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Novel rapid switching and bleaching electrochromic polyimides containing triarylamine with 2-phenyl-2-isopropyl groups

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ABSTRACT

A series of novel organosoluble polyimides and copolyimides with a propeller-shaped triarylamine unit were prepared from diamine and various aromatic dianhydrides *via* direct polycondensation. All of the polymers possessed tough, flexible, and strong films with high molecular weights. The polyimide and copolyimide films revealed electrochromic characteristics, with a color change from pale yellowish at its neutral state, to green, and finally to blue at its oxidized state, at applied potentials ranging from 0 to 1.50 V. The polyimide (**Ib**) film exhibited switching times of 4.5 s at 1.08 V at 424 and 877 nm and 1.9 s for fast bleaching due to a pendent substituted 2-phenyl-2-isopropyl group. Cyclic voltammetry (CV) of the polymer films showed two reversible redox couples at potentials of 0.91–0.99 V and 1.30–1.38 V, respectively. The CV results of the model compound **M1** and model polyimide **M2**, were not a match to the oxidation peaks of polyimide **Ib**, indicating that the contribution of the oxidation was not only from the electron removal of nitrogen atoms.

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1. Introduction

Polvimides continually attract wider interest because of their unique mechanical properties, thermal stability, and morphological properties [1–7]. Conventional polyimides such as Kapton (produced by DuPont) have been applied to microelectronic devices and aerospace applications. However, these polyimides are generally insoluble in organic solvents. Solubility is a key property of polyimides when used as a coating material. A general approach to overcome this drawback, was to introduce bulky lateral substituents, flexible linkages, and noncoplanar biphenylene moieties into the polymer [8-15]. The introduction of propeller-shaped triarylamine units into the polyimide backbone as a structural modification to the rigid polyimides has the potential to form an amorphous structure exhibiting excellent solubility and film-forming capabilities. Copolymerization is another approach to improving the solubility without sacrificing the thermal properties [16].

Electrochromism is known as the alternation of color by the application of a potential [15,17,18]. This interesting property has

* Corresponding author. E-mail address: liawdj@mail.ntust.edu.tw (D.-J. Liaw). led to many technological applications such as smart windows, automatic antiglazing mirrors, large-scale electrochromic screens, and chameleon materials [19-23]. Triarylamine-based derivatives have been used as hole-transporting materials in optoelectronics. photoreceptor devices [24], polymer memory [25-27], and organic light-emitting diodes as well [28,29]. Although triphenylamine (TPA) has many advantages, Adams and coworkers [30] reported that TPA could be easily dimerized to form tetraphenylbenzidine during the anodic oxidation pathway. If a TPA-based electrochromic material undergoes dimerization, it can cause irreversible defects after several redox switches. To avoid this behavior, incorporating electron-donating substituents such as alkyl or alkoxy groups at the para-position of TPA group could prevent the coupling reactions and create stable cationic radicals with lower potentials [31]. These polymers, derived from N,N,N',N'-tetrasubstituted-1,4-phenylenediamines with redox, electrochromism and photoelectrochemical behaviors, exhibit ease of processability and useful mechanical properties [32-35]. It is well-known that the electrochromic properties result from the redox state of the polymers [36]. Therefore, the computational study of the electronic state of polymer is important and useful for electrochromic researches.

In this article, we will report the synthesis and characterization of polyimides derived from six kinds of commercial dianhydrides and the novel triarylamine containing diamine (**4**), *N*,*N*,-bis(4-





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aminohenyl)-*N'*,*N'*-bis[4-(2-phenyl-2-isopropyl)-phenyl]-1,4-phenylene-diamine. In addition, organosoluble copolyimides were also prepared from rigid fluorine-containing dianhydrides. To gain more insight into the oxidation mechanism, the computational study on the electronic structures of the basic unit, **M3**, was also studied based on DFT(B3LYP/6-31G(d)) calculations.



Propeller-shaped triarylamine units

2. Experimental

2.1. Materials

Bis[4-(2-phenyl-2-isopropyl)phenyl]amine (OUCHI SHINKO), 4-fluoro-nitrobenzene (ACROS), cesium fluoride (ACROS), sodium hydride (95%; dry; ALDRICH), 10% Pd/C (MERCK), and hydrazine monohydrate (MERCK) were used as received. N,N-Dimethylacetamide (DMAc; MERCK), dimethyl sulfoxide (DMSO; MERCK), *N*-methyl-2-pyrrolidinone (NMP; MERCK), and pyridine (MERCK), were dried over calcium hydride overnight, distilled under reduced pressure, and stored over 4 Å molecular sieves in a sealed bottle. Iodobenzene, bis(dibenzylideneacetone) palladium [Pd (dba)₂], 1,1'-bis(diphenylphosphino)-ferrocene (DPPF), sodium tert-butoxide were purchased from ACROS. Commercially available aromatic tetracarboxylic dianhydrides such as 4,4'-hexafluoroisopropylidenediphathalic dianhydride (5a; CHRISKEV) (6FDA), 4,4'-oxydiphthalic anhydride (5b; TCI) (ODPA), 3,3',4,4'diphenyl sulfone-tetracarboxylic dianhydride (5c; TCI) (DSDA), 3,3',4,4'-benzophenone tetracarboxylic dianhydride (5d; CHRIS-KEV) (BTDA), 3,3',4,4'-biphenyltetracarboxylic dianhydride (5e; CHRISKEV) (BPDA), and pyromellitic dianhydride (5f; CHRISKEV) (PMDA were purified by vacuum sublimation. Tetra-n-butylammonium perchlorate (TBAP) was obtained from ACROS and recrystallized twice from ethyl acetate and then dried under vacuum before use. All other reagents were used as received from commercial sources.

