

Transparent Electrochromic Polyimides and Their Devices for Electrochromic Applications

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Abstract

A series of new electroactive polyimides and their copolyimides were readily prepared from the 4-methoxytriphenylamine-based diamine and/or bis(etheramine) monomers with various cyclic aliphatic dianhydrides via the one-step direct polymerization. These polyimides are readily soluble in many organic solvents and can be solution-coated into tough and amorphous films. These polyimides derived large-scale device showed reversible electrochemical oxidation accompanied by strong color changes with high contrast from transparent neutral state to deep blue oxidation state.

Keywords: Transparent Polyimides, Redox Polymers, Electrochromism, Electrochemic Devices

Introduction

Electrochromic devices are attractive in green energy industries due to their low driving voltage and bistable properties. Major electrochromic materials are inorganic oxide for longer lifetime and endurance, however, films thereof are prepared by expensive processes and equipment such as vacuum deposition, spray pyrolysis, or sputtering. Even ignoring the cost of processing, the inorganic oxide still has shortcomings such as slow electrochromic rate, less color variation, and the likes. Most electrochromic organic materials are conjugated polymer with more color variation and fast electrochromic response time. However, the electrochromic conjugated polymer has shortcomings such as expensive monomers, a complicated synthesis, and formation by electro-polymerization. Therefore, the conjugated polymer with a low molecular weight has a size limited by the electrode size of the electro-polymerization. In other words, it is difficult to form the organic electrochromic material with a large area. On the other hand, the electrochromic conjugated polymers (such as poly(3,4-alkylenedioxythiophene)s^{1,2} and poly(3,4-alkylenedioxyppyrrrole)s³⁻⁶ and their derivatives) have an appearance of deep color due to their conjugated length. Although the deep color can be lightened by applying a voltage, the conjugated polymers cannot be fully transparent in neutral state. In other words, the conjugated polymer must be electrified to affect a transparent state, thereby leading to the problem of high energy consumption. For the normally transparent electrochromic devices in neutral state, short conjugated length must be necessary. Thus, many triarylamine-based electrochromic polymers (e.g., aromatic polyamides and polyimides) have been reported in the literature.⁷⁻¹³ Because of the incorporation of packing disruptive, propeller-shaped triphenylamine (TPA) units along the polymer backbone, most of these polymers exhibited good solubility in polar organic solvents. They may form uniform, transparent amorphous thin films by solution-casting and spin-coating methods. This is advantageous for their ready fabrication of large-area thin-film devices. However, TPA-based polyimides have deep color in neutral state due to strong charge transfer complex (CTC) effect from triphenylamine donor and phthalimide acceptor. In order to overcome this difficulty, we introduced the cyclic aliphatic dianhydride into polyimide backbone to decrease the CTC effect and lead to good solubility. Therefore, we synthesized the new semi-aromatic polyimide and its derived polycopolyimides containing electroactive TPA units. The cyclic aliphatic dianhydrides

are expected to reduce the charge transfer complex effect and increase the organosolubility of polyimides. We anticipated that the electrochromic device prepared from the present polyimides would be highly transparent in the neutral state and have high optical contrast in opaque state.

Experiment

Monomer Synthesis.

61.58 g (0.5mole) of 4-methoxyaniline, 167.1 g (1.1mole) of cesium fluoride, and 141.1 g (1.0mole) of *p*-fluoronitrobenzene (1.0mole) were weighted and put into a 2 L reaction tank. 0.6 L of DMSO was then added into the reaction tank. The mixture in the reaction tank was heated to 120°C and reacted at 120°C for 8 hours under nitrogen, and then cooled to room temperature. The cooled reaction was poured into ethanol to precipitate a solid, and then filtered to collect the solid. The solid was washed by ethanol and then dried to obtain a dinitro compound. 54.8 g (0.15mole) of the dinitro compound, 680 mL of ethanol, and 0.5 g of 10% active carbon palladium (Pd/C) were put into a 2 L reaction tank under nitrogen. The mixture was heated to reflux for 4 hours, and 60 mL of hydrazine was gradually added into the reaction tank to chemically reduce the dinitro compound. The refluxed reaction was immediately filtered to remove the active carbon palladium, and the filtration was cooled to obtain a white diamine crystal. The white diamine crystal was collected by filtering and then dried for following polyimides and copolyimides. IR (KBr): 3454, 3339 cm⁻¹ (N–H stretch). ¹H NMR (DMSO-*d*₆, ppm): 3.65 (s, 3H, OCH₃), 4.82 (s, 4H, NH₂), 6.48 (d, 2H), 6.68 (d, 2H), 6.69–6.73 (m, 4H). ¹³C NMR (DMSO-*d*₆, d, ppm): 55.4 (OCH₃), 114.5, 115.0, 121.2, 125.8, 137.7, 143.2, 144.5, 153.0.

