–6846.
- 24 B. Dasgupta, S. K. Sen, S. Maji, S. Chatterjee, S. Banerjee, *J. Appl. Polym. Sci.* **2009**, *112*, 3640–3651.
- 25 B. Dasgupta, S. K. Sen, S. Banerjee, *J. Membr. Sci.* **2009**, *345*, 249–256.
- 26 X. Zhao, Y.-F. Li, S.-J. Zhang, Y. Shao, X.-L. Wang, *Polymer* **2007**, *48*, 5241–5249.
- 27 X. Zhao, Y.-F. Li, Y. Shao, T. Ma, C.-L. Gong, C.-S. Huang, *J. Appl. Polym. Sci.* **2008**, *107*, 3119–3126.
- 28 M. Ghaemy, R. Alizadeh, *Eur. Polym. J.* **2009**, *45*, 1681–1688.
- 29 M. Ghaemy, R. Alizadeh, F. H. Nasr, *J. Appl. Polym. Sci.* **2010**, *118*, 3407–3415.
- 30 W.-T. Chen, K.-L. Wang, *Macromol. Res.* **2010**, *18*, 821–827.
- 31 L. Cheng, X. G. Jian, *J. Appl. Polym. Sci.* **2004**, *92*, 1516–1520.
- 32 H. B. Zheng, Z. Y. Wang, *Macromolecules* **2000**, *33*, 4310–4312.
- 33 K. C. Chuang, J. M. Criss, E. A. Mintz, In 42nd Central Regional Meeting of the American Chemical Society, Dayton, OH, June 16–19 (**2010**), Abstr. CERMACS-361.
- 34 J. A. Young, B. L. Farmer, J. A. Hinkley, *Polymer* **1999**, *40*, 2787–2795.
- 35 C. Park, Z. Ounaies, K. E. Wise, J. S. Harrison, *Polymer* **2004**, *45*, 5417–5425.
- 36 B. Gonzalo, J. L. Vilas, T. Breczewski, M. A. Pérez-Jubindo, M. R. De La Fuente, M. Rodriguez, L. M. León, *J. Polym. Sci. Part A: Polym. Chem.* **2009**, *47*, 722–730.
- 37 Z. Ounaies, C. Park, J. S. Harrison, J. G. Smith, J. Hinkley, *SPIE Proc.* **1999**, *3669*, 171–178.
- 38 Saxena, P. V. Prabhakaran, V. L. Rao, K. N. Ninan, *Polym. Int.* **2005**, *54*, 544–552.
- 39 J. Lu, C. P. Wong, *IEEE Trans Dielectr Electr Insul* **2008**, *15*, 1322–1328.
- 40 L. Li, R. Kikuchi, M.-A. Kakimoto, M. Jikei, A. Takahashi, *High Perform. Polym.* **2005**, *17*, 135–147.
- 41 C. Hamciuc, E. Hamciuc, M. Ignat, G. Zarnescu, *High Perform. Polym.* **2009**, *21*, 205–218; (b) C. Hamciuc, E. Hamciuc, M. Ignat, G. Zarnescu, *High Perform. Polym.* **2010**, *22*, 225–236.
- 42 H. A. Kang, I. S. Chung, M.-A. Kakimoto, S. Y. Kim, *Polym. J.* **2001**, *33*, 284–289.
- 43 H. R. Kricheldorf, In *Handbook of Polymer Synthesis, Part A*; H. R. Kricheldorf, Ed.; Marcel Dekker: New York, (**1992**); pp 588–590 and references therein.
- 44 R. H. B. Galt, J. Horbury, Z. S. Matusiak, R. J. Pearce, J. S. Shaw, *J. Med. Chem.* **1989**, *32*, 2357–2362.
- 45 J. Thurmond, M. E. R. Butchbach, M. Palomo, B. Pease, M. Rao, L. Bedell, M. Keyvan, G. Pai, R. Mishra, M. Haraldsson, T. Andresson, G. Bragason, M. Thosteinsdottir, J. M. Bjornsson, D. D. Coovert, A. H. M. Burghes, M. E. Gurney, J. Singh, *J. Med. Chem.* **2008**, *51*, 449–469.
- 46 F. W. Mercer, M. T. McKenzie, A. Easteal, S. J. Moses, *Polymer* **1994**, *35*, 5355–5363; (b) F. W. Mercer, A. Easteal, M. Bruma, *Polymer* **1997**, *38*, 707–714.
- 47 (a) For the ground-breaking work using the asymmetric diamines and dianhydrides in lowering the melt-viscosity of thermosetting imide oligomers, see (a) R. Yokota, S. Yamamoto, S. Yano, T. Sawaguchi, M. Hasegawa, H. Yamaguchi, H. Ozawa, R. Sato, *High Perform. Polym.* **2001**, *13*, S61–S72; (b) T. Ogasawara, T. Ishikawa, R. Yokota, H. Ozawa, M. Taguchi, R. Sato, Y. Shigenari, K. Miyagawa, *Adv. Compos. Mater.* **2003**, *11*, 277–286.
- 48 (a) Industrial Summit Technology Corporation, "Colorless Polyimide Films" Industrial Summit Technology Corporation web site, http://www.istcorp.jp/en/div_el_cpifl.htm, accessed on 09/11/2013; (b) "DuPont Kapton Colorless Polyimide Film Enables World Record for Flexible CdTe Photovoltaic Efficiency", DuPont web site, http://www2.dupont.com/Photovoltaics/en_US/news_events/article20110601.html, accessed on 09/11/2013.
- 49 J. D. Jacobs, M. J. Arlen, D. H. Wang, Z. Ounaies, R. Berry, L.-S. Tan, P. H. Garrett, R. A. Vaia, *Polymer* **2010**, *51*, 3139–3146; (b) M. Arlen, D. Wang, D. Jacobs, R. Justice, A. Trionfi, J. Hsu, D. Schaefer, L.-S. Tan, R. Vaia, *Macromolecules* **2008**, *41*, 8053–8062.