2.2. Monomer synthesis

2.2.1. Synthesis of bis[4-(2-phenyl-2-isopropyl)phenyl]-4-nitrophenylamine (**1**)

A 500 mL three neck round-bottom flask was filled with bis[4-(2-phenyl-2-isopropyl)phenyl]amine (20.0 g, 49 mmol), 4-fluoro-nitrobenzene (5.23 g, 49 mmol), sodium hydride (1.18 g, 49 mmol), and 120 mL DMSO. The mixture was heated and stirred at 120 °C for 24 h. The reaction mixture was then cooled and poured into 1 L of methanol. The yellow precipitate was collected by filtration and dried under vacuum. The product was purified by silica gel column chromatography (*n*-hexane:dichloromethane = 2 : 1) resulting in the nitro compound **1** 16.3 g in a 63% yield; mp 150–151 °C by DSC (10 °C/min).

IR (KBr) 1585, 1342 cm⁻¹(NO₂ stretch) ¹H NMR. (CDCl₃): δ (ppm) = 1.77 (s, 12H, H_d), 6.93–6.95 (d,4H, H_f, *J* = 9.4 Hz), 7.12–7.14 (d, 4H, H_e, *J* = 10.05 Hz), 7.24–7.27 (m, 2H, H_a), 7.28–7.30 (d, 2H, H_h, *J* = 10.05 Hz), 7.35–7.36 (m, 4H, H_b), 7.37–7.38 (d, 4H, H_c, *J* = 5.02 Hz), 8.05–8.08 (d, 2H, H_g, *J* = 9.3 Hz). ¹³C NMR (CDCl₃): δ (ppm) = 30.6 (C₆), 42.6 (C₅), 117.4 (C₁₂), 125.3 (C₁₃), 125.7 (C₁), 125.9 (C₉), 126.6 (C₂), 128.0 (C₃), 128.1 (C₈), 139.6 (C₁₄), 142.8 (C₁₀), 148.2 (C₇), 150.0 (C₄), 153.4 (C₁₁). ELEM. ANAL. Calcd. for C₃₆H₃₄N₂O₂: C, 82.10%; H, 6.51%; N, 5.32%. Found: C, 81.67%; H, 6.39%; N, 5.21%.



2.2.2. Synthesis of bis[4-(2-phenyl-2-isopropyl)phenyl]-4aminophenylamine (**2**)

In a 500 mL three neck round-bottom flask the nitro compound **1** (20 g, 38 mmol), Pd/C (0.4 g), and ethanol (200 mL) were added. After the addition of 14 mL of hydrazine monohydrate, the solution was stirred at reflux temperature for 12 h. After the solution was cooled down to room temperature, the solution was filtered to remove the catalyst, and the crude product was recrystallized from ethanol yielding 12.5 g (yield: 66%) of the compound **2**, mp 110–114 °C by DSC (10 °C/min).

IR (KBr) 3432, 3356 cm⁻¹ (NH₂ stretch). ¹H NMR (DMSO-*d*₆): δ (ppm) = 1.57 (s, 12H, H_d), 5.02 (s, 2H, NH₂), 6.56–6.58 (d, 2H, H_g, J = 10 Hz), 6.77 (s, 4H, H_f), 6.79 (s, 4H, H_e), 6.98–7.00 (d, 2H, H_h, J = 10 Hz), 7.09–7.12 (m, 2H, H_a), 7.19–7.20 (d, 4H, H_b, J = 5 Hz), 7.20–7.21(d, 4H, H_c, J = 5 Hz). ¹³C NMR (DMSO-*d*₆): δ (ppm) = 30.3 (C₆), 41.7 (C₅), 114.9 (C₁₃), 120.73 (C₉), 125.3 (C₁), 126.2 (C₃), 126.9 (C₈), 127.8 (C₂), 127.9 (C₁₂), 135.2 (C₁₄), 142.5 (C₁₀), 145.4 (C₇), 145.9 (C₁₁), 150.3 (C₄). ELEM. ANAL. Calcd. for C₃₆H₃₆N₂: C, 87.05%; H, 7.31%; N, 5.64%. Found: C, 86.9%; H, 7.13%; N, 5.61%.



2.2.3. Synthesis of N,N,-bis(4-nitrophenyl)-N',N'-bis[4-(2-phenyl-2-isopropyl)phenyl]-1,4-phenylene-diamine (**3**)

In a 250 mL three neck round-bottom flask, bis-[4-(2-phenyl-2isopropyl)phenyl]-4-aminophenylamine (**2**) (7.26 g, 14.63 mmol), 4-fluoro-nitrobenzene (4.13 g, 29.27 mmol), cesium fluoride (4.41 g, 29.27 mmol), and 80 mL DMSO were added. The mixture was heated and stirred at 120 °C for 24 h. The reaction mixture was cooled and then poured into 500 mL of methanol. The red precipitate was collected by filtration and dried under vacuum. The product was purified by silica gel column chromatography (*n*-hexane:dichloromethane = 1:1) resulting in dinitro compound (**3**) in a 65% yield; mp 224–225 °C (by DSC; 10 °C/min).