Polymer Synthesis.

5.77 g of 4-methoxytriphenylamine-based diamine and 4.24 g of hydrogenated pyromellitic dianhydride (H-PMDA) were mixed in a reaction flask. 23.3g of NMP serving as a solvent was added into the reaction flask, and 0.2 g of isoquinoline serving as a catalyst was then added into the reaction flask. The mixture in the reaction flask was heated to 210°C for 4 hours to obtain a yellow viscous solution. The spectra data of dried thin film derived from the yellow viscous solution is shown as follows. IR (film, cm⁻¹): 2935, 2935, 1774, 1709. ¹H-NMR (DMSO-*d*₆, δ, ppm): 2.14 (4H), 3.11 (4H), 3.73 (3H), 6.97 (2H), 7.03 (4H), 7.10 (2H), 7.17 (4H). ¹³C-NMR (DMSO-*d*₆, δ, ppm): 36.8, 55.4, 68.4, 115.4, 122.0, 126.0, 128.2, 139.1, 147.2, 156.8, 178.4. GPC data: M_w = 168,469, M_n = 131,026.

Copolymer Synthesis.

4.28 g of 4-methoxytriphenylamine-based diamine, 2.46 g of 2,2'-bis[4-(4-aminophenoxy)phenyl]propane (BAPP), and 4.96 g of bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride were mixed in a reaction flask. 27.3 g of NMP serving as a solvent was added into the reaction flask, and 0.2 g of isoquinoline serving as a catalyst was then added into the reaction flask. The mixture in the reaction flask was heated to 210 °C for 4 hours to obtain a yellow viscous solution. It should be understood that the product in Formula 13 is a random copolymer other than a block copolymer. The spectra data of the dried thin film derived from yellow viscous solution is shown as follows. IR (film, cm⁻¹): 2964, 2837, 1772, 1712. ¹H-NMR (DMSO-*d*₆, δ, ppm): 1.94, 3.36, 3.51, 3.72, 6.24, 6.93~7.01, 7.12, 7.24. ¹³C-NMR (DMSO-*d*₆, δ, ppm): 34.0, 41.8, 55.3, 63.3, 65.6, 68.3, 69.2, 69.9, 115.4, 118.5, 122.0, 125.7, 127.0, 127.8, 128.1,

