Synthesis of a New Class of Triphenylamine-Containing Poly(ether-imide)s for Electrochromic Applications

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ABSTRACT: A novel triphenylamine (TPA)-containing bis(ether anhydride) monomer, namely 4,4'-bis(3,4-dicarboxyphenoxy)triphenylamine dianhydride, was synthesized and reacted with various aromatic diamines leading to a series of new poly-(ether-imide)s (PEI). Most of these PEIs were soluble in organic solvents and could be easily solution cast into flexible and strong films. The polymer films exhibited good thermal stability with glass-transition temperatures in the range 211–299 °C. The polymer films exhibited reversible electrochemical processes and stable color changes (from transparent to navy blue) with high coloration efficiency and contrast ratio upon electro-

INTRODUCTION Electrochromic materials comprise redoxactive species that exhibit significant, lasting, and reversible changes in color upon reduction or oxidation.¹ Research in electrochromic devices has received a great deal of attention because of the importance of this interesting phenomenon in applications such as electrochromic windows,² displays,³ memory devices,⁴ electronic papers,⁵ and adaptive camouflages.⁶ There is a huge amount of chemical species that exhibited electrochromic properties,⁷ including metal coordination complexes,⁸ metal oxide (especially tungsten oxide),9 viologens (4,4'-bipyridium salts),10 and conducting polymers (such as polyanilines, polypyrroles, and polythiophenes).¹¹ The use of conjugated polymers as active layers in electrochromic devices became popular because of the outstanding electrochromic properties such as fast switching time, ease of synthesis, and wide range of colors, which can be achieved by simple chemical synthesis.¹² For efficient operation of an electrochromic device, it is necessary to take a number of properties into consideration: electrochromic efficiency, optical contrast, response time, stability, and durability.^{11(b)} The difficulty in achieving satisfactory values for all these parameters at the same time stimulates the development of new methods of preparation of electrochromic films, new materials, and components for the devices.¹³

oxidation. During the electrochemical oxidation process, a crosslinked polymer structure was developed due to the coupling reaction between the TPA radical cation moieties in the polymer chains. These polymers can be used to fabricate electrochromic devices with high coloration efficiency, high redox stability, and fast response time. © 2013 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2014**, *52*, 825–838

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Triarylamine derivatives are important organic materials for electronic and optoelectronic devices. Owing to the electrondonating nature of the nitrogen atom in triarylamines, they act as hole-transport materials in various applications like xerography, light-emitting diodes, and solar cells.¹⁴ Polymers bearing triarylamine units have attracted much attention as ideal hole-transporting materials in various optoelectronic device applications such as organic light-emitting diodes because of the strong electron-donating and hole-transporting/injecting properties of triarylamine units.¹⁵ Triarylamines can be easily oxidized to form stable radical cations, and the oxidation process is always associated with a strong change of coloration. Various triarylamine-based polymer systems have been reported to be potential electrochromic materials.¹⁶

Aromatic polyimides are known for their outstanding properties, such as unique high thermal stability, good mechanical and electrical properties as well as excellent chemical resistance.¹⁷ They are commercially important materials used extensively in photoresists, alignment layers in liquid crystal displays, and high-temperature coatings. However, wholly aromatic polyimides are difficult to process because of limited solubility and extremely high softening temperatures that stem from the rigidity of the backbone and strong interchain interactions. To overcome these drawbacks, various

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attempts have been made to develop structurally modified polymers existing increased solubility with retention of their good thermal stability.¹⁸ Several major approaches include the incorporation of flexible linkages, noncoplanar moieties, asymmetric units, or bulky pendant groups into the polyimide backbones.¹⁹ In recent years, Liou and coworkers have carried out extensive studies on the design and synthesis of triarylamine-based high-performance polymers such as aromatic polyimides²⁰ and polyamides²¹ for potential application in electrochromic devices. The triarylamine-containing monomers such as diamines and dicarboxylic acids could be easily prepared using a well-established procedure, and they could react with the corresponding comonomers through conventional polycondensation techniques, producing the desired triarylamine-based polymers. In general, these polymers exhibit good solubility to organic solvents due to the introduction of bulky, packing-disruptive triarylamine moieties. Thus, they could be readily solution-cast into flexible electrochromic films with good mechanical property and high thermal stability. Thus, incorporation of threedimensional, packing-disruptive triarylamine units into the polyimide backbone not only resulted in enhanced solubility but also led to new electronic functions of polyimides such as electrochromic characteristics.

It has also been demonstrated that triarylamine-based polyimides generally exhibited poor electrochemical and electrochromic stability as compared to their polyamide analogs because of the strong electron-withdrawing imide group, which increases the oxidation potential of the triarylamine unit and destabilizes the resultant amino radical cation upon oxidation.²² Incorporating a spacer between the triarylamine core and the imide ring may improve the electrochemical and elcetrochromic stability of this kind of electroactive polymers. Thus, a new kind of triphenylamine (TPA)-containing bis(ether anhydride), namely 4,4'-bis(3,4-dicarboxyphenoxy)triphenylamine dianhydride, was synthesized and led to a series of poly(ether-imide)s (PEIs) with main-chain TPA groups. By the incorporation of the phenoxy spacer between the TPA and imide units, the resulting PEIs are expected to exhibit enhanced electrochemical and electrochromic properties. The threedimensional TPA kinked structure is certainly responsible for decreasing interchain interactions, thus improving the solubility of polyimides. Physical, thermal, electrochemical, and electrochromic properties of these PEIs were also investigated.

EXPERIMENTAL

Materials

N,*N*-Dimethylacetamide (DMAc, Fluka) was dried over calcium hydride overnight, distilled under reduced pressure, and stored over 4 Å molecular sieves in a sealed bottle. According to a literature method,²³ 4,4'-dihydroxytriphenylamine (**2**) was prepared by demethylation of 4,4'-dimethoxytriphenylamine (**1**) which was obtained from Ullmann reaction between aniline and 4-iodoanisole. Commercially available diamine monomers including *p*-phenylenediamine (**6a**), 4,4'-diaminodiphenyl ether (**6b**), 3,4-diaminodiphenyl ether (6c), and 9,9-bis(4-aminophenyl)fluorene (6e) were used as received from Tokyo Chemical Industry. According to a procedure reported previously,²⁴ 2-triflouromethyl-4,4'diaminodiphenyl ether (6d, mp: 112-113 °C) was synthesized by the chloro-displacement reaction of 2-chloro-5nitrobenzotrifluoride with p-nitrophenol in the presence of potassium carbonate, followed by the hydrazine palladiumcatalyzed reduction of the intermediate dinitro compound. 4,4'-Diaminotriphenylamine (6f, mp: 186-188 °C) and 4,4'diamino-4"-tert-butyltriphenylamine (6g, mp: 113-115 °C)²⁵ were synthesized by the cesium fluoride-mediated condensation of *p*-fluoronitrobenzene with aniline and 4-tert-butylaniline, respectively, followed by a palladium-catalyzed hydrazine reduction of the dinitro intermediates. Tetrabutylammonium perchlorate, Bu₄NClO₄, were recrystallized from ethyl acetate under nitrogen atmosphere and then dried in vacuo before use. All other reagents and solvents were used as received from commercial sources.