IR (KBr) 1580, 1341 cm⁻¹ (NO₂ stretch). ¹H NMR (CDCl₃): δ (ppm) = 1.70 (s, 12H, H_d); 6.97–6.99 (d, 2H, H_h, *J* = 10.0 Hz); 7.04–7.05 (d, 4H, H_f, *J* = 5.0 Hz); 7.05–7.07 (d, 2H, H_g, *J* = 10.0 Hz); 7.15–7.17 (d, 4H, H_e, *J* = 10.0 Hz); 7.19–7.20 (d, 4H, H_i, *J* = 5.0 Hz); 7.20–7.21 (m, 2H, H_a); 7.28–7.29 (d, 4H, H_c, *J* = 5.0 Hz); 7.30–7.31 (d, 4H, H_b, *J* = 5.0 Hz);

8.14–8.17 (d, 4H, H_j, J = 15.0 Hz). ¹³C NMR (CDCl₃): δ (ppm) = 30.7 (C₆), 42.5 (C₅), 121.8 (C₁₆), 123.2 (C₁₂), 124.3 (C₉), 125.4 (C₁₇), 125.6 (C₁), 126.6 (C₃), 127.7 (C₈), 127.9 (C₂), 128.0 (C₁₃), 137.2 (C₁₄), 142.3 (C₁₈), 144.3 (C₁₀), 146.1 (C₇), 147.0 (C₁₁), 150.4 (C₄), 151.7 (C₁₅). ELEM. ANAL Calcd. for C₄₈H₄₂N₄O₄: C, 78.03%; H, 5.73%; N, 7.58%. Found: C, 77.57%; H, 5.63%; N, 7.45%.



2.2.4. Synthesis of N,N,-bis(4-aminohenyl)-N',N'-bis[4-(2-phenyl-2-isopropyl)phenyl]-1,4-phenylene-diamine (**4**)

The dinitro compound (**3**) (5 g, 6.77 mmol), Pd/C (0.2 g), and 150 mL ethanol were added into a three-necked flask and hydrazine monohydrate (10 mL) was added dropwise over a period of 30 min at 90 °C. Upon completing the addition, the solution was stirred at reflux temperature for 12 h. After the solution was cooled down to room temperature, the solution was filtered to remove the catalyst, and the crude product was purified by silica gel column chromatography (*n*-hexane:ethyl acetate = 2:1) to produce diamine monomer (**4**) 2.3 g (yield: 50%), mp 149–151 °C by DSC (10 °C/min).

IR (KBr) 3445, 3360 cm⁻¹ (NH₂ stretch). ¹H NMR (DMSO- d_6): δ (ppm) = 1.56 (s, 12H, H_d); 4.93 (s, 4H, amino); 6.53–6.55 (d, 4H, H_f, J = 10.1 Hz); 6.56–6.58 (d, 2H, H_h, J = 10.1 Hz); 6.75–6.77 (d, 2H, H_g, J = 10.1 Hz); 6.77–6.79 (d, 4H, H_i, J = 10.1 Hz); 6.80–6.82 (d, 4H, H_e, J = 10.1 Hz); 6.99–7.01 (d, 4H, H_j, J = 10.1 Hz); 7.09–7.12 (m, 2H, H_a); 7.19–7.20 (d, 4H, H_c, J = 5.1 Hz); 7.21–7.23 (d, 4H, H_bJ = 10.1 Hz). ¹³C NMR (DMSO- d_6): δ (ppm) = 30.3 (C₆), 41.7 (C₅), 114.8 (C₈), 117.8 (C₁₃), 121.3 (C₁₆), 125.3 (C₁), 126.2 (C₃), 126.7 (C₁₂), 127.0 (C₉), 127.1 (C₁₇), 127.8 (C₂), 136.0 (C₁₀), 137.2 (C₁₄), 143.0 (C₁₈), 145.2 (C₁₅), 145.3 (C₇), 146.2 (C₁₁), 150.2 (C₄). ELEM. ANAL. Calcd. for C₄₈H₄₆N₄: C, 84.92%; H, 6.83%; N, 8.25%. Found: C, 84.11%; H, 6.77%; N, 8.17%.



2.2.5. Synthesis of model compound (M1)

lodobenzene (1.4 g, 7 mmol), bis[4-(2-phenyl-2-isopropyl) phenyl]amine (2.4 g, 6 mmol), Pd(dba)₂ (0.07 g, 0.12 mmol), DPPF (0.13 g, 0.24 mmol), sodium *tert*-butoxide (2.6 g, 27 mmol) and dry toluene (10 mL) were charged in a three-necked flask under nitrogen. The mixture was heated to reflux for 8 h. After the completion of the reaction, the solvent was removed under vacuum and the residue was extracted with dichloromethane and water. The organic layer was dried over MgSO₄ and filtered. After removing the solvent, the residue was purified by silica gel column chromatography (toluene:*n*-hexane = 1:6). Then the viscous product was obtained in a 55% yield.

¹H NMR (CDCl₃): δ (ppm) = 1.67 (s, 12H, H_d); 6.96–6.98 (m, 6H, H_g + H_f); 7.06–7.09 (m, 5H, H_e + H_i); 7.15–7.24 (m, 4H, H_a + H_h); 7.27–7.30 (d, 8H, H_b + H_c, *J* = 10.0 Hz). ¹³C NMR (CDCl₃): δ (ppm) = 30.8 (C₆), 42.4 (C₅), 122.2 (C₁₂), 123.5 (C₉), 123.7 (C₁₄), 125.5 (C₁), 126.7 (C₃), 127.5 (C₈), 127.9 (C₂), 129.0 (C₁₃), 144.8 (C₁₁), 145.2 (C₁₀), 147.9 (C₇), 150.7 (C₄).



