

This article was downloaded by: [University Of Gujrat]

On: 11 December 2014, At: 13:43

Publisher: Taylor & Francis

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gmcl20>

Electrochromism Properties of Polyimides Possessing Triphenylamine Moieties with Different Substituents

Seung Hun Lee^a, Jun Bae^a, Hye Mi Seo^a, Ji Hyuk Im^a, Hyung Sub Shin^a, Eun Joo Yoo^a & Seung Woo Lee^a

^a School of Chemical Engineering, Yeungnam University, Gyeongsan, Korea

Published online: 17 Nov 2014.

To cite this article: Seung Hun Lee, Jun Bae, Hye Mi Seo, Ji Hyuk Im, Hyung Sub Shin, Eun Joo Yoo & Seung Woo Lee (2014) Electrochromism Properties of Polyimides Possessing Triphenylamine Moieties with Different Substituents, *Molecular Crystals and Liquid Crystals*, 598:1, 6-15, DOI: [10.1080/15421406.2014.932674](https://doi.org/10.1080/15421406.2014.932674)

To link to this article: <http://dx.doi.org/10.1080/15421406.2014.932674>

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at <http://www.tandfonline.com/page/terms-and-conditions>

Electrochromism Properties of Polyimides Possessing Triphenylamine Moieties with Different Substituents

SEUNG HUN LEE, JUN BAE, HYE MI SEO, JI HYUK IM,
HYUNG SUB SHIN, EUN JOO YOO, AND SEUNG WOO LEE*

School of Chemical Engineering, Yeungnam University, Gyeongsan, Korea

Two diamine monomers with methyl (CH₃TPA) and methoxy (OCH₃TPA) group substituents in the para position of the triphenylamine (TPA) moiety were synthesized by nucleophilic aromatic substitution using 4-fluoronitrobenzene with p-toluidine and p-anisidine, respectively. From these diamine monomers, electroactive polyimides (PI)s were prepared by the chemical imidization of poly(amic acid) solutions, which were prepared with 4,4'-oxydiphthalic anhydride (ODPA). ¹H nuclear magnetic resonance and Fourier transform infrared spectroscopy confirmed that both PIs had been synthesized successfully. The measured inherent viscosity for ODPA-CH₃TPA PI and ODPA-OCH₃TPA PI was 0.42 and 0.49 dL/g, respectively. The glass transition temperatures for ODPA-CH₃TPA PI and ODPA-OCH₃PDA PI were 236°C and 238°C, respectively, and the thermal degradation temperature of both PIs was above 390°C. The band gaps of ODPA-CH₃PDA and ODPA-OCH₃PDA were 3.00 and 2.72 eV, respectively. The oxidation onset potential E_{ox} of ODPA-CH₃PDA PI and ODPA-OCH₃PDA PI from cyclic voltammetry was 0.73 V and 0.65 V, respectively. The highest occupied molecular orbital and lowest unoccupied molecular orbital values differed according to the groups substituted into the triphenylamine moiety. After applying a voltage, the absorption peak intensity at 723 nm and 752 nm for ODPA-CH₃TPA and ODPA-OCH₃TPA, respectively, increased. The electrical properties varied according to the chemical structure of synthesized diamines.

Keywords Electroactive polyimide; HOMO; LUMO; triphenyl amine moiety; spectroelectrochemical behaviors

Introduction

Organic charge transporting materials play important roles in many electrical and optical applications, such as organic photoconductors, electroluminescence (EL) and electrochromic devices [1–5]. In particular, electrochromic devices exhibit a reversible optical change in absorption or transmittance after being oxidized or reduced electrochemically by applying an external voltage using electrochromic materials, such as transition-metal oxides, inorganic coordination complexes, organic molecules, and conjugated polymers [6–11]. In general, studies of electrochromic materials focusing on the optical changes in the visible

*Address correspondence to Prof. Seung Woo Lee, School Chemical Engineering, Yeungnam University, 280 Daehak-ro, Gyeongsan 712-749, Korea (ROK). Tel.: (+82)53-810-3972; Fax: (+82)53-810-4631. E-mail: leesw1212@ynu.ac.kr

region have been useful for variable reflectance mirrors, sunglasses, controllable aircraft canopies, smart windows, and electrochromic displays [11].

Triphenylamine (TPA) derivatives have attracted considerable interest over the past few decades owing to their excellent charge transporting properties as hole transporting materials in thin layer electro-optical devices, such as organic light-emitting diodes, solar cells, organic field effect transistors and photorefractive holography [1–4, 12–16]. The basic electrical properties of the TPA derivatives are the easy oxidizability of the amino center and its ability to transport the positive charge centers via cationic radical species [17]. As a result, significant research effort is currently being invested in the development of electrochromic polymer materials with the properties and chemical structure of TPA derivatives. Several studies on such polymer materials have been reported [18–23].