Monomer Synthesis

4,4'-Bis(3,4-dicyanophenoxy)triphenylamine (3)

A mixture of 6.93 g (0.025 mol) of bisphenol **2**, 8.66 g (0.050 mol) of 4-nitrophthalonitrile, and 6.91 g (0.050 mol) of K₂CO₃ in 60 mL of DMF was stirred at room temperature for about 48 h. Then, the reaction mixture was poured into 600 mL of water, and the precipitated light brown solid was collected and washed thoroughly with methanol and water. The yield of bis(ether dinitrile) **3** was 12.34 g (93%), mp = 223–225 °C. IR (KBr) (Supporting Information Fig. S1): 2231 cm⁻¹ (C \equiv N stretch).

¹H NMR (500 MHz, DMSO- d_6 , δ , ppm) (Supporting Information Fig. S2): 7.08 (t, J = 7.5 Hz, 1H, H_a), 7.12 (d, J = 8.0 Hz, 2H, H_c), 7.15 (s, 8H, H_d + H_e), 7.35 (t, J = 10.0 Hz, 2H, H_b), 7.45 (d, J = 10.0 Hz, 2H, H_f), 7.80 (s, 2H, H_h), 8.55 (d, J = 8.5 Hz, 2H, H_g). ¹³C NMR (125 MHz, DMSO- d_6 , δ , ppm): 107.98 (C¹²), 115.39 (-CN), 115.89 (-CN), 116.66 (C¹³), 121.60 (C⁷), 121.75 (C¹⁰), 122.28 (C¹⁴), 123.34 (C¹), 123.86 (C³), 125.36 (C⁶), 129.66 (C²), 136.24 (C¹¹), 144.75 (C⁵), 146.96 (C⁴), 148.79 (C⁸), 161.34 (C⁹).



4,4'-Bis(3,4-dicarboxyphenoxy)triphenylamine (4)

In a 250-mL flask, a suspension of bis(ether dinitrile) **3** (10.59 g, 0.020mol) in an ethanol/water mixture (100 mL/ 100 mL) containing 27 g (0.48 mol) of dissolved KOH was heated at a reflux temperature. Refluxing was continued for 48 h until the evolution of ammonia had ceased. The resulting clear solution was filtered hot to remove any possible insoluble impurities. The filtrate was allowed to cool and was then acidified by hydrochloric acid to a pH of 2–3. The

precipitated pale green product was filtered off, washed with water until it was neutral, and dried. The yield of bis(ether diacid) 4 was 10.29 g (85%).

IR (KBr) (Supporting Information Fig. S1): 2500–3500 cm⁻¹ (0—H stretch), 1714 cm⁻¹ (C=0 stretch). ¹H NMR (500 MHz, DMSO- d_6 , δ , ppm) (Supporting Information Fig. S3): 7.05 (t, J = 7.3 Hz, 1H, H_a), 7.07 (d, J = 7.7 Hz, 2H, H_c), 7.11 (s, 8H, H_d and H_e), 7.15 (d, J = 8.6 Hz, 2H, H_f), 7.24 (s, 2H, H_h), 7.33 (t, J = 7.6 Hz, 2H, H_b), 7.85 (d, J = 8.6 Hz, 2H, H_g). ¹³C NMR (125 MHz, DMSO- d_6 , δ , ppm): 117.04 (C¹⁴), 118.64 (C¹⁰), 121.16 (C⁷), 122.94 (C¹), 123.35 (C³), 125.52 (C⁶), 126.14 (C¹²), 129.67 (C²), 132.01 (C¹¹), 136.82 (C¹³), 143.96 (C⁵), 147.31 (C⁴), 150.41 (C⁸), 159.48 (C⁹), 167.49 (-COOH), 168.44 (-COOH).



4,4'-Bis(3,4-dicarboxyphenoxy)triphenylamine Dianhydride (5)

In a 200-mL flask, a mixture of 9.08 g (0.015 mol) of bis(ether diacid) **4** dissolved in 50 mL of acetic anhydride was heated at a reflux temperature for 3 h. The resulting clear solution was filtered to remove any insoluble impurities. After cooling to room temperature, the precipitated olivine product was filtered and dried at 120 °C *in vacuo*. The yield of bis(ether anhydride) **5** was 5.00 g (67%). IR (KBr) (Supporting Information Fig. S1): 1849 cm⁻¹ (asymmetric C=O stretch), 1774 cm⁻¹ (symmetric C=O stretch).

¹H NMR (500 MHz, DMSO- d_6 , δ , ppm) (Fig. 1): 7.09 (t, J = 7.3 Hz, 1H, H_a), 7.13 (t, J = 8.1 Hz, 2H, H_c), 7.17 (s, 8H, H_d + H_e), 7.36 (t, J = 7.6 Hz, 2H, H_b), 7.50 (s, 2H, H_h), 7.56 (d, J = 8.4 Hz, 2H, H_f), 8.08 (d, J = 8.4 Hz, 2H. H_g). ¹³C NMR (125 MHz, DMSO- d_6 , δ , ppm): 112.35 (C¹⁴), 121.61 (C⁷), 123.39 (C¹), 123.93 (C³), 124.36 (C¹⁰), 124.56 (C¹²), 125.36 (C⁶), 127.80 (C¹¹), 129.68 (C²), 134.04 (C¹³), 144.70 (C⁵), 146.98 (C⁴), 149.24 (C⁸), 162.39 (anhydride carbonyl), 162.60 (anhydride carbonyl), 164.18 (C⁹). Anal. Calcd. For C₃₄H₁₉NO₈ (569.53): C, 71.70%; H, 3.36%; N, 2.46%. Found: C, 71.45%; H, 3.29%; N, 2.41%.



Polymer Synthesis

A typical polymerization procedure is as follows. The diamine **6d** (0.3202 g, 1.19 mmol) was dissolved in 9.5 mL of



anhydrous DMAc in a 50-mL round-bottom flask. Then bis(ether anhydride) 5 (0.6798 g, 1.19 mmol) was added to the diamine solution in one portion. Thus, the solid content of the solution is approximately 10 wt %. The mixture was stirred at room temperature for about 18 h to yield a viscous poly(amic acid) solution. The inherent viscosity of the resulting poly(amic acid) was 0.68 dL g^{-1} , measured in DMAc at a concentration of 0.50 g dL⁻¹ at 30 °C. The poly(amic acid) film was obtained by casting from the reaction polymer solution onto a glass Petri-dish and drying at 90 °C overnight. The poly(amic acid) in the form of solid film was converted to PEI 7d by successive heating under vacuum at 150 °C for 30 min, 200 $^\circ\text{C}$ for 30 min, 250 $^\circ\text{C}$ for 30 min and then 300 °C for 1 h. The inherent viscosity of the resulting PEI 7d was 0.44 dL g^{-1} , measured at a concentration of 0.5 g dL⁻¹ in DMAc at 30 °C. The IR spectrum of 7d (Supporting Information Fig. S4) exhibited characteristic imide absorption bands at 1776 cm⁻¹ (asymmetric C=O stretch) and 1722 cm⁻¹ (symmetric C=O stretch).

¹H NMR (500 MHz, CDCl₃, δ , ppm) (Supporting Information Fig. S5): 7.03 (d, J = 8.5 Hz, 4H, H_e), 7.10 (t, J = 7.0 Hz, 1H, H_a), 7.15 (d, 1H, H_k), 7.18 (d, J = 7.0 Hz, 6H, H_c, and H_d), 7.21 (d, J = 10.5 Hz, 2H, H_j), 7.33 (t, J = 8.0 Hz, 2H, H_b), 7.39 (d, J = 7.5 Hz, 2H. H_f), 7.46 (d, J = 8.5 Hz, 2H, H_i), 7.48 (s, 2H, H_h), 7.57 (d, J = 8.0 Hz, 1H, H_l), 7.79 (s, 1H, H_m), 7.91 (d, J = 7.5 Hz, 2H, H_g).