2.2.6. Synthesis of the model polymer (M2)

The model polymer **M2** was prepared according to the reported literature [37].



2.2.7. Synthesis of homopolyimides

The polyimides were prepared using similar procedures. one example is described below

To a stirring solution of diamine (**4**) (0.6 g, 0.883 mmol) in DMAc (5 mL), 6FDA (0.382 g, 0.883 mmol) was gradually added. The mixture was stirred at room temperature for 4 h under nitrogen atmosphere to form poly(amic acid). Chemical cyclodehydration was carried out by adding an equal molar mixture of acetic anhydride and pyridine into the above-mentioned poly(amic acid) solution. This mixture was stirred at room temperature for 1 h, and then treated at 100 °C for 4 h. The polymer solution was poured into 500 mL of methanol. The precipitate was collected by filtration, washed thoroughly with methanol, and then dried at 100 °C under vacuum. Yield: 98%.

The IR spectrum of **Ia** (film) exhibited characteristic imide absorption at 1779 (asymmetrical carbonyl stretching), 1726 (symmetrical carbonyl stretching) and 744 cm⁻¹ (imide ring deformation). ¹H NMR (CDCl₃): δ (ppm) = 1.70 (s, 12H, H_d); 7.02–7.04 (d, 4H, H_f); 7.04–7.10 (d, 4H, H_h + H_g); 7.13–7.14 (d, 4H, H_e); 7.16–7.20 (m, 2H, H_a); 7.27–7.28 (d, 4H, H_i); 7.27–7.30 (d, 8H, H_b + H_c); 7.32–7.33 (d, 4H, H_j); 7.88–7.90 (d, 2H, H_l); 7.99 (s, 2H, H_k); 8.05–8.07 (d, 2H, H_m). ELEM. ANAL. Calcd. for (C₆₇H₄₈N₄O₄F₆)_n: C, 74.02%; H, 4.45%; N, 5.15%. Found: C, 73.01%; H, 4.23%; N, 5.02%.

2.2.8. Synthesis of copolyimides

The copolyimides were prepared using similar procedures. One example is described below:

To a stirring solution of diamine ($\mathbf{4}$) (0.5 g, 0.736 mmol) in DMAc (3.2 mL), 6FDA (0.16 g, 0.368 mmol) and BTDA (0.11 g, 0.368 mmol) were gradually added. The mixture was stirred at room temperature for 4 h under nitrogen atmosphere to form poly(amic acid). Chemical cyclodehydration was carried out by adding equal molar mixture of acetic anhydride and pyridine into the above-mentioned poly(amic acid) solution. This mixture stirred at room temperature

for 1 h, and then treated at 100 °C for 4 h. The polymer solution was poured into 500 mL of methanol. The precipitate was collected by filtration, washed thoroughly with methanol, and then dried at 100 °C under vacuum. Yield: 95%.

2.3. Measurements

IR spectra were recorded in the range of $4000-400 \text{ cm}^{-1}$ on a JASCO IR-700 spectrometer. Elemental analyses were conducted on a Perkin Elmer 2400 instrument. The ¹H and ¹³C NMR spectra were obtained by BRUKER AVANCE 500 NMR operated at 500 MHz for proton and 125 MHz for carbon. The inherent viscosities of all polymers were measured using Capillary Ubbelohde viscometer. Thermogravimetric data were obtained on a TA instrument Dynamic TGA 2950 under nitrogen flowing condition at a rate of 30 cm³ min⁻¹ and conducted from 30 to 800 °C at a heating rate of 20 °C min⁻¹. Differential scanning calorimetric analysis was performed on a differential scanning calorimeter (TA instrument TA 910) under nitrogen flowing condition at a rate of 30 cm³ min⁻¹ and conducted from 50 to 350 °C at a heating rate of 10 °C min $^{-1}$ Tensile properties were determined from stress-strain curves obtained with an Instron mode 5544 based on ASTM D412 method. The dielectric constants were measured by the parallel-plate capacitor method with a TA Instruments DEA 2970 dielectric analyzer. UV-vis spectra of the polymer films or solutions were recorded on a JASCO V-550 spectrophotometer at room temperature in air. Weight-average (M_w) and number-average (M_n) molecular weights were determined by gel permeation chromatography (GPC). Four Waters (Ultrastyragel) columns $(300 \text{ mm} \times 7.7 \text{ mm}, \text{guard}, 10^5, 10^4, 10^3, \text{and } 500 \text{ Å in series})$ were used for GPC analysis with tetrahydrofuran (THF; 1 mL min⁻¹) as the eluent. The eluents were monitored with a UV detector (JMST Systems, VUV-24, USA) at 254 nm. Polystyrene was used as the standard. Cyclic voltammetry (CV; CHI model 619A) was conducted using a three-electrode cell in which ITO was used as a working electrode. The electrochemical cell was composed of a 1cm cuvette, ITO as a working electrode, a platinum wire as an auxiliary electrode, and an Ag/Ag⁺ as a reference electrode. The spectroelectrochemical cell was composed of a 1 cm cuvette, ITO as a working electrode, a platinum wire as an auxiliary electrode, and an Ag/Ag⁺ reference electrode. Absorption spectra in spectroelectrochemical analysis were measured with a JASCO V-550 spectrophotometer.