The electrochemical properties of TPA derivatives are affected by the substitution group at the *para* position of the TPA moiety. The oxidation potential and π - π^* band gap of the product are different from that of the chemical structures of TPA derivatives [24]. For example, unsubstituted TPA undergoes coupling deprotonation to form tetraphenylbenzidine after the formation of the initial monocationic radical [25, 26]. When TPA derivatives with electron-donating substituents, such as methoxy groups at the *para* position of TPA, prevents coupling reactions and affords stable cationic radicals [25–27].

Aromatic polyimides (PIs) have excellent thermal stability, dimensional stability, and mechanical properties [28–31]. Commonly, PIs are prepared using dianhydride and diamine monomers in a polar aprotic solvent, such as N-methylpyrrolidinone (NMP), N,N-dimethylformamide (DMF), and N,N-dimethylacetamide (DMAc) to synthesize poly(amic acid), which is a precursor of PI. The PAA precursor obtained is then converted to PI by thermal imidization or chemical imidization.

In this study, PAAs were prepared using different TPA derivatives with electron-donating methyl groups and methoxy groups in the *para* position of the TPA moiety, with a dianhydride monomer in NMP. The PIs were then synthesized by the chemical imidization of PAAs solutions. The chemical structures of the synthesized monomers were characterized by ^1H nuclear magnetic resonance (NMR) spectroscopy. The chemical structures and thermal properties of the synthesized PIs were determined using spectroscopic methods including ^1H NMR and Fourier transform infrared (FTIR) spectroscopy and differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), respectively. In addition, the electrical properties and spectroelectrochemical behavior was investigated in terms of the chemical structure of the TPA derivatives.

Experimental

Materials

The materials, *p*-toluidine (TCI), potassium permanganate (Aldrich), 4-fluoronitrobenzene (from Alfa Aesar), cesium fluoride (Aldrich), hydrazine monohydrate (Aldrich), tetrabutylammonium perchlorate (TPBA) and 10% palladium on activated carbon (Aldrich) were used as received. The solvents, dimethyl sulfoxide (DMSO), acetonitrile and pyridine (Py), were purchased from Aldrich, and used as received. The solvent for polymerization, N-methyl-2-pyrrolidinone (NMP), was purchased from Aldrich, purified by distillation over calcium hydride and stored over 4 Å molecular sieves.

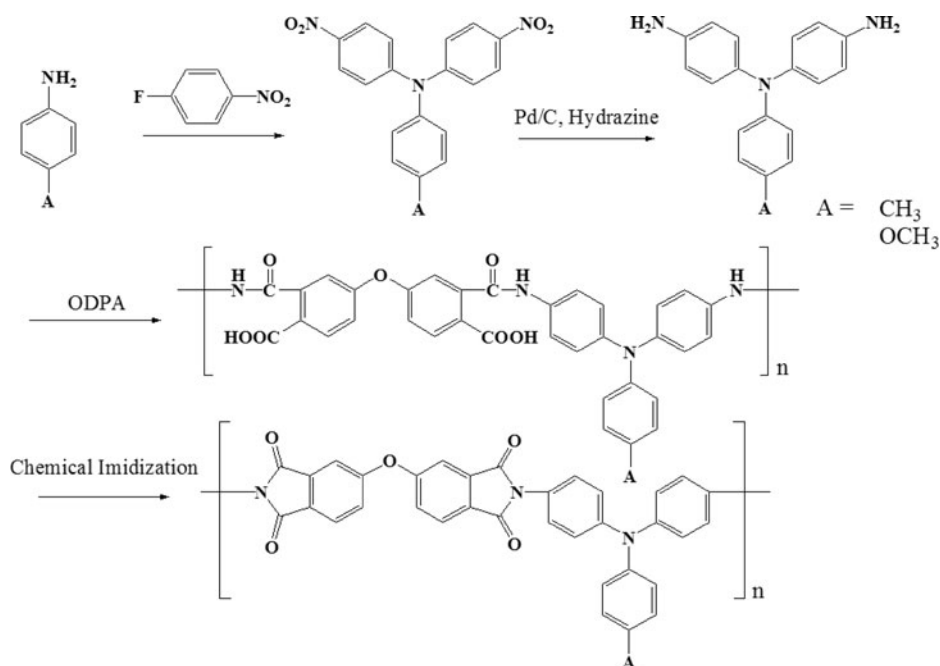
Measurements

The ^1H NMR spectra were obtained using a Bruker AM 300 spectrometer. The FTIR (BOMEM DA8 FTIR) spectra were obtained on a spectrometer equipped with a Diamond