For the chemical imidization method, 4 mL of acetic anhydride and 2 mL of pyridine were added to the poly(amic acid) solution obtained by a similar process as above, and the mixture was heated at 100 °C for 1 h to effect a complete imidization. The homogenous polymer solution was poured slowly into 150 mL of stirring methanol giving rise to yellow precipitate that was collected by filtration, washed thoroughly with hot water and methanol, and dried. A polymer solution was made by the dissolution of about 0.5 g of the polyimide sample in 10 mL of hot DMAc. The homogeneous solution was poured into a 9-cm glass Petri dish, which was placed in a 90 °C oven overnight for the slow release of the solvent, and then the film was stripped off from the glass substrate and further dried in vacuum at 160 °C for 6 h.

Fabrication of Electrochromic Devices

Electrochromic polymer films were prepared by dropping solution of the PEIs (3 mg mL⁻¹ in DMAc) onto an ITOcoated glass substrate ($20 \times 30 \times 0.7$ mm, $50-100 \Omega$ cm⁻²). A gel electrolyte based on PMMA (Mw: 120,000) and LiClO₄ was plasticized with propylene carbonate to form a highly transparent and conductive gel. PMMA (1 g) was dissolved in dry acetonitrile (4 mL), and LiClO₄ (0.1 g) was added to the polymer solution as supporting electrolyte. Then propylene carbonate (1.5 g) was added as plasticizer. The mixture was then gently heated until gelation. The gel electrolyte was spread on the polymer-coated side of the electrode, and the electrodes were sandwiched. Finally, an epoxy resin was used to seal the device.

Measurements

Infrared (IR) spectra were recorded on a Horiba FT-720 FTIR spectrometer. ¹H and ¹³C NMR spectra were measured on a Bruker AVANCE 500 FT-NMR system with tetramethylsilane as an internal standard. Elemental analysis was performed on a Heraeus VarioEL III CHNS elemental analyzer. The inherent viscosities were determined with a Cannon-Fenske viscometer at 30 °C. Wide-angle X-ray diffraction (WAXD) measurements were performed at room temperature (ca. 25 °C) on a Shimadzu XRD-6000 X-ray diffractometer with a graphite monochromator (operating at 40 kV and 30 mA), using nickelfiltered Cu-K α radiation ($\lambda = 1.5418$ Å). The scanning rate was 2° min⁻¹ over a range of $2\theta = 10-40^{\circ}$. Thermogravimetric analysis (TGA) was performed with a Perkin-Elmer Pyris 1 TGA. Experiments were carried out on approximately 4-6 mg of samples heated in flowing nitrogen or air (flow rate = 40 $\text{cm}^3 \text{ min}^{-1}$) at a heating rate of 20 °C min⁻¹. DSC analyses were performed on a Perkin-Elmer Pyris 1 DSC at a scan rate of 20 $^{\circ}\text{C}\ \text{min}^{-1}$ in flowing nitrogen. Thermomechanical analysis (TMA) was determined with a Perkin-Elmer TMA 7 instrument. The TMA experiments were carried out from 50 to 400 $^\circ\text{C}$ at a scan rate of 10 $^\circ\text{C}$ min $^{-1}$ with a penetration probe 1.0 mm in diameter under an applied constant load of 10 mN. Softening temperatures (T_s) were taken as the onset temperatures of probe displacement on the TMA traces. Electrochemistry was performed with a CHI 750A electrochemical analyzer. Cyclic voltammetry was conducted with the use of a three-electrode cell in which ITO (polymer films area about $0.8 \times 1.25 \text{ cm}^2$) was used as a working electrode. A platinum wire was used as an auxiliary electrode. All cell potentials were taken with the use of a home-made Ag/AgCl, KCl (sat.) reference electrode. Ferrocene was used as an external reference for calibration (+0.48 V vs. Ag/AgCl). Voltammograms are presented with the positive potential pointing to the left and with increasing anodic currents pointing downwards. Spectroelectrochemistry analyses were carried out with an electrolytic cell, which was composed of a 1 cm cuvette, ITO as a working electrode, a platinum wire as an auxiliary electrode, and a Ag/AgCl reference electrode. Absorption spectra in the spectroelectrochemical experiments were measured with an Agilent 8453 UV-visible diode array spectrophotometer. Color measurements were performed by using a Konica Minolta CS-100 ChromaMeter with viewing geometry as recommended by Commision Internationale de l'Eclairage.

RESULTS AND DISCUSSION

Monomer Synthesis

The new triphenylamine-based bis(ether anhydride) **5** was synthesized via the synthetic route outlined in Scheme 1. According to a reported method,²³ the 4,4'-dimethoxytriphenylamine (**1**) was synthesized by Ullmann condensation between aniline and 4-iodoanisole by using Cu and K_2CO_3 in tri(ethylene glycol) dimethyl ether (TEGDME). Demethylation of dimethoxy compound **1** with boron tribromide (BBr₃) gave the 4,4'-dihydroxy-triphenylamine (**2**). 4,4'-Bis(3,4-dicyanophenoxy)triphenylamine (**3**) was obtained from the nitro-displacement of 4-nitrophthalonitrile with the potassium salt of compound **2**



SCHEME 1 Synthetic route to the target bis(ether anhydride) monomer **5**.

formed in situ by treatment of K₂CO₃ in DMF. Alkaline hydrolysis of the bis(ether dinitrile) 3 with aqueous potassium hydroxide in ethanol followed by acidification with aqueous HCl led to 4,4'bis(3,4-dicarboxyphenoxy)triphenylamine (4), which was subsequently cyclodehydrated with acetic anhydride to generate the target bis(ether anhydride) monomer 5. The yield in each step was reasonable, and the molecular structure of the synthesized compounds could be affirmed by IR and NMR spectroscopic techniques. The FTIR spectra of intermediate compounds 3 and 4 and the target monomer 5 are included in Supporting Information (Fig. S1). The proton and carbon-13 NMR spectra of intermediate compounds 3 and 4 are also shown in SI (Supporting Information Figs. S2 and S3). Figure 1 depicts the proton and carbon-13 NMR spectra of bis(ether anhydride) 5 in dimethyl sulfoxide- d_6 . Assignments of each carbon and proton assisted by the two-dimensional NMR spectroscopy are also indicated in these spectra, and they are in good agreement with the proposed molecular structures of these compounds.