3. Results and discussion

3.1. Monomer Synthesis

The monomer preparation is shown in Scheme 1. Amine compound (2) was prepared by the condensation of bis[4-(2phenyl-2-isopropyl)phenyl]amine with 4-fluoro-nitrobenzene, followed by hydrazine Pd/C catalytic reduction. Diamine monomer (4) was successfully synthesized by the reaction of compound (2) with 4-fluoro-nitrobenzene, using hydrazine Pd/C as the reducing agent. Elemental analysis, IR, ¹H NMR and ¹³C NMR spectroscopic techniques were used to identify the structures of the intermediates (1), (2), (3) and the diamine (4). The nitro group of compound (1) and (3) gave nitro group characteristic bands at 1580 (asymmetrical stretching) and 1340 cm^{-1} (symmetrical stretching) in the IR spectra. After reduction, the characteristic absorptions of the nitro group disappeared, and the amino group showed a typical N–H stretching absorption pair at 3465 and 3374 cm^{-1} . The structures of intermediates and the diamine were also confirmed by high-resolution NMR spectra. The ¹H, ¹³C and COSY NMR spectra of diamine (4) are given in Fig. 1. Assignments of each proton and carbon are also given in the figure, and these spectra as well as elemental analysis indicate the diamine compound (4) agree with the proposed molecular structure.

3.2. Polymer synthesis

Polyimides and copolyimides were prepared using a conventional two-step method by reactions of equal molar amounts of diamine (4) with various dianhydrides to form viscous poly(amic



Scheme 1. Synthesis of novel diamine (4).



Fig. 1. (A) ¹H NMR (B) ¹³C NMR (C) COSY spectra of diamine monomer 4 in DMSO-d₆.

acid)s, followed by chemical cyclodehydration as shown in Scheme 2. These polymers exhibited inherent viscosities between 0.34 and 0.62 dL/g, could be cast into flexible and tough films. Number-average (M_n) and weight-average (M_w) molecular weights of the polyimides were found to be in the range $2.2-6.9 \times 10^4$ and $3.4-11.7 \times 10^4$, respectively. However, polyimide **Id–Ifs'** inherent visocity and molecular weight could not be measured due to their poor solubility. All the results are summarized in Table 1. The complete imidization of polymer was confirmed by IR and NMR spectra. All the polymers showed the characteristic absorption bands of the imide absorption at 1779 (asymmetrical carbonyl

stretching), 1726 (symmetrical carbonyl stretching) and 744 cm⁻¹ (imide ring deformation). Fig. 2 shows a typical ¹H NMR spectrum of polyimide **Ia** in CDCl₃, in which all the peaks have been readily assigned to the hydrogen atoms of the repeating unit. The mole ratio of the 6FDA and BTDA was 1.18:1.00, which is very close to the experimental feed (see Supplementary materials Figure S1).

3.3. Basic characterization

The solubility behaviors of polymers were tested qualitatively, and the results are summarized in Table 2. Polyimides Ia-Ic were found to be highly organosoluble in common organic solvents such as NMP, DMAc, and even in CHCl₃. Polyimide Ib has shown to have better solubility than M2 [38] and M4 [38]. This phenomenon could be attributed to the bulky pendent 4,4'-substituted 2-phenyl-isopropyl group in the repeating unit, which retards dense chain packing and leads to a decreased chain-chain interaction. However, when the dianhydrides were 5d, 5e or 5f the polyimides were soluble only in CHCl₃. However, soluble copolyimides IId-IIf were successfully synthesized by using 5a (6FDA) as a comonomer to improve the solubility of Id-If. All the copolyimides were soluble and able to be cast into film. The good solubility of these polymers in low boiling point solvents is a benefit when preparing polymer films or coatings at low processing temperature [39]. These films were subjected to tensile testing, and the results are given in Table 3. The tensile strengths, elongations to break, and high initial moduli of these films were in the ranges 40–54 MPa. 2.8–4.2%. 2.2–2.4 GPa, respectively. The crystallinity of the polyimides were carried out by wide-angle X-ray diffraction (WAXD) patterns and the results indicated that the polymers were essentially amorphous, revealing that the 4,4'-substituted 2-phenyl-2-isopropyl disturbed the packing of the polymers which had excellent solubility.

3.4. Thermal properties of polyimides

The thermal behaviors of the polymers evaluated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) are tabulated in Table 4. There were no melting peaks (T_m) detected by DSC and the absence of a peak in DSC supported the generally amorphous nature of the polymers. Typical DSC and TGA curves for polyimide Ia are illustrated in Fig. 3. The DSC thermograms of polymers obtained from the second heating trace showed glass transition temperatures (T_g) in the range 241–267 °C. There was a negative correlation between T_{g} and chain flexibility. For example, the polyimide **Ib** from ODPA showed the lowest T_g (241 °C) because of the presence of a flexible ether linkage between the phthalimide units. All the polymers exhibited excellent thermal stability showed higher T_{d10} in nitrogen than in air. Polymers were stable up to 470 °C and the 10% weight loss temperature was between 504 and 536 °C in nitrogen atmosphere. These polymers exhibited high char yield in the range of 51-68% at 800 °C in a nitrogen atmosphere. The polyimide prepared from fluorine-based tetracarboxylic dianhydrides (Ia) exhibited higher T_d values than the one prepared from sulfone-based tetracarboxylic dianhydrides (Ic). This increase may be a result of stronger C-F bonding of the CF₃ groups in polyimide Ia.