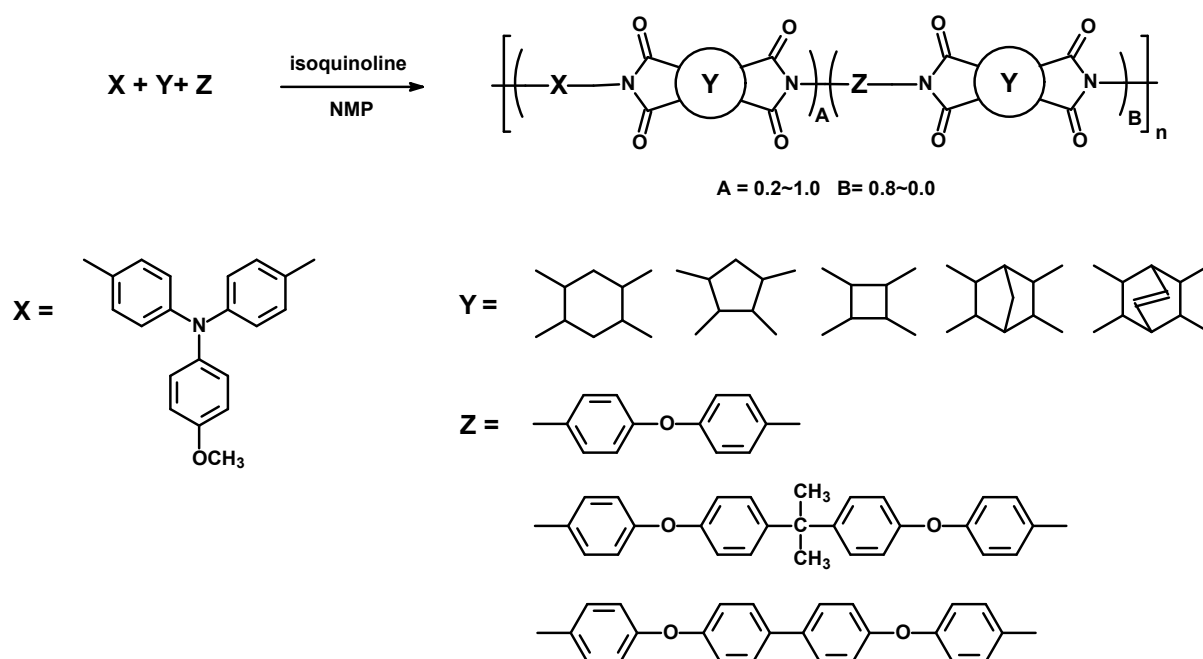
128.2, 128.6, 131.0, 139.1, 145.8, 147.2, 153.9, 156.8, 176.8. GPC data: $M_w = 129,234$, $M_n = 119,499$.

Device Fabrication.

An electrochromic polymer film was prepared by blade coating solutions of the polyimide (solid content was about 20wt% in DMAc) onto an ITO-coated glass substrate (200 x 300 x 0.7 mm, 7–15 Ω /square). The polymers were blade-coated onto an active area (about 190 mm x 290 mm) then dried in vacuum. A gel electrolyte based on PMMA (M_w : 120,000) and LiClO_4 was plasticized with propylene carbonate to form a highly transparent and conductive gel. PMMA (50 g) was dissolved in dry acetonitrile (250 g), and LiClO_4 (5.0 g) was added to the polymer solution as supporting electrolyte. Then, propylene carbonate (PC) (75 g) was added as plasticizer. The mixture was then slowly heated until gelation. The gel electrolyte was spread on the polymer-coated side of the electrode, and the electrodes were sandwiched. Finally, a transparent epoxy resin was used to seal the device.

Results and discussion

Polyimides were prepared in a one-step procedure by the reactions of equal molar amounts of diamine with commercially available cyclic aliphatic tetracarboxylic dianhydrides in NMP by isoquinoline catalyst cyclodehydration. The reaction route is shown in Scheme 1.



Scheme 1. Synthesis of TPA-based polyimides and copolyimides.

These polyimides were prepared by a one-pot, high-temperature solution polymerization of TPA-diamine and dianhydride in NMP at 180 °C in the presence of isoquinoline as the catalyst. The chemical structure of the polyimides was confirmed by means of FTIR and NMR spectroscopy as shown in Fig. 1 and 2, respectively. In high frequency region shows aliphatic C–H stretching peaks at 2935 and 2837 cm^{-1} . The absorption bands around 1774 and 1709 cm^{-1} arising from the unsymmetrical and symmetrical carbonyl stretching vibrations of the imide groups were found in all the polyimides.

There was no existence of the characteristic absorption bands of the amide and carboxyl groups in the region of 3200–3500 cm^{-1} (N–H and O–H stretching), and this indicated that a virtually complete imidization had been obtained. The absorption bands in the range of 2837–2935 cm^{-1} were assigned to methylene and methine C–H stretching of the cyclohexane groups. The ^1H and ^{13}C NMR spectra of a representative polyimide are reproduced in Fig. 2 and agrees well with the desired polymer structure. Fig. 3 exhibited the photographs of thin film of H-PMDA and 6FDA-based polyimides with highly flexibility. By introducing the cyclic aliphatic dianhydrides can be efficiency to diminish the charge transfer complex effect from the electron donor and acceptor system of polyimide. Comparison with the TPA-based 6FDA polyimide, the cutoff wavelengths (absorption edge; λ_0) from the UV-Vis-NIR transmittance spectra of semi-polyimides (H-PMDA PI) or copolyimide (BAPP coPI) exhibited lighter color and higher optical transparency due to the low inter- or intra-interaction from polymer chain (Fig. 4).