Polymer Synthesis

PEIs **7a-7g** were prepared in a conventional two-step method by the reactions of equal molar amounts of bis(ether anhydride) monomer **5** with various aromatic diamines (**6a-6g**) to form poly(amic acid)s, followed by thermal or chemical cyclodehydration (Scheme 2). As shown in Table 1, the



FIGURE 1 (a) ¹H NMR, (b) ¹³C NMR, (c) H-H COSY, and (d) C-H HMQC spectra of the target bis(ether anhydride) **5** in DMSO- d_6 . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]





TABLE 1 Inherent Viscosity and Solubility Behavior of Poly(ether-imide)s Prepared via Thermal (-T) or Chemical (-C) Imidization

	η_{inh} (dL g	Solubility in Various Solvents ^b							
Polymer Code	Poly(amic acid)	Polyimide	NMP	DMAc	DMF	DMSO	<i>m</i> -Cresol	THF	CHCl₃
7a-T	0.50	-	-	_	_	_	+-	-	_
7a-C		-	+-	+-	+-	+-	+h	+-	-
7b-T	0.69	-	+-	+-	+-	+-	+h	_	+-
7b-C		0.54	++	++	++	+h	+h	+-	++
7c-T	0.35	-	+h	+-	+-	+-	+h	+-	++
7c-C		0.37	++	++	++	+h	+h	++	++
7d-T	0.68	-	+-	+-	+-	+-	+-	+-	-
7d-C		0.44	++	++	++	+h	+h	++	++
7e-T	0.44	_	+-	+-	+-	+-	+-	+-	+-
7e-C		0.36	++	++	++	+h	+h	++	++
7f-T	0.64	-	-	-	-	-	+-	-	+-
7f-C		0.36	++	++	+h	+h	+h	++	++
7g-T	0.60	_	+-	+-	+-	-	+-	+-	+-
7g-C		-	+h	+h	+h	+h	+h	++	+-

 $^{\rm a}$ Inherent viscosity measured at a concentration of 0.5 dL g^{-1} in DMAc at 30 $^\circ\text{C}.$

^b The qualitative solubility was tested with 10 mg of a sample in 1 mL of stirred solvent.++, soluble at room temperature; +h, soluble on heating; +-, partially soluble; -, insoluble even on heating.

poly(amic acid) precursors had inherent viscosities in the range of 0.35–0.69 dL g^{-1} . The resulting poly(amic acid) solutions were poured into a clean glass Petri-dish and dried to form thin solid films. The thermal conversion to polyimides was carried out by step-by-step heating of the poly(amic acid) films to 300 °C. The transformation from poly(amic acid) to a polyimide could also be carried out via chemical cyclodehydration by using acetic anhydride and pyridine. All the polyimides showed the characteristic absorption bands of the imide ring near 1776 (asymmetric C=O stretching) and 1722 cm⁻¹ (symmetric C=O stretching). Typical IR spectra of PEI 7d and its poly(amic acid) precursor are illustrated in Supporting Information Figure S4. The ¹H NMR and ¹H-¹H COSY spectra of a representative PEI **7d** are illustrated in Supporting Information Figure S5. Assignments of each proton are in good agreement with the structure of its repeating unit.

Polymer Properties

Basic Characterization

As evidenced by their WAXD patterns (see Supporting Information Fig. S6), all the PEI films exhibited an amorphous nature. This can be attributed in part to the bulky, packingdisruptive TPA unit along the polymer backbone, which does not favor their close chain packing. The solubility behavior of the polyimides depended on their chain packing ability and intermolecular interactions that was affected by the rigidity, symmetry, and regularity of the molecular backbone. PEI **7a** derived from more rigid *p*-phenylenediamine showed a poor solubility in all the test solvents. The other PEIs exhibited a better solubility to organic solvents. As shown in ^c Solvent: NMP: *N*-methyl-2-pyrrolidone; DMAc: *N*,*N*-dimethylacetamide; DMF: *N*,*N*-dimethylformamide; DMSO: dimethyl sulfoxide; THF: tetrahydrofuran.

Table 1, most of the chemically imidized samples of **7b-7g** are soluble in NMP, DMAc, DMF, and THF. The good solubility of these polyimides can be attributed to the presence of three-dimensional TPA units, together with the flexible ether linkage along the polymer backbone. In addition, the chemically imidized samples generally revealed a higher solubility than those prepared by the thermal imidization method. The lower solubility of the thermally cured PEIs may be attributed to the presence of partial interchain crosslinking or an aggregation of the polymer chains during thermal curing process.

Thermal Properties

The thermal stability and phase-transition temperatures of these PEIs were determined by TGA, DSC, and TMA techniques. The thermal behavior data are included in Table 2. Typical TGA and TMA curves of the representative PEI 7f are shown in Figure 2. The TGA results showed an excellent thermal stability of these PEIs, even though they revealed high solubility. All of these polymers exhibited a similar TGA pattern with no significant weight loss below 500 °C in air or nitrogen atmosphere. The decomposition temperatures $(T_{\rm d})$ at 10% weight-loss in nitrogen and air were recorded in the range of 539-598 and 551-596 °C, respectively. The amount of carbonized residue (char yield) of these polymers in nitrogen atmosphere was more than 58% at 800 °C. The glass-transition temperatures (T_g) of all the polymers were observed in the range of 211-299 °C by DSC (Supporting Information Fig. S7). The decreasing order of $T_{\rm g}$ generally correlated with that of chain flexibility. As expected, the polymer **7e** showed the highest $T_{\rm g}$ due to the presence of rigid

TABLE 2 Thermal Properties of the Poly(ether-imide)s^a

			T _d at 5% Weight Loss (°C) ^d		T _d at 10% Weight Loss (°C) ^d		
Polymer Code	$T_{g} (^{\circ}C)^{b}$	T_s (°C) ^c	N ₂	Air	N_2	Air	Char Yield (wt %) ^e
7a	239	232	505	518	539	557	61
7b	227	227	536	526	563	569	58
7c	211	208	513	513	542	551	60
7d	227	224	572	562	598	596	66
7e	299	300	571	571	597	595	66
7f	252	252	527	513	555	552	65
7g	260	256	536	509	558	555	60

 $^{\rm a}$ All the polymer films were heated at 300 $^\circ\text{C}$ for 1 h before DSC, TMA, and TGA experiments.

^b Midpoint temperature of the baseline shift on the second DSC heating trace (rate = 20 °C min⁻¹) of the sample after quenching from 400 to 50 °C (rate = 200 °C min⁻¹) in nitrogen.

9,9-diphenylfluorene segments. Polymer **7c** exhibited the lowest $T_{\rm g}$ value of 211 °C because of the presence of flexible *m*-phenoxy linkage in its diamine residue. The softening temperatures ($T_{\rm s}$) (may be referred to as apparent $T_{\rm g}$) of the polymer film samples determined by the TMA method with a loaded penetration probe are also listed in Table 2. They were obtained from the onset temperature of the probe displacement on the TMA trace. As a representative example, the TMA trace of PEI **7f** is illustrated in the inset of Figure 2. In most cases, the $T_{\rm s}$ values of the PEI films obtained by TMA are comparable to the $T_{\rm g}$ values measured by the DSC experiments. The $T_{\rm g}$ values of the present PEIs are similar to those of analogous ones in which the bis(phenoxy)triphenylamine segment is in the diamine side;^{23(b)} however, they are lower than those ($T_{\rm g} = 298-351$ °C) reported for the polyi-



FIGURE 2 TMA and TGA curves of poly(ether-imide) **7f** with a heating rate of 10 and 20 °C min⁻¹, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

 $^{\rm c}$ Softening temperature determined by TMA at a heating rate of 10 $^{\circ}$ C min $^{-1}.$ $^{\rm d}$ Decomposition temperature at which a 5 or 10% weight loss was recorded by TGA at a heating rate of 20 $^{\circ}$ C min $^{-1}$ and a gas flow rate of 20 cm³ min $^{-1}.$

^e Residual weight % at 800 °C at a scan rate 20 °C min^{−1} in nitrogen.

mides based on N,N-bis(3,4-dicarboxyphenyl)aniline dianhydride²⁶ due to the incorporation of more flexible phenoxy spacer in the dianhydride component.