3.5. Optical properties and dielectric constants of polyimides

The optical properties of the polymers were investigated by UV–vis and photoluminescence spectroscopy. The results are summarized in Table 5. The UV–vis absorption of these polymers exhibited strong absorption at 308–327 nm in NMP solutions, which are assigned to a π – π * transition resulting from the



Scheme 2. Synthesis of polyimides I and copolyimides II.

conjugation between the aromatic rings and nitrogen atoms. The UV–vis absorption of the polymer films also showed similar absorbance at 307–325 nm. Their PL spectra in NMP solutions showed maximum bands around 385–419 nm. The cutoff

Table 1

Inherent viscosity and molecular	weight of polyimides	and copolyimides.

Polymer	$\eta_{\rm inh} ({ m dL} { m g}^{-1})^{ m a}$	$M_{ m w} imes 10^{-4 m b}$	$M_{ m n} imes 10^{-4b}$	PDI ^c
la	0.62	11.7	6.4	1.74
Ib	0.47	3.4	2.2	1.54
Ic	0.49	10.5	6.9	1.51
IId	0.34	_d	d	_d
IIe	0.43	d	d	_d
llf	0.40	_d	_d	_d

^a Measured at a polymer concentration of 0.5 dL/g in DMAc at 30 °C.

^b Measured by GPC in THF; polystyrene was used as standard.

^c PDI = M_w/M_n . ^d Insoluble in THF. wavelengths (absorption edge) from UV–vis transmittance spectra were in the range 414–492 nm. The dielectric constants of polyimides are tabulated in Table 5. Dielectric constants of polyimides were measured at 1 KHz, being in the range 3.43–3.68, the polyimide **Ia** containing hexafluoro dianhydride having the lowest value.

3.6. Electrochemical properties of polyimides

The electrochemical behavior of the polymers was investigated by cyclic voltammetry conducted by film cast on an ITO-coated glass substrate as the working electrode in dry acetonitrile (CH₃CN) containing 0.1 M of TBAP as an electrolyte, under nitrogen atmosphere. Fig. 4 indicates the electrochemical behavior for polyimide **Ib** and model compounds **M1** and **M2**. They have reversible oxidation redox couples at $E_{1/2} = 0.93$ V and 1.32 V for polyimide **Ib**,



Fig. 2. ¹H NMR of polyimide Ia in CDCl₃.

0.75 V for **M1**, and 1.25 V for **M2**. The energy of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of the investigated polymers could be determined from the oxidation onset potentials and the onset absorption wavelengths of the polymer films. The results are listed in Table 6. For example, the oxidation onset potential for polyimide **Ib** was determined to be 0.87 V vs Ag/Ag⁺. The external ferrocene/ferrocenium (Fc/Fc⁺) redox standard onset potential (Fc/Fc⁺) was 0.66 V vs Ag/Ag⁺ in CH₃CN. Under the assumption that the HOMO energy for the ferrocene standard was -4.8 eV with respect to the zero vacuum level, the HOMO energy for polyimide **Ib** was evaluated to be -5.01 eV.

The cyclic voltammograms of **M1**, **M2**, and polyimide **Ib** are shown in Fig. 4. The oxidation peaks of **M1** and **M2** were not close to the oxidation peaks of polyimide **Ib**, indicating that the oxidations were not only resulting from the electron removal of nitrogen atoms. Many literatures have previously proposed the triarylamine polymer oxidation mechanism, in which the first electron was removed from the nitrogen atom with the larger electron density, and the second electron was removed from the other nitrogen atom, which is closer to the atomic orbital opinion [40,41]. However, from the electrochemical study of model compounds and the polymer **Ib** (Fig. 4), it is not suitable to explain the mechanism

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Solubility	behavior	of pol	vimides	and co	polvimides	. a

Polymer	Ia	lb	lc	Id	Ie	lf	IId	lle	llf	M2 ^b	M4 ^b
NMP	S	S	S	+h	Р	+h	S	S	S	+h	S
DMAc	S	S	S	+h	Р	Р	S	S	S	+h	S
DMF	S	S	S	Р	Р	Р	+h	S	S	I	Р
DMSO	+h	+h	+h	Р	Ι	Р	+h	Р	+h	+h	+h
CHCl ₃	S	S	S	S	S	S	S	S	S	I	S
THF	S	S	S	Р	Ι	Р	+h	+h	+h	I	Р
m-Cresol	+h	+h	+h	Р	Р	Р	+h	Р	+h	+h	+h
Toluene	S	Р	Р	Р	Р	I	S	S	S	n.a.	n.a.
Xylene	S	Р	Р	Ι	Р	I	S	S	S	n.a.	n.a.
γ-Butylactone	S	+h	S	+h	Ι	Р	+h	Р	Р	n.a.	n.a.

S: soluble at room temperature, +h: soluble on heating to 70 $^\circ$ C, P: partially soluble on heating 70 $^\circ$ C, I: insoluble.

n.a.: not available.

^a The solubility was determined with a 1 mg sample in 1 mL of a solvent.
 ^b Reference [38].

Table 3

Mechanical properties of polyimides and copolyimdies.