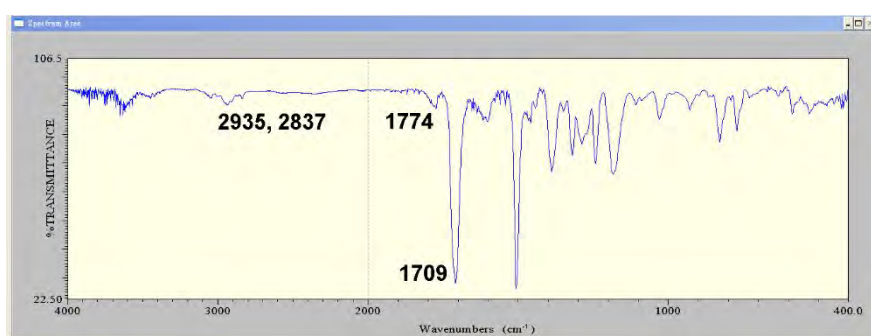


Fig. 1. IR spectra of H-PMDA-based polyimide.

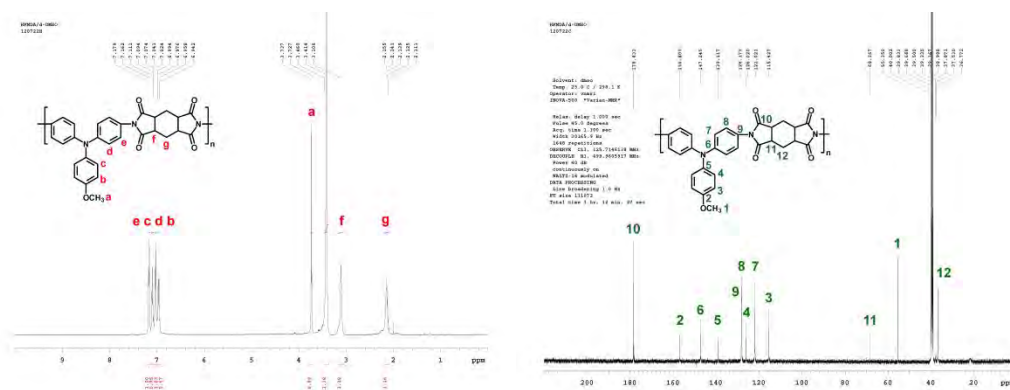


Fig. 2. ^1H and ^{13}C NMR spectra of H-PMDA-based polyimide.



Fig. 3. Photographs of TPA-based H-PMDA (Left) and 6FDA (Right) polyimides.

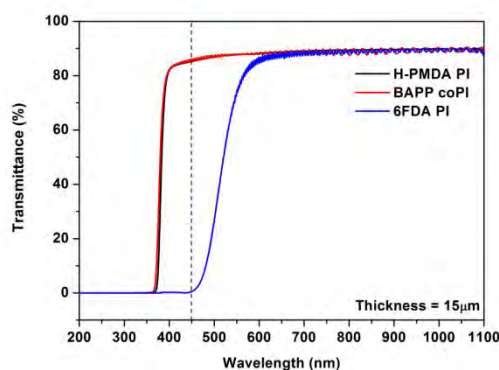


Fig. 4. Transmittance spectra of thin films of TPA-based polyimides and copolyimides.