Electrochemical Properties

The electrochemical behavior of each PEI was investigated by CV conducted for the cast film on the ITO-coated glass substrate as the working electrode in dry acetonitrile (for the anodic scan) or DMF (for the cathodic scan) containing Bu_4NCIO_4 as an electrolyte and saturated Ag/AgCl as the reference electrode under nitrogen atmosphere. Figure 3 depicts the CV diagrams for **7d**, which was representative for the other **7a–7e** analogs. PEI **7d** exhibited an amphoteric redox behavior because of the presence of both the electron-



FIGURE 3 Cyclic voltammograms of the cast film of poly(etherimide) **7d** on an ITO-coated glass substrate in 0.1 M Bu₄NClO₄/ CH₃CN (for the anodic process) and DMF (for the cathodic process) solution at a scan rate of 50 and 100 mV s⁻¹, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE 3 C	Optical an	d Electrochemical	Properties of t	he Poly(ether-imide)s
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	Thin Film (nm) ^a		Oxidation Potential (V) ^b		Reduction Potential (V) ^c		Bandgap (eV) ^{d,e}		Energy Level (eV) ^e	
Polymer Code	λ_{\max}^{Abs}	λonset Abs	Eonset ^{ox}	$E_{1/2}^{\text{ox}}$	<i>E</i> onset ^{red}	E _{1/2}	E_{g}^{opt}	E_{g}^{ec}	НОМО	LUMO
7a	298	557	0.89	1.01	-1.05	-1.35	2.23	2.36	5.37	3.01
7b	297	585	0.88	0.97	-1.03	-1.29	2.12	2.26	5.33	3.07
7c	302	647	0.87	0.94	-0.96	-1.28	1.92	2.22	5.30	3.08
7d	298	566	0.93	1.02	-1.03	-1.29	2.19	2.31	5.38	3.07
7e	301	574	0.95	0.99	-0.89	-1.28	2.16	2.27	5.35	3.08
7f	298	606	0.97	1.01	-1.13	-1.30	2.05	2.31	5.37	3.06
7g	302	556	0.94	1.02	-1.08	-1.30	2.23	2.32	5.38	3.06
7d′	304	613	0.79	0.86, 0.96	-0.96	-1.24	2.79	2.20	5.32	3.12

 $^{\rm a}$ Versus Ag/AgCl in CH_3CN. $E_{\rm 1/2}={\rm average}$ potential of the redox couple peaks.

^b Versus Ag/AgCl in DMF.

 c Bandgaps calculated from absorption edge of the polymer films: E_{g}^{opt} = 1240/ $\lambda_{onset}.$

rich TPA moiety and the electron-deficient imide ring in its repeating unit. The anodic peak at 1.14 V is ascribed to the oxidation of the TPA units, and the cathodic peak at -1.34V can be attributed to the formation of radical anion of the imide unit. For the first positive scan, we observed an oxidation peak at about 1.14 V. From the first reverse negative potential scan, we detected two cathodic peaks one at 0.89 V and the other at 0.80 V. After the second scan, a new oxidation potential appeared at about 0.90 V that was the complementary anodic process for the second cathodic peak at 0.8 V. The observation of a new oxidation couple in the second potential scan indicates that the polymer 7d radical cations were involved in very fast electrochemical reactions that produced a substance that was easier to oxidize than was the parent 7d. The other 7a-7e analogs showed a similar CV behavior to that of 7d, and their redox potential according to the first CV diagrams are summarized in Table 3.

The cyclic voltammograms and differential pulse voltammograms (DPV) of PEIs 7f and 7g are illustrated in Figures 4 and 5, respectively. For comparison, the CV diagrams of structurally related polyimides 7d and 8 are also included in Figure 4. Polymers 7f and 7g with a TPA unit in both the dianhydride and diamine components are expected to display two oxidation processes due to the different electronic characters of these two TPA segments in their repeating units. However, these two oxidation processes occurred almost simultaneously by a two-electron loss event. Therefore, these two oxidation waves emerged (around 1.1-1.2 V) and were not well resolved even in their DPV diagrams. The repetitive CV diagrams of polymer 7g shown in Figure 5 reveal another new oxidation couple at lower potentials (waves at about 0.90 and 0.76 V). This behavior is similar to that observed for PEIs 7a-7e and can be attributed to the concomitant dimerization of the TPA units upon oxidation of these PEIs.

 $^{\rm d}$ $E_g^{\rm ec,}$ electrochemical band gap is derived from the difference between HOMO and LUMO values.

^e The HOMO and LUMO energy levels were calculated from $E_{1/2}^{ox}$ and $E_{1/2}^{red}$ values of CV curves and were referenced to ferrocene (4.8 eV relative to the vacuum energy level).

The energy levels of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the corresponding polymers were estimated from the $E_{1/2}^{\text{ox}}$ values. Assuming that the HOMO energy level for the ferrocene/ferrocenium (Fc/Fc⁺) standard is 4.80 eV with respect to the zero vacuum level, the HOMO and LUMO values for these PEIs were calculated to be in the range of 5.30–5.38 and 3.01–3.08 eV, respectively (Table 3).

Spectroelectrochemical Studies

The electro-optical properties of the polymer films were investigated using the changes in electronic absorption spectra at various applied voltages. As a typical example, the result of the 7d film upon electro-oxidation (p-doping) is presented in Figure 6 as a series of UV-vis-NIR absorption curves correlated to electrode potentials. In the neutral form, polymer 7d exhibited strong absorption at wavelength around 310 nm, characteristic for triphenylamine, but it almost transparent in the visible region. When the applied voltage was stepped from 0 to 1.14 V, the intensity of the absorption peak around 310 nm decreased gradually, and new peaks at 367 and 741 nm gradually increased in intensity [Fig. 6(a)]. Consequently, the film turned from colorless to blue. We attribute these spectral changes to the formation of a cation radical of the TPA moiety. As shown in Figure 6(b), when the applied voltage returned from 1.14 to 0.80 V, the absorption peaks at 367 and 741 nm decreased in intensity while a new absorption band at 478 nm appeared. Meanwhile, the film changed color from blue to yellow-orange. After the first electrochemical series of 7d was recorded from 0.00 to 1.02 V and then back to 0 V, we reapplied the electrode voltage and recorded its absorption profile. As shown in Figure 6(c), an additional yellow-orange oxidized state was observed in the rescan film at applied voltage of 0.89 V. The film showed a multicolored electrochromism from colorless neutral state to yellow-orange (L: 82; *a*: 6; *b*: 40) and blue (*L*: 80; *a*: -20; *b*: -16) oxidized states.



FIGURE 4 (a) Cyclic voltammograms of the cast films of polyimides **7d**, **7f**, and **8** on an ITO-coated glass substrate in 0.1 M Bu_4NCIO_4/CH_3CN solution at a scan rate of 50 mV s⁻¹. (b) Differential pulse voltammogram (DPV) of **7f**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

For the explanation of this spectral change, repetitive CV diagrams of **7d** are also included in Figure 6(d). The new yelloworange state should be related to the oxidation of the benzidine group formed by the oxidative coupling between TPA units.^{16(c)}

Electrochemical Crosslinking of the Poly(ether-imide)s

To obtain a crosslinked film of PEI **7d**, the solution of **7d** in Bu_4NClO_4/CH_2Cl_2 was repeated scanned between 0 and 1.4 V. Upon repetitive scanning, we observed a progressive growth in all peak currents and an insoluble polymer film being deposited on the ITO glass surface (Fig. 7). This behavior suggests that the oxidative coupling of the radical cations of TPA units in the polymer chain which might produce a tetraphenylbenzidine (TPB) structure (Scheme 3).^{16(a,c),27} Thus, the linear PEI **7d** may formed a partially crosslinked structure (we coded the partially crosslinked polymer as **7d**') after repeated CV scans.