Polymer ^a	Tensile strength (MPa)	Elongation at break (%)	Tensile modulus (GPa)	Film property
la Ib Ic	40 54 50	2.8 4.2 3.9	2.2 2.2 2.2	Tough and flexible Tough and flexible Tough and flexible
IId IIe IIf	41 54 54	3.8 4.0 4.0	2.3 2.4 2.4	Tough and flexible Tough and flexible Tough and flexible
	01	110	2	rough und nembre

^a The polyimide films **Id**-**If** are too brittle to be measured.

by atomic orbital opinion. If the oxidations occurred only in the nitrogen atoms, the oxidation peaks should appear in the same bias potential. We combined experimental and theoretical studies to prove that the oxidation mechanism is another pathway. A more reasonable oxidation mechanism reported in the previous literature [42] (see Supplementary materials Scheme S1) also interpret the oxidation behavior well, in where the first electron was removed from the HOMO of the molecule instead of the lone pair electron of the nitrogen atom. The first electron was removed from HOMO to form a single occupied molecular orbital (SOMO), and the second electron was removed from SOMO to form a second oxidation state.

3.7. Computational study for oxidation mechanism

All theoretical calculations in this study were carried out using Gaussian 03 [43,44]. Equilibrium structure of basic unit **M3** was determined using DFT with the B3LYP functional and the 6-31G(d) basis set. The atomic charge was determined by Mulliken population analysis.

The sketch map containing the studied structure **M3** and optimized structure by DFT (B3LYP/6-31G(d)) are plotted in Fig. 5. Part of the selected electronic properties was summarized in Table 7 (see detailed distribution in the Supplementary materials). The main atomic charge difference was located on 1 N, 9C, 29C, and 32 N atoms. For the first oxidation (losing first electron), the 1 N, 9C, 29C and 32 N atoms contributed 3.5%, 2.1%, 3.9% and 4.3% of an electron, respectively. For the second oxidation (losing second electron), the 1 N, 9C, 29C and 32 N atoms contribute 2.1%, 1.4%, 1.4% and 1.6% of an electron, respectively. The electron density contour of the ground state and first oxidation state are plotted by Gauss View as shown in Fig. 6, which indicates that the electron lone pair of the nitrogen atoms have strong coupling with π electrons. The electron density distribution of the first oxidation state was a little

Table	4
-	

Thermal properties of polyimides and copolyimides.

Polymer	$T_{\rm g} (°C)^{\rm a}$	$T_{d10\%}$ (°C)	b	Char yield(%) ^c
		in N ₂	in Air	
Ia	266	528	466	68
Ib	241	519	424	62
Ic	267	504	446	54
Id	241	517	466	56
Ie	257	535	505	60
If	_d	521	493	55
IId	245	536	488	64
Ile	251	520	456	55
llf	259	524	446	51

^a From DSC measurements conducted at a heating rate of 10 °C/min.

 $^{\rm b}\,$ Temperature at 10% weight loss ($T_{\rm d10\%}$) was determined by TGA at a heating rate of 20 °C/min.

^c Residual weight percentage at 800 °C in nitrogen.

d Not observed.



Fig. 3. (A) DSC curves of polyimides Ia and Ib and (B) TGA curves of polyimides Ia and Ic.

broader than that of the ground state, and the main distribution was located on *N*,*N*,*N*',*N*'-tetraphenyl phenylene-diamine.

3.8. Electrochromic characteristics

Electrochromic behavior of these polymer thin films was examined by use of an optically transparent thin-layer electrode coupled with UV-vis spectroscopy. The electrode preparations and solution conditions were identical to those used in cyclic voltammetry. All of the polymers exhibited similar electrochromic properties, and the typical electrochromic spectra of polyimide Ib is shown in Fig. 7. When the applied potentials increased positively from 0 to 1.20 V, the peak of absorbance at 317 nm, a characteristic peak for neutral form polyimide **Ib**, decreased gradually. Two new bands appeared at 405 and 879 nm, which was due to the first stage oxidation. When the potential was adjusted to a more positive value of 1.50 V, corresponding to the second step oxidation, the characteristic peak of absorbance decreased gradually and a new band appeared at 705 nm. Correspondingly, the film changed from its original pale yellowish color to green and then to blue, correlating to the oxidized form. The copolyimide IIf also showed a similar spectra to homopolyimide **Ib**, indicating that the electrochromic characteristic resulted from the triarylamine only and was independent of the dianhydride (see Supplementary materials

Table 5

Optical properties and dielectric constants of polyimides and copolyimides.

Polymer	Solution	$\lambda (nm)^{a}$		Film λ (nm)			
	$\lambda_{abs.max}$ $(nm)^{a}$	PL _{max} (nm) ^b	Cutoff wavelength ^c	λ _{abs.max} (nm)	λ _{abs.onset} (nm)	Dielectric constant ^d	
la	315	419	414	324	396	3.43	
Ib	327	407	429	308	419	3.68	
Ic	308	404	415	307	402	3.66	
Id	315	394	492	320	432	_e	
Ie	322	385	482	325	422	_e	
If	318	391	485	318	435	_e	
IId	309	399	491	311	411	3.53	
Ile	316	391	426	320	436	3.57	
IIf	310	398	446	314	447	3.61	

^a Measured at a concentration of 10^{-5} mol/L in NMP.

 $^{\rm b}$ They were excited at the $\lambda_{\rm abs.max}$ for the solution state.