ATR system (Harrick Scientific). The glass transition temperature (T_g) and degradation temperature (T_d) of each film were measured by DSC (model DSC-7, Perkin-Elmer, USA) and TGA (model TGA-7, Perkin-Elmer, USA), respectively. In the DSC and TGA measurements, dry nitrogen gas was purged at a flow rate of 100 cc/min and a ramping rate of 10.0°C/min was used. The UV-visible absorption spectra were obtained as a function of the exposure dose using a Hewlett-Packard 8453 spectrophotometer. The inherent viscosity of each PI product in NMP with a concentration of 0.50 g/dL was measured at 25.0°C using an Ubbelohde suspended-level capillary viscometer. Cyclic voltammetry (Epsilon) was performed using a three-electrode cell, in which indium tin oxide (ITO, the polymer film area was ca. $0.5 \times 1.1 \text{ cm}^2$) was used as the working electrode. The electrochemical cell was composed of a 1 cm cuvette, ITO as the working electrode, platinum wire as the auxiliary electrode, and Ag/AgCl as the reference electrode.

Synthesis of 4,4'-dinitro-4''-methyltriphenylamine¹

p-Toluidine (2.5 g, 23.3 mmol), 4-fluoronitrobenzene (7.24 g, 51.3 mmol) and cesium fluoride (7.79 g, 51.3 mmol) were dissolved in dried 100 mL DMSO, and the reactant mixture was stirred at 120°C for 48 h (Scheme 1). The reaction mixture was cooling to room temperature, poured into 500 ml of cold water and the precipitated orange solid was then collected by filtration and washed with methanol. The yield of the product was 5.91 g (66%); ¹H NMR (DMSO-*d*₆, ppm): 2.35 (s, Ar-CH₃, 3H), 7.13–7.16 (d, Ar-H, 2H), 7.16–7.19 (d, Ar-H, 4H), 7.30–7.33 (d, Ar-H, 2H), 8.15–8.18 (d, Ar-H, 4H).



Scheme 1. Synthesis route of diamines with methyl and methoxy substituents into the para position of triphenylamine derivatives and chemical structures of polyimides.

Synthesis of 4,4'-dinitro-methoxytriphenylamine³²

p-Anisidine (2.5 g, 20.3 mmol), 4-fluoronitrobenzene (6.30 g, 44.6 mmol) and cesium fluoride (6.78 g, 44.6 mmol) were dissolved in dried 100 mL DMSO, and stirred at 150°C

for 24 h (Scheme 1). The reaction mixture was cooled to room temperature, and poured into methanol. The precipitated orange solid was collected by filtration and washed with methanol. The product yield was 5.71 g (70%); ^1H NMR ($\text{DMSO}-d_6$, ppm): 3.67 (s, Ar-OCH₃, 3H), 7.03–7.06 (d, Ar-H, 2H), 7.13–7.16 (d, Ar-H, 4H), 7.18–7.21 (d, Ar-H, 2H), 8.12–8.15 (d, Ar-H, 4H).

Synthesis of 4,4'-diamino-4''-methyltriphenylamine (CH3TPA)¹

A mixture of 5.0 g (14.3 mmol) of 4,4'-dinitro-4''-methyltriphenylamine, 2.52 g (40.0 mmol) of hydrazine monohydrate, 0.2 g of 10% Pd-C and 100 ml of ethanol was stirred at 120°C for 8 h (Scheme 1). The reaction mixture was filtered through Celite to remove Pd-C, and the filtrate was added to 100 ml of water to obtain precipitates that were filtered and dried. The crude product was recrystallized from ethanol. The product yield was 3.93 g (95%); ^1H NMR ($\text{DMSO}-d_6$, ppm): 2.16 (s, Ar-CH₃, 3H), 4.84 (s, Ar-NH₂, 4H), 6.50–6.53 (d, Ar-H, 2H), 6.56–6.59 (d, Ar-H, 4H), 6.72–6.75 (d, Ar-H, 2H), 6.87–6.90 (d, Ar-H, 4H).

Synthesis of 4,4'-diamio-methoxytriphenylamine (OCH3TPA)

The reaction of OCH3TPA was conducted in a similar manner of CH3TPA except that 5.0 g (13.7 mmol) of 4,4'-dinitro-methoxytriphenylamine was used (Scheme 1). The product yield was 3.80 g (91%); 3.67 (s, Ar-OCH₃, 3H), 4.72 (s, Ar-NH₂, 4H), 6.47–6.50 (d, Ar-H, 2H), 6.67–6.70 (d, Ar-H, 4H), 6.68–6.71 (d, Ar-H, 6H).