The CV and DPV diagrams of the electrochemically crosslinked film of 7d' on the ITO glass substrate in 0.1 M Bu₄N-ClO₄/CH₃CN are displayed in Figure 8. The CV diagram reveals one emerged oxidation peak at 1.04 V and two associated cathodic waves at 0.78 and 0.89 V. As mentioned above, the first anodic peak (by DPV) corresponds to oxidations of the TPB units to form radical cations, followed subsequently by oxidation to dicationic species. In addition, the oxidation process of the unreacted TPA units in polyimide 7d' probably occurred concurrently with the second oxidation of TPB units. Upon oxidation of the 7d' film, an obvious electrochromic behavior was observed. The film in the neutral state is almost colorless. It changed color to yellowish orange at an applied voltage of 0.90 V and to blue at 1.10 V.

Spectroelectrochemical and Electrochromic Properties of the 7d' Film

The result of the 7d' film upon electro-oxidation (p-doping) is presented in Figure 9 as a series of UV-vis-NIR absorption curves correlated to electrode potentials. In the neutral form, polymer 7d' exhibited strong absorption at wavelength around 303 nm, characteristic for triphenylamine, but it almost transmissive in the visible region. When the applied voltage was stepped from 0 to 0.91 V, the new peaks at 485 nm gradually increased intensity. Meanwhile, the film changed color from colorless to yellowish orange (L: 82; a: 6; b: 40). This spectral and color change can be attributed to the first oxidation of the TPB units in the 7d' film. When the applied potential became more anodic at 1.03 V, the absorbance at 485 nm decreased and a strong broadband centered at 839 nm appeared, which we assigned to the formation of TPA radical cations and TPB dications. Meanwhile, the film changed color to blue (L: 80; a: -20; b: -16).



FIGURE 5 (a) Repetitive cyclic voltammograms of the cast film of poly(ether-imide) **7g** on an ITO-coated glass substrate in 0.1 M Bu_4NCIO_4/CH_3CN solution at a scan rate of 50 mV s⁻¹. (b) Differential pulse voltammograms of **7g**. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



FIGURE 6 (a) Absorption spectra of thin film of poly(ether-imide) **7d** on an ITO electrode at various applied voltages from 0 to 1.14 V, (b) spectral change from 1.14 back to 0.80 V, (c) the second spectroelectrochemical series, and (d) the color changes and repetitive cyclic voltammograms of the **7d** film. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Electrochromic switching studies for the PEI films were performed to monitor the percent transmittance changes (ΔT %) as a function of time at their absorption maximum (λ_{max}) and to determine the response time by stepping potential repeatedly between the neutral and oxidized states. The active area of the polymer film on ITO glass is about 1 cm^2 . Figure 10 depicts the optical transmittance as a function of time, current densities monitored and the first cycle optical transmittance changes for the 7d' film at 485 and 839 nm by applying square-wave potential steps between 0 and 0.91 V for a resident time of 10 s and between 0 and 1.03 V for a resident time of 11 s. The response time was calculated at 90% of the full-transmittance change, because it is difficult to perceive any further color change with naked eye beyond this point. As shown in Figure 10(c), the 7d' film attained 90% of a complete orange coloring and bleaching in 4 and 2.3 s, respectively. The optical contrast measured as $\Delta T\%$ of 7d' between neutral colorless and oxidized yellow states was found to be 22% at 485 nm. The 7d' film attained 90% of a complete blue coloring and bleaching in 4.6 and 3.5 s, respectively [Fig. 10(c)]. The optical contrast measured as



FIGURE 7 Repeated cyclic voltammograms of poly(ether-imide) **7d** between 0 and 1.4 V in 0.1 M Bu₄NCIO₄/CH₂Cl₂ solution, with a scan rate of 150 mV s⁻¹. The resulting partially crosslinked polymer is coded as **7d**'. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



SCHEME 3 Proposed coupling reaction of the TPA radical cations in the PEIs, together with the following oxidation reactions.

 $\Delta T\%$ of polyimide **7d**' between neutral colorless and oxidized blue states was found to be 81% at 839 nm. The electrochromic coloring efficiency (CE) for the yellowish orange coloring ($\eta = \Delta OD_{485}/Q$) was estimated to be 391 cm² C⁻¹, and that for the blue coloring ($\eta = \Delta OD_{839}/Q$) of the **7d**' film was estimated to be 384 cm² C⁻¹ (Table 4).

Finally, we fabricated as preliminary investigations single layer electrochromic cells (Fig. 11). The polyimide films were spray-coated onto ITO-glass and then dried. Afterward, the gel electrolyte was spread on the polymer-coated side of the electrode and the electrodes were sandwiched. To prevent leakage, an epoxy resin was applied to seal the device. As a typical example, an electrochromic cell based on PEI 7d' was fabricated. The polymer film is colorless in neutral form. When the voltage was increased (to a maximum of 1.29 V), the color changed to yellowish orange and blue due to



FIGURE 8 Cyclic voltammograms of the deposited film of electrochemically crosslinked PEI **7d**' on an ITO-coated glass substrate in 0.1 M Bu_4NCIO_4/CH_3CN at a scan rate of 50 mV s⁻¹. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

electro-oxidation, the same as was already observed for the solution spectroelectrochemistry experiments. When the potential was subsequently set back at 0 V, the polymer film turned back to original colorless. We believe that optimization could further improve the device performance and fully explore the potential of these electrochromic PEIs.

CONCLUSIONS

A new bis(ether anhydride) monomer containing the triphenylamine group, namely 4,4'-bis(3,4-dicarboxyphenoxy)triphenylamine dianhydride, was successfully synthesized and was polymerized with aromatic diamines to a series of electroactive PEIs. Most of these PEIs were easily soluble in polar organic solvents and could afford flexible and strong films with high thermal stability. The PEIs could be further converted into a crosslinked film via oxidative coupling of their TPA radical cations in an electrochemical cell. The



FIGURE 9 Spectroelectrochemistry of the **7d**' thin film on the ITO-coated glass substrate in 0.1 M Bu₄NCIO₄/CH₃CN. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



FIGURE 10 (a) Optical transmittance changes, (b) current densities monitored and (c) the first cycle optical transmittance changes for the **7d**' film at 485 and 839 nm on the ITO-glass slide (coated area: 1 cm^2) (in CH₃CN with 0.1 M Bu₄NClO₄ as the supporting electrolyte). The dotted line represents the applied voltage. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE 4 Electrochromic Properties of the 7d' Film

			Respon	Response Time ^b			
Polymer	λ_{\max}^{a} (nm)	$\Delta\%T$	$t_{\rm c}$ (s)	t _b (s)	ΔOD^c	$Q_{ m d}~(m mC~cm^{-2})^{ m d}$	CE (cm ² C ⁻¹) ^e
7d′	485	22	4	2.3	0.133	0.34	391
	839	81	4.6	3.5	0.529	1.38	384

^a Wavelength of absorption maximum.

^b Time for 90% of the full-transmittance change.

 $^{\rm c}$ Optical Density ($\Delta {\rm OD}) = \log[{\cal T}_{\rm bleached}/{\cal T}_{\rm colored}]$, where ${\cal T}_{\rm colored}$ and ${\cal T}_{\rm bleached}$ are the maximum transmittance in the oxidized and neutral states, respectively.

(a)



FIGURE 11 (a) Photos of single-layer ITO-coated glass electrochromic device, using **7d**' as active layer. (b) Schematic diagram of polyimide ECD sandwich cell. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

 $^{\rm d}$ $\textit{Q}_{\rm d}$ is ejected charge, determined from the in situ experiments.