The electrochemical properties of the polyimide films were then measured to monitor colors of the polyimide films under different voltages. The DMAc solution of the polyimide or copolymer thereof was coated on an ITO glass to serve as a working electrode. 0.1 M acetonitrile (CH_3CN) solution of TBAP served as an electrolyte, and ferrocene (Fc) served as a standard. The polyimide films of **H-PMDA PI** or **BAPP coPI** were applied a voltage from 0V to 1.25 V, such that the appearance of the polyimide films was transferred from transparent (colorless) to deep blue. The polyimide film of **6FDA PI** was applied a voltage from 0V to 1.25 V, such that the appearance of the polyimide film was transferred from opaque yellow to blue. The redox behavior was monitored by cyclic voltammetry (CV) conducted for the cast film on an ITO-coated glass substrate as working electrode in dry acetonitrile (CH_3CN) containing 0.1 M of TBAP as an electrolyte under nitrogen atmosphere. A pair of reversible redox couple could be observed on the CV scans of all polymers. Typical CV curves for polyimide **H-PMDA PI** and copolyimide **BAPP coPI** are shown in Fig. 5. The polyimides exhibited $E_{1/2}$ values in the range of 0.93–0.94 V, corresponding to electroactive triphenylamine (TPA) core oxidation.

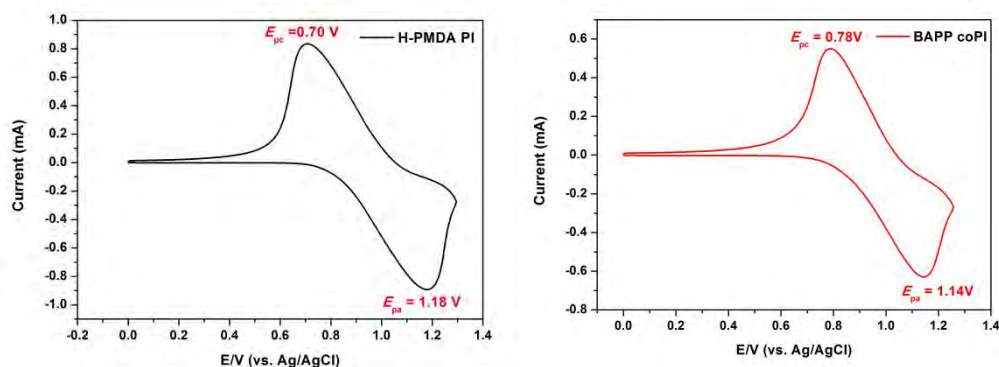


Fig. 5. Cyclic voltammograms of the cast film of **H-PMDA PI** (Left) and **BAPP coPI** (Right) polyimide on an indium–tin oxide (ITO)-coated glass substrate at a scan rate of 100 mV/s in 0.1 M TBAP/acetonitrile.

Spectroelectrochemical analysis of the polyimide and copolyimide thin films was carried out on an ITO-coated glass substrate in an acetonitrile solution of 0.1 M TBAP by applying the desired potential. All the polymer films showed a strong coloration change when the applied potential was changed. The

typical changes of the absorption spectra of polyimide **H-PMDA PI** are shown in Fig. 6. When the applied potential increased from 0.85 to 1.25 V, the peak of characteristic absorbance at 342 nm for polyimide **H-PMDA PI** decreased gradually while new band grew up at 738 nm, and the color of the film changed to deep blue. The spectral changes were clearly due to the formation of the cationic species of polyimide.

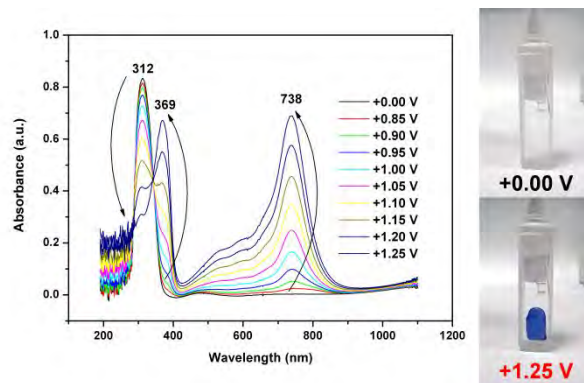


Fig. 6. Spectral change of polyimide **H-PMDA PI** thin film on the ITO-coated glass substrate (in CH_3CN with 0.1 M TBAP as the supporting electrolyte) along with increasing of the applied voltage (vs. Ag/AgCl couple as reference). The inset shows the photographic images of the film at indicated applied voltages.