Synthesis of Polyimide

Polymerization was conducted by the conventional two-step solution imidization process. Poly(amic acid)s (PAA) was prepared by adding 1 equivalent of 4,4'-oxydiphthalic anhydride (ODPA) in an anhydrous NMP solution and 1 equivalent of a diamine, which was pre-dissolved in NMP to form a 10.0 wt.% solution, under nitrogen with vigorous stirring (Scheme 1). Once addition was complete, the reaction flask was sealed tightly and stirring was continued for 48 h until the polymerization mixture was homogeneous and viscous. A small excess of acetic anhydride and pyridine was added to the PAA solutions at room temperature and allowed to stir for 12 h at 150°C. After dilution with 5 mL of NMP, the solutions were poured into 1000 mL of methanol with vigorous stirring. The solids formed were filtered, washed repeatedly with hot methanol, and dried at 150°C for 12 h *in vacuo*. The yields were almost quantitative in polymerizations using the two different diamines.

Results and Discussion

4,4'-Dinitro-4''-methyltriphenylamine and 4,4'-dinitro-methoxytriphenylamine were synthesized *via* a nucleophilic aromatic substitution reaction in the presence of cesium fluoride between 4-fluoronitrobenzene and p-toluidine and p-anisidine, respectively. The obtained dinitro group-containing molecules were characterized by ^1H NMR spectroscopy. The spectra were coincident with the expected chemical structure. A characteristic chemical shift at 2.35 ppm for the methyl group was observed on the ^1H NMR spectrum for 4,4'-dinitro-4''-methyltriphenylamine. A chemical shift at 3.67 ppm for the methoxy group in 4,4'-dinitro-methoxytriphenylamine was observed.

The monomers with diamino groups for polymerization were prepared in the presence of hydrazine monohydrate with a catalytic amount of a Pd/C catalyzed reduction reaction of dinitro group containing compounds. The prepared diamine compounds were characterized

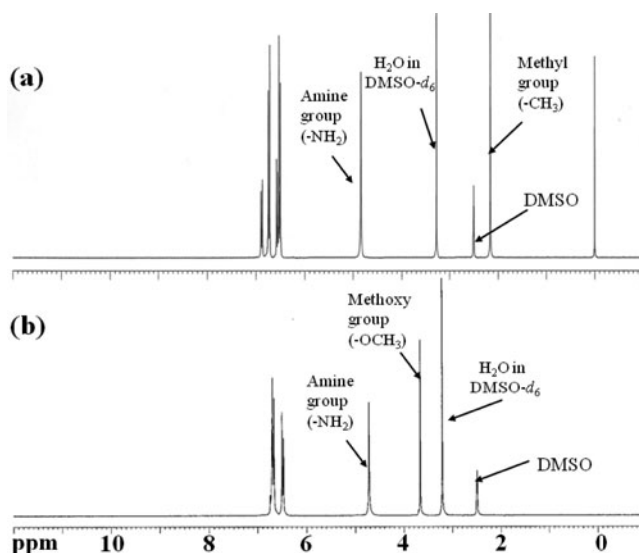


Figure 1. ^1H NMR spectra of two triphenylamine derivatives with diamine groups dissolved in dimethyl- d_6 sulfoxide ($\text{DMSO}-d_6$): (a) CH_3TPA and (b) OCH_3TPA .

by ^1H NMR spectroscopy. After the reduction reaction, singlet peaks at 4.84 and 4.72 ppm for CH_3TPA and OCH_3TPA , respectively, were observed and assigned to the amino proton from the reduction of nitro groups (Figure 1). The proton peaks from aromatic rings were shifted to high field after the reduction reaction. These results suggest that the two diamine compounds, CH_3TPA and OCH_3TPA , were synthesized successfully.

Imidization was conducted using a two steps solution polymerization process. The precursor PAAs were prepared via a room temperature reaction between each diamine and the ODPA at room temperature in NMP. Imidization of the PAA precursors to PIs was carried out by a chemical treatment with acetic anhydride. The obtained PIs were identified by IR spectroscopy (Figure 2). The characteristic absorption bands of the imide group were observed near 1773 and 1713 cm^{-1} (asymmetry and symmetry stretch of carbonyl ($\text{C}=\text{O}$), imide I) and 1371 cm^{-1} ($\text{C}-\text{N}-\text{C}$ stretch, imide II). The carbonyl stretch bands of amide and carboxylic acid in the PAA precursors were not detected in the IR spectra of the resulting PIs, indicating that the PAA precursors had been converted completely to the corresponding PIs [28–31].

The synthesized PIs were characterized by ^1H NMR spectroscopy (Figure 3). Both PIs showed aromatic proton peaks at 6.8–8.2 ppm. A characteristic chemical shift at 2.35 ppm and 3.81 ppm for the methyl group and methoxy substituents of TPA moiety, respectively, was observed on the ^1H NMR spectra for ODPA- CH_3PDA PI and ODPA- OCH_3PDA PI. In addition, unreacted acid, amine and amide group from PAA were not detected in the ^1H NMR spectra. These spectroscopic characterizations confirmed that the imidization reactions had proceeded completely after treating the polymers with acetic anhydride at 150°C . For PIs, the measured inherent viscosities of ODPA- CH_3TPA PI and ODPA- OCH_3TPA PI were 0.42 and 0.49 dL/g, respectively. Considering the spectroscopy results and inherent viscosity, it can be inferred that the PIs had been synthesized successfully with a reasonably high molecular weight.