^c Cutoff wavelength from the transmission UV-vis absorption spectra of the polymer films.

^d Dielectric constants were obtained in the frequency 1 kHz on thin films.

^e The polyimide films **Id ~ If** are too brittle to be measured.



Fig. 4. Cyclic voltammograms of (A) ferrocene and (B) model compound **M1**, **M2** and polyimide **Ib** in CH_3CN containing 0.1 M TBAP. The scan rate was 0.1 V/s.

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Electrochemical properties of polyimides and copolyimides.

Polymer	Oxidation (V) ^a		Band gap ^b (eV)	HOMO ^c (eV)	LUMO ^c (eV)
code	First	Second			
Ia	0.97	1.30	3.13	-4.98	-1.85
Ib	0.93	1.32	2.96	-5.01	-2.05
Ic	0.94	1.32	3.08	-5.00	-1.92
Id	0.94	1.31	2.87	-4.98	-2.11
Ie	0.95	1.30	2.93	-4.96	-2.03
If	0.97	1.34	2.85	-4.95	-2.10
IId	0.98	1.38	3.01	-5.04	-2.03
IIe	0.91	1.34	2.84	-5.00	-2.16
IIf	0.99	1.36	2.77	-5.05	-2.28
M1	0.75	-	-	-	-
M2	1.25	-	-	-	-

^a From cyclic votammograms vs Ag/Ag⁺ in CH₃CN.

^b Band gap = $1240/\lambda_{abs.onset}$ of the polymer film.

^c Calculated from the equation: HOMO = $-(E_{onset}^{ex} - E_{onset}^{ec}) - 4.8$, LUMO = HOMO + Band gap.



Fig. 5. Sketch map containing the studied structure and optimized structure by (DFT/ B3LYP/6-31G(d)).

Table 7

Atomic charge distribution of selected atoms in ground state, fist oxidation state, second oxidation state, and the charge difference of $\Delta Q1$ and $\Delta Q2$.

	G. S ^a	Ox1 ^b	Ox2 ^c	$\Delta Q1^{d}$	$\Delta Q2^{e}$
1 N	-0.659	-0.624	-0.603	0.035	0.021
9 C	0.309	0.330	0.344	0.021	0.014
29 C	0.291	0.330	0.344	0.039	0.014
32 N	-0.661	-0.618	-0.602	0.043	0.016

^a G. S: ground state.

^b Ox1: losing one electron.

^c Ox2: losing two electrons.

^d $\Delta Q1$ = atomic charge difference of Ox1 and G. S.

^e $\Delta Q2 =$ atomic charge difference of Ox2 and Ox1.



Fig. 6. Electronic density contours of the frontier orbitals for optimized basic unit M3 at ground state and first oxidation state.



Fig. 7. Electrochromic behavior of polyimide **Ib** film (in CH₃CN with 0.1 M TBAP as the supporting electrolyte) at (1) 0.00. (2) 1.00. (3) 1.05. (4) 1.20. (5) 1.30. (6) 1.34. (7) 1.38. (8) 1.50 V.

Figure S2). The color switching times were estimated by applying a potential step, and the absorbance profiles were followed (Fig. 8). The switching time was defined as the time required for reaching 90% of the full change in absorbance after the switching of the potential. Thin film from polyimide **Ib** required 4.5 s at 1.08 V for switching absorbance at 405 and 879 nm and 1.9 s for fast bleaching due to the pendent substituted 2-phenyl-2-isopropyl group. Thin film of polymer **Ib** revealed a switching time of 4.5 s for $\lambda_{max} = 879$ nm and 1.9 s for bleaching, reflecting the different redox rates between the neutral and oxidized forms of the **Ib** film. Comparing the bleaching time of analogous polymers shown in Scheme 3, polyimide **Ib** exhibited a faster bleaching time than **M4** [38], which does not contain any substituents, and **M2**, which contains only one triphenylamine group. The reason for this difference is not clear in this stage, however, it must be related to



Fig. 8. (A) Potential step absorptometry (B) current consumption of polyimide **lb** (in CH₃CN with 0.1 M TBAP as the supporting electrolyte) by the application of a potential step 0–1.20 V.







Scheme 3. Analogous polyimides with (Ib) and without (M2 and M4) 2-phenyl-2-isopropyl group.

the introduction of electron-donating 2-phenyl-2-isopropyl groups, that lower the oxidation potential making oxidation easier.

4. Conclusions

A series of novel polyimides with pendent 2-phenyl-2-isopropyl substituted triarylamine moieties were readily prepared from the newly synthesized N',N'-bis[4-(2-phenyl-2-isopropyl)phenyl]-1,4phenylene-diamine with various aromatic dianhydride via the polycondensation reaction. The color changes from the pale yellowish neutral state to the green and blue oxidized state when scanning potentials positively from 0.00 to 1.20 V with short switching time. These properties suggest that these novel polyimides have a great potential as a new type of hole-transporting, and electrochromic material such as smart windows, automatic antiglazing mirrors, large-scale electrochromic screens, and chameleon materials. The molecular orbital theory and quantum simulation results suggest that the electron removal (oxidation) of the molecule was contributed by all atoms of the molecule but not by the nitrogen atom only. The electron was removed from HOMO to form SOMO, and the second electron was removed from SOMO to form second oxidation state.

Appendix. Supplementary material

Supplementary material associated with this article can be found in the on-line version, at doi:10.1016/j.polymer.2010.07.023.

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