The color of the polyimide films turned from transparent to deep blue upon oxidation. 12 inch of polyimide film was coated on the conductive surface of the ITO glass, and then baked to remove the solvent thereof. The electrolyte gel was coated on the transparent electrochromic film, and then attached to another ITO glass. Thereafter, the attaching portions of the two transparent conductive layers were coated by sealing epoxy resin to complete a simple electrochromic device. Only a very low DC voltage of 2.4 V was applied to the polyimide film through an external line and the ITO layer, such that the appearance of the electrochromic device was transferred from transparent (colorless) to deep blue in few seconds. The typical changes of the transmittance spectra of polyimide **H-PMDA PI** derived electrochromic device are shown in Fig. 7. When the applied potential increased from 1.6 to 2.4 V, the peak of characteristic absorbance at 342 nm for polyimide **H-PMDA PI** decreased gradually while new band grew up at 738 nm, and the color of the film changed to deep blue. The spectral changes were clearly due to the formation of the cationic species of polyimide. Compared with the solution type electrochromic test cell from the CV method, the electrochromic device have higher driving voltage from 1.25 to 2.4V due to the lower diffusion rate between gel-type electrolyte and polyimide.

Conclusions

The new triphenylamine-based series of electroactive semiaromatic polyimides and copolyimides with triphenylamine groups were synthesized from the polycondensation reactions of this diamine monomer with various cyclic aliphatic tetracarboxylic dianhydrides. The three-dimensional triphenylamino group can disrupt the coplanarity of aromatic units in chain packing, and increases the between- chains spaces or free volume; consequently, all the polymers were amorphous with good solubility in many polar solvents and exhibited excellent film-forming ability. In addition to high glass transition temperature, high thermal stability, and good mechanical properties, these polyimides also

revealed excellent stability of electrochromic characteristics. As a result, the present polyimides and copolyimides may find applications as new type organic electrochromics.

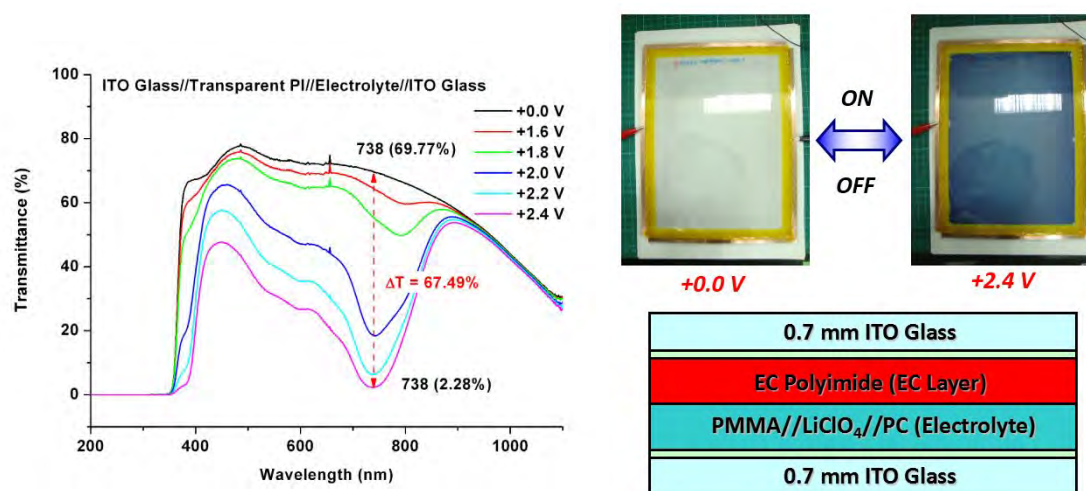


Fig. 7. Transmittance change of polyimide **H-PMDA PI** thin film on the ITO-coated glass substrate (in gel electrolyte) along with increasing of the applied voltage (vs. Ag/AgCl couple as reference). The right side shows the photographic images and diagram of the transparent electrochromic device (Size = 300mm x 200mm) at indicated applied voltages.

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