^e Coloration efficiency (CE) = $\Delta OD/Q_d$.

crosslinked PEI films exhibit reversible electrochemical oxidation accompanied by strong color changes that can be switched through modulation of the applied potential. Electrochemical and spectral results showed that these polymers can be employed as potential anodically coloring materials in the development of electrochromic devices. Further development of materials of this type would seem to be warranted by the encouraging initial results presented here.

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REFERENCES AND NOTES

1 Electrochromism and Electrochromic Devices; P. M. S. Monk, R. J. Mortimer, D. R. Rosseinsky; Cambridge University Press: Cambridge, UK, **2007**.

2 (a) R. D. Rauch, *Electrochim. Acta* **1999**, *44*, 3165–3176; (b) A. Michaelis, H. Berneth, D. Haarer, S. Kostromine, R. Neigl, R. Schmidt, *Adv. Mater.* **2001**, *13*, 1825–1828; (c) H. W. Heuer, R.

Wehrmann, S. Kirchmeyer, Adv. Funct. Mater. 2002, 12, 89–94;
(d) C.-G. Granqvist, Nat. Mater. 2006, 5, 89–90; (e) R. Baetens,
B. P. Jelle, A. Gustavsen, Sol. Energy Mater. Sol. Cells 2010, 94, 87–105.

3 (a) D. R. Rosseinsky, R. J. Mortimer, *Adv. Mater.* **2001**, *13*, 783–793; (b) G. Sonmez, F. Wudl, *J. Mater. Chem.* **2005**, *15*, 20–22; (c) R. J. Mortimer, A. L. Dyer, J. R. Reynolds, *Displays* **2006**, *27*, 2–18; (d) P. Andersson, R. Forchheimer, P. Tehrani, M. Berggren, *Adv. Funct. Mater.* **2007**, *17*, 3074–3082.

4 G. Sonmez, H. B. Sonmez, *J. Mater. Chem.* 2006, *16*, 2473–2477.

5 (a) U.Bach, D. Corr, D. Lupo, F. Pichot, M. Ryan, *Adv. Mater.* **2002**, *14*, 845–848; (b) N. Kobayashi, S. Miur, M. Nishimura, H. Urano, *Sol. Energy Mater. Sol. Cells* **2008**, *92*, 136–139; (c) P. Tehrani, L.-O. Hennerdal, A. L. Dyer, J. R. Reynolds, M. Berggren, *J. Mater. Chem.* **2009**, *19*, 1799–1802.

6 S. Beaupre, A.-C. Breton, J. Dumas, M. Leclerc, *Chem. Mater.* 2009, *21*, 1504–1513.

7 (a) R. J. Mortimer, *Chem. Soc. Rev.* **1997**, *26*, 147–156; (b) R. J. Mortimer, *Electrochim. Acta* **1999**, *44*, 2971–2981; (c) P. S. Somani, S. Radhakrishnan, *Mater. Chem. Phys.* **2002**, *77*, 117–133.

8 (a) F. S. Han, M. Higuchi, D. G. Kurth, *Adv. Mater.* 2007, *19*, 3928–3931; (b) T. Zhang, S. Liu, D. G. Kurth, C. F. J. Faul, *Adv. Funct. Mater.* 2009, *19*, 642–652; (c) A. Maier, A. R. Rabindranath, B. Tieke, *Adv. Mater.* 2009, *21*, 959–963.

9 (a) W. C. Dautremont-Smith, *Displays* **1982**, *3*, 3–20; (b) W. C. Dautremont-Smith, *Displays* **1982**, *3*, 67–80; (c) G. A. Niklasson, C. G. Granqvist, *J. Mater. Chem.* **2007**, *17*, 127–156.

10 (a) P. M. S. Monk, The Viologens: Synthesis, Physicochemical Properties and Applications of the Salts of 4,4'-Bipyridine; Wiley: Chichester, **1998**; (b) H. C. Ko, M. Kang, B. Moon, H. Lee, *Adv. Mater.* **2004**, *16*, 1712–1716; (c) H. C. Ko, S. Kim, H. Lee, B. Moon, *Adv. Funct. Mater.* **2005**, *15*, 905– 909.

11 (a) L. Groenendaal, G. Zotti, P. H. Aubert, S. M. Waybright, J. R. Reynolds, *Adv. Mater.* **2003**, *15*, 855–879; (b) A. A. Argun, P. H. Aubert, B. C. Thompson, I. Schwendeman, C. L. Gaupp, J. Hwang, N. J. Pinto, D. B. Tanner, A. G. MacDiarmid, J. R. Reynolds, *Chem. Mater.* **2004**, *16*, 4401–4412; (c) R. M. Walczak, J. R. Reynolds, *Adv. Mater.* **2006**, *18*, 1121–1131; (d) G. Sonmez, *Chem. Commun.* **2005**, 5251–5259; (e) A. Patra, M. Bendikov, *J. Mater. Chem.* **2010**, *20*, 422–433; (f) A. Balan, D. Baran, L. Toppare, *Polym. Chem.* **2011**, *2*, 1029–1043.

12 (a) P. M. Beaujuge, J. R. Reynolds, *Chem. Rev.* **2010**, *110*, 268–320; (b) P. M. Beaujuge, C. M. Amb, J. R. Reynolds, *Acc. Chem. Res.* **2010**, *43*, 1396–1407; (c) C. M. Amb, A. L. Dyer, J. R. Reynolds, *Chem. Mater.* **2011**, *23*, 397–415.

13 (a) D. Cummins, G. Boschloo, M. Ryan, D. Corr, S. Rao, D. Fitzmaurice, J. Phys. Chem. B 2000, 104, 11449-11459; (b) S. I. Cho, W. J. Kwon, S.-J. Choi, P. Kim, S.-A. Park, J. Kim, S. J. Son, R. Xiao, S.-H. Kim, S. B. Lee, Adv. Mater. 2005, 17, 171-175; (c) S.-H. Lee, R. Deshpande, P. A. Parilla, K. M. Jones, B. To, A. H. Mahan, A. C. Dillon, Adv. Mater. 2006, 18, 763-766; (d) M. A. Invernale, Y. Ding, D. M. D. Mamangun, M. S. Yavuz, G. A. Sotzing, Adv. Mater. 2010, 22, 1379-1382; (e) P. M. Beaujuge, S. Ellinger, J. R. Reynolds, Nat. Mater. 2008, 7, 795-799; (f) A. Balan, D. Baran, G. Gunbas, A. Durmus, F. Ozyurt, L. Toppare, Chem. Commun. 2009, 6768-6770; (g) S. Y. Park, J. M. Lee, C. Noh, S. U. Son, J. Mater. Chem. 2009, 19, 7959-7964; (h) M. Icli, M. Pamuk, F. Algi, A. M. Onal, A. Cihaner, Chem. Mater. 2010, 22, 4034-4044; (i) F. Baycan Koyuncu, E. Sefer, S. Koyuncu, E. Ozdemir, Macromolecules 2011, 44, 8407-8414.

14 (a) Y. Shirota, *J. Mater. Chem.* **2000**, *10*, 1–25; (b) M. Thelakkat, *Macromol. Mater. Eng.* **2002**, *287*, 442–461; (c) Y. Shirota, *J. Mater. Chem.* **2005**, *15*, 75–93; (d) Y. Shirota, H. Kageyama, *Chem. Rev.* **2007**, *107*, 953–1010.