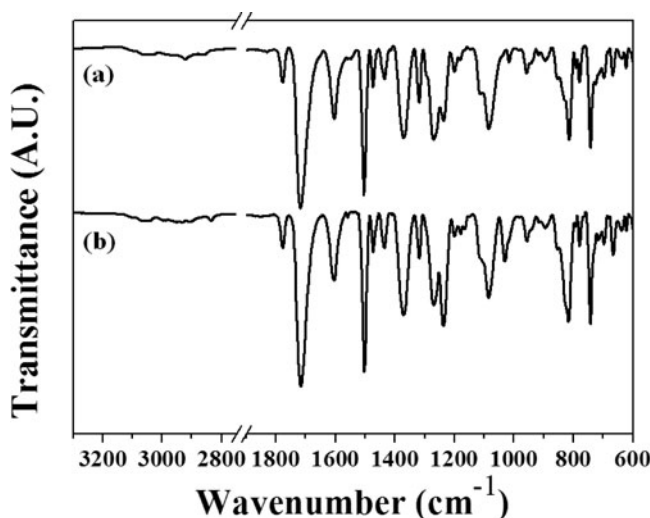


Figure 2. ATR-FTIR spectra of polyimide films: (a) ODPA-CH3TPA PI and (b) ODPA-OCH3TPA PI.

The thermal properties of the PIs were determined, and the results are listed in Table 1. The T_g of ODPA-CH3TPA PI and ODPA-OCH3PDA PI measured by DSC were 236°C and 238°C, respectively. These glass transition behaviors might come from the similar chemical structures of both PIs. The two PIs have similar T_d s (394–407°C). Of these polymers, ODPA-CH3PDA PI had a higher T_d .

The PI films were examined by UV-vis spectroscopy and cyclic voltammetry (CV). From the UV-vis spectra, the band gap (which is the difference between the highest occupied molecular orbital (HOMO) level and lowest unoccupied molecular orbital (LUMO)) was

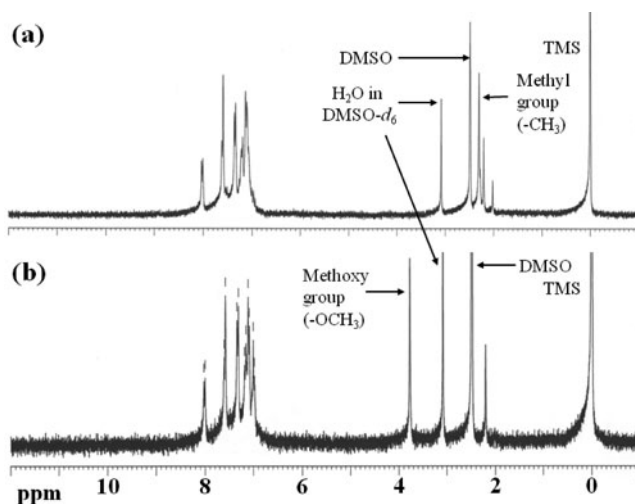


Figure 3. ^1H NMR spectra of polyimides dissolved in dimethyl- d_6 sulfoxide ($\text{DMSO}-d_6$): (a) ODPA-CH3TPA PI and (b) ODPA-OCH3TPA PI.

Table 1. Inherent viscosity, glass transition temperatures (T_g), and decomposition temperatures (T_d) of polyimides

Sample designation	Inherent viscosity ^a	T_g (°C) ^b	T_d (°C) ^c
ODPA-CH3TPA PI	0.42	236	407
ODPA-OCH3TPA PI	0.49	238	394

^aMeasured in NMP at a concentration of 0.5g/dL at room temperature.

^bMeasured by DSC with a heating rate of 10.0°C/min.

^cDetermined by TGA at a heating rate of 10.0°C/min under a nitrogen atmosphere: T_d = temperature of 5.0% weight loss.

determined using the λ_{onset} value from the measured UV-vis spectroscopy. The band gap was estimated to be 3.00 eV for ODPA-CH3PDA PI, and 2.72 eV for ODPA-OCH3PDA PI [33]. The electrochemical behavior of the PIs were examined by CV of the coated film on ITO-coated glass substrates as the working electrode in dry acetonitrile containing 0.1 M of TBAP as an electrolyte under a nitrogen atmosphere. Figure 4 shows the typical CVs for ODPA-CH3TPA and ODPA-OCH3TPA PI films. CV analysis showed that the oxidation onset potential E_{ox} of ODPA-CH3PDA PI and ODPA-OCH3PDA PI were 0.73 V and 0.65 V, respectively. The external ferrocene/ferrocenium (F_c/F_{c+}) redox standard half-wave potential ($E_{1/2}$) was 0.48 V versus the Ag/AgCl electrode in acetonitrile. The HOMO of ODPA-CH3TPA PI and ODPA-OCH3PDA PI was determined to be 5.55 eV and 5.52 eV, respectively. From these band gap and HOMO values, LUMO value of ODPA-CH3TPA PI and ODPA-OCH3PDA PI were estimated to be 2.11 eV and 2.33, respectively. The

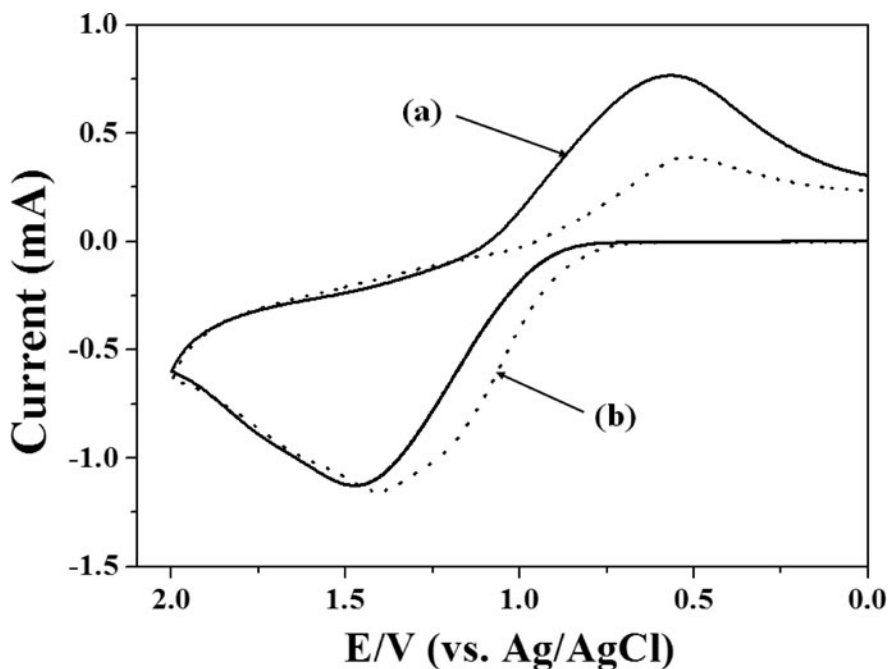


Figure 4. CV responses of (a) ODPA-CH3TPA PI and (b) ODPA-OCH3TPA PI films coated on indium tin oxide glass substrates in acetonitrile containing 0.1 M tetrabutylammonium perchlorate.

Table 2. Redox potentials and energy levels of the polyimides

Sample	Thin film (nm)		Oxidation potential (V) ^a		E _g (eV) ^b	HOMO (eV) ^c	LUMO (eV)
	λ_{\max}	λ_{onset}	E _{1/2}	E _{onset}			
ODPA-CH3TPA	306	413	1.17	0.73	3.00	5.55	2.55
ODPA-OCH3TPA	308	456	1.14	0.65	2.72	5.03	2.80

^aMeasured by cyclic voltammograms (CV) versus Ag/AgCl in acetonitrile containing 0.1 M tetrabutylammonium perchlorate. E_{1/2}: Oxidation half-wave potential from CV

^bCalculated from polyimide films by the equation: E_g (energy band gap between HOMO and LUMO) = 1240/ λ_{onset}

^cCalculated from E_{1/2} of CV. This value were referenced to ferrocene (4.8 eV)

differences between the band gaps and HOMO/LUMO levels of the PIs might be due to the differences in their substituent effects in the same position of the TPA moiety.

Both the oxidation of PIs occurred at the nitrogen center of the TPA unit. On the other hand, the introduction of more electron-donating methoxy substituents into the para-position of TPA not only stabilizes the cationic radicals but also reduces the oxidation potentials [32]. The HOMO and LUMO levels of the PIs investigated could be determined from the oxidation onset or half-wave potentials and the onset absorption wavelength of polymer films (Table 2).

Spectroelectrochemical experiments were carried out to reveal the optical characteristics of the electrochromic films. The electrode preparations and solution conditions were the same as the CV experimental condition. Figure 5 shows the spectroelectrochemical results using UV-vis spectroscopy for ODPA-OCH3TPA PI. In the neutral state, ODPA-OCH3TPA

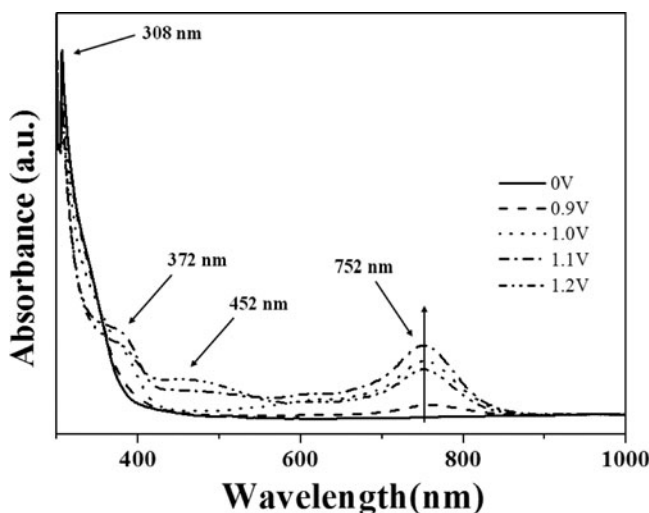


Figure 5. Spectroelectrochemical behavior at the applied potentials of ODPA-OCH3TPA PI thin film coated on indium tin oxide glass substrates in acetonitrile containing 0.1 M tetrabutylammonium perchlorate.

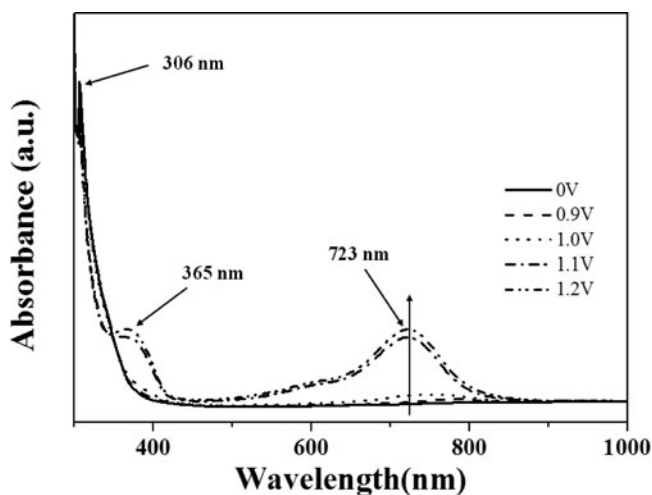


Figure 6. Spectroelectrochemical behavior at the applied potentials of ODPA-CH₃TPA PI thin film coated on indium tin oxide glass substrates in acetonitrile containing 0.1 M tetrabutylammonium perchlorate.

PI has strong absorption at wavelengths around 308 nm, which is characteristic for the TPA moiety, but is almost transparent in the visible region. The neutral ODPA-OCH₃TPA PI film showed an absorption maximum at 308 nm ($\lambda_{\text{max}} = 308$ nm), but no absorbance in the visible region. This UV absorption might have originated from the TPA moiety in the polymer. The absorption peak intensity at $\lambda_{\text{max}} = 308$ nm decreased drastically with increasing applied voltage, whereas a new peak at 752 nm increased gradually. The increasing new peak is due to the formation of a stable cationic radical of the methoxy group-substituted TPA unit [32].

Figure 6 shows the spectroelectrochemical behavior of an ODPA-CH₃TPA PI film. The $\lambda_{\text{max}} = 306$ nm for the ODPA-CH₃TPA PI film decreased gradually with increasing applied positive potential, whereas new bands grew at 723 nm. This new absorbance peak was assigned to a cationic radical TPA with a methyl substituent. Furthermore, when the λ_{max} of ODPA-OCH₃PDA and ODPA-CH₃PDA in neutral state were compared, a 2 nm blue-shift was observed for ODPA-OCH₃PDA PI. This means that ODPA-OCH₃PDA PI has a shorter conjugation length than ODPA-CH₃PDA PI.

Conclusions

Two diamine monomers with a methyl (CH₃TPA) and methoxy (OCH₃TPA) group substituent in the para- position of triphenylamine (TPA) moiety were synthesized by nucleophilic aromatic substitution. From these diamine monomers, electroactive polyimides (PIs) were prepared via the chemical imidization of poly(amic acid) (PAA) solutions, which were prepared with 4,4'-oxydiphthalic anhydride (ODPA). Both PIs were synthesized successfully and showed good thermal stability. The band gaps of the PIs were 3.00 and 2.72 eV for ODPA-CH₃PDA and ODPA-OCH₃PDA, respectively. The HOMO and LUMO values differed according to the substituent groups into the TPA moiety. The spectroelectrochemical behavior varied according to the chemical structure of the diamines and applied voltage.

Acknowledgment

This study was supported by Yeungnam University Research Grants in 2012 and a Human Resources Development Program of Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant (No. 20104010100580) funded by the Korean Ministry of Knowledge Economy.

References

- [1] Wang, K.-L., Huang, S.-T., Hsieh, L.-G., & Huang, G.-S. (2008). *Polymer* 49, 4087.
- [2] Ha, J., Lee, H. C., Lee, S. H., Kimura, N., & Sato, H. (2004). *Polym. J.* 36, 219.
- [3] Wang, B. C., Liao, H. R., Chang, J. C., Chen, L., & Yeh, J. T. J. (2007). *Lumin.* 124, 333.
- [4] Liu, C. B., Li, J., Li, B., Hong, Z. R., Zhao, F. F., Liu, S. Y., & Li, W. L. (2007). *Chem. Phys. Lett.* 435, 54.
- [5] Xiang, N. J., Lee, T. H., Gong, M. L., Tong, K. L., So, S. K., & Leung, L. M. (2006). *Synth. Met.* 156, 270.
- [6] Mortimer, R. J. (1997). *Chem. Soc. Rev.* 26, 147.
- [7] Rosseinsky, D. R., & Mortimer, R. J. (2001). *Adv. Mater.* 13, 783.
- [8] Liu, S., Kurth, D. G., Mohwald, H., & Volkmer, D. (2002). *Adv. Mater.* 14, 225.
- [9] Zhang, T., Liu, S., Kurth, D. G., & Faul, C. F. J. (2009). *Adv. Funct. Mater.* 19, 642.
- [10] Maier, A., Rabindranath, A. R., & Tieke, B. (2009). *Adv. Mater.* 21, 959.
- [11] Yen, H.-J., & Liou, G.-S. (2010). *Org. Electron.* 11, 299.
- [12] Drobizhev, M., Karotki, A., Dzenis, A. R., Suo, Z. Y., Spangler, C. W. J. J. (2003). *Phys. Chem. B* 107, 7540.
- [13] Stampor, W., & Mroz, W. (2007). *Chem. Phys.* 331, 261.
- [14] Ichikawa, M., Hibino, K., Yokoyama, N., Miki, T., Koyama, T., & Taniguchi, Y. (2006). *Synth. Met.* 156, 1383.
- [15] Shirota, Y. J. (2005). *Mater. Chem.* 15, 75.
- [16] Katsuma, K., & Shirota, Y. (1998). *Adv. Mater.* 19, 223.
- [17] Hsiao, S.-H., Liou, G.-S., Kung, Y.-C., & Lee, Y.-J. (2010). *Eur. Polym. J.* 46, 1355.
- [18] Shirota, Y., & Kageyama, H. (2007). *Chem. Rev.* 107, 953.
- [19] Beaupre, S., Dumas, J., & Leclerc, M. (2006). *Chem. Mater.* 18, 4011.
- [20] Natera, J., Otero, L., Sereno, L., Fungo, F., Wang, N.-S., Tsai, Y.-M., Hwu, T.-Y., & Wong, K.-T. (2007). *Macromolecules* 40, 4456.
- [21] Liou, G.-S., Hsiao, S.-H., Ishida, M., Kakimoto, M., & Imai, Y. J. (2002). *Polym. Sci. Part A: Polym. Chem.* 40, 2810.
- [22] Liou, G.-S., & Lin, K.-H. J. (2009). *Polym. Sci. Part A: Polym. Chem.* 47, 1988.
- [23] Hsiao, S.-H., Liou, G.-S., & Wang, H.-M. J. (2009). *Polym. Sci. Part A: Polym. Chem.* 47, 2330.
- [24] Hsiao, S.-H., Liou, G.-S., Kung, Y.-C., & Yen, H.-J. (2008). *Macromolecules* 41, 2800.
- [25] Seo, E. T., Nelson, R. F., Fritsch, J. M., Marcoux, L. S., Leedy, D. W., & Adams, R. N. J. (1966). *Am. Chem. Soc.* 88, 3498.
- [26] Nelson, R. F., & Adams, R. N. J. (1968). *Am. Chem. Soc.* 90, 3925.
- [27] Zhao, H., Tanjutco, C., & Thayumanavan, S. (2001). *Tetrahedron Lett.* 42, 4421.
- [28] Lee, S. W., Lee, S. J., Hahm, S. G., Lee, T. J., Lee, B., Chae, B., Jung, J. C., Kim, S. B., & Ree, M. (2005). *Macromolecules* 38, 4331.
- [29] Lee, S. W., Kim, S. I., Lee, B., Kim, H. C., Chang, T., & Ree, M. (2003). *Langmuir* 19, 10381.
- [30] Chae, B., Lee, S. W., Lee, B., Choi, W., Kim, S. B., Jung, Y. M., & Ree, M. (2003). *Langmuir* 19, 9459.
- [31] Jung, E. Y., Chae, B., Kwon, S. J., Kim, H.-C., & Lee, S. W. (2012). *Solid State Ionics* 216, 95.
- [32] Chang, C.-W., Liou, G.-S., & Hsiao, S.-H. J. (2007). *Mater. Chem.* 17, 1007–1015.
- [33] Park, S., Kim, K., Lim, J. C., Kwon, W