15 (a) Q. Zhao, Y.-H. Kim, T. T. Mai Dang, D.-C. Shin, H. You, S.-K. Kwon, *J. Polym. Sci. Part A: Polym. Chem.* **2007**, *45*, 341–347; (b) C.-Y. Chuang, P.-I Shih, C.-H. Chien, F.-I. Wu, C.-F. Shu, *Macromolecules* **2007**, *40*, 247–252; (c) J. H. Park, J. O. Huh, Y. Do, M. H. Lee, *J. Polym. Sci. Part A: Polym. Chem.* **2008**, *46*, 5816–5825; (d) C. C. Chiang, H.-C. Chen, C.-s. Lee, M.-k. Leung, K.-R. Lin, K.-H. Hsieh, *Chem. Mater.* **2008**, *20*, 540–552; (e) B.-Y. Hsieh, Y. Chen, *J. Polym. Sci. Part A: Polym. Chem.* **2009**, *47*, 1553–1566; (f) G. Nursalim, Y. Chen, *Polymer* **2010**, *51*, 3187–3195.

16 (a) M.-Y. Chou, M.-k. Leung, Y. O. Su, C. L. Chiang, C.-C. Lin, J.-H. Liu, C.-K. Kuo, C.-Y. Mou, *Chem. Mater.* 2004, *16*, 654–661; (b) S. Beaupre, J. Dumas, M. Leclerc, *Chem. Mater.* 2006, *18*, 4011–4018; (c) J. Natera, L. Otero, L. Sereno, F. Fungo, N.-S. Wang, Y.-M. Tsai, T.-Y. Hwu, K.-T. Wong, *Macromolecules* 2007, *40*, 4456–4463; (d) J. Natera, L. Otero, F. D'Eramo, L. Sereno, F. Fungo, N.-S. Wang, Y.-M. Tsai, K.-T. Wong, *Macromolecules* 2009, *42*, 626–635; (e) H.-J. Yen, G.-S. Liou, *Polym. Chem.* 2012, *3*, 255–264.

17 (a) Polyimides; D. Wilson, H. D. Stenzenberger, P. M. Hergenrother, Eds.; Blackie: Glasgow and London, **1990**; (b) C. E. Sroog, *Prog. Polym. Sci.* **1991**, *16*, 561–694; (c) Polyimides: Fundamentals and Applications; M. M. Ghosh, K. L. Mittal, Eds.; Marcel Dekker: New York, **1996**.

18 (a) J. de Abajo, J. G. de la Campa, *Adv. Polym. Sci.* **1999**, *140*, 23–59; (b) M. X. Ding, *Prog. Polym. Sci.* **2007**, *32*, 623–668; (c) M. G. Dhara, S. Banerjee, *Prog. Polym. Sci.* **2010**, *35*, 1022–1077; (d) D.-J. Liaw, K.-L. Wang, Y.-C. Huang, K.-R. Lee, J.-Y. Lai, C.-S. Ha, *Prog. Polym. Sci.* **2012**, *37*, 907–974.

19 (a) Y.-T. Chern, J.-Y. Tsai, J.-J. Wang, *J. Polym. Sci. Part A: Polym. Chem.* **2009**, *47*, 2443–2452; (b) S. J. Zhang, Y. F. Li, T. Ma, J. J. Zhao, X. Y. Xu, F. C. Yang, X. Y. Xiang, *Polym. Chem.* **2010**, *1*, 485–493; (c) M. Calle, M.; A. E. Lozano, J. G. de la Campa, J. de Abajo, *Macromolecules* **2010**, *43*, 2268–2275; (d) C. H. Lin, S. L. Chang, P. W. Cheng, *J. Polym. Sci. Part A: Polym. Chem.* **2011**, *49*, 1331–1340; (e) H. B. Wei, X. L. Pei, X. Z. Fang, *J. Polym. Sci. Part A: Polym. Chem.* **2011**, *49*, 2484–2494; (f) S.-H. Hsiao, H.-M. Wang, W.-J. Chen, T.-M. Lee, C.-M. Leu, *J. Polym. Sci. Part A: Polym. Chem.* **2011**, *49*, 3109–3120; (g) Y. J. Hou, G. F. Chen, X. L. Pei, X. Z. Fang, *J. Polym. Res.* **2012**, *19*, 9955.

20 (a) S.-H. Cheng, S.-H. Hsiao, T.-H. Su, G.-S. Liou, *Macromolecules* **2005**, *38*, 307–316; (b) G.-S. Liou, S.-H. Hsiao, H.-W. Chen, *J. Mater. Chem.* **2006**, *16*, 1831–1842; (c) H.-M. Wang, S.-H. Hsiao, *Polymer* **2009**, *50*, 1692–1699; (d) Y.-C. Kung, S.-H. Hsiao, *J. Mater. Chem.* **2011**, *21*, 1746–1754; (e) Y.-C. Kung, W.-F. Lee, S.-H. Hsiao, G.-S. Liou, *J. Polym. Sci. Part A: Polym. Chem.* **2011**, *49*, 2210–2221.

21 (a) Y.-C. Kung, S.-H. Hsiao, J. Mater. Chem. **2010**, 20, 5481– 5492; (b) S.-H. Hsiao, G.-S. Liou, Y.-C. Kung, Y.-M. Chang, J. Polym. Sci. Part A: Polym. Chem. **2010**, 48, 2798–2809; (c) H.-M. Wang, S.-H. Hsiao, G.-S. Liou, C.-H. Sun, J. Polym. Sci. Part A: Polym. Chem. **2010**, 48, 4775–4789; (d) H.-M. Wang, S.-H. Hsiao, J. Polym. Sci. Part A: Polym. Chem. **2011**, 49, 337–351; (e) Y.-C. Kung, S.-H. Hsiao, J. Polym. Sci. Part A: Polym. Chem. **2011**, 49, 3475–3490.

22 (a) Y.-C. Kung, G.-S. Liou, S.-H. Hsiao, *J. Polym. Sci. Part A: Polym. Chem.* **2009**, *47*, 1740–1755; (b) S.-H. Hsiao, G.-S. Liou, Y.-C. Kung, H.-Y. Pan, C.-H. Kuo, *Eur. Polym. J.* **2009**, *45*, 2234–2248.

23 (a) M. Faccini, M. Balakrishnan, M. B. Diemeer, Z.-p. Hu, K. Clays, I. Asselberghs, A. Leinse, A. Driessen, D. N. Reinhoudt, W. Verboom, *J. Mater. Chem.* 2008, *18*, 2141–2149; (b) S.-H. Hsiao, H.-M. Wang, P.-C. Chang, Y.-R. Kung, T.-M. Lee, *J. Polym. Sci. Part A: Polym. Chem.* 2013, *51*, 2925–2938.

24 C.-P. Yang, R.-S. Chen, K.-H. Chen, *Colloid Polym. Sci.* 2003, 281, 505–515.

25 S.-H. Hsiao, Y.-M. Chang, H.-W. Chen, G.-S. Liou, *J. Polym. Sci. Part A: Polym. Chem.* **2006**, *44*, 4579–4592.

26 W. M. Li, S. H. Li, Q. Y. Zhang, S. B. Zhang, *Macromolecules* 2007, *40*, 8205–8211.

27 (a) E. T. Seo, R. F. Nelson, J. M. Fritsch, L. S. Marcoux, D. W. Leedy, R. N. Adams, *J. Am. Chem. Soc.* **1966**, *88*, 3498–3503; (b) R. F. Nelson, R. N. Adams, *J. Am. Chem. Soc.* **1968**, *90*, 3925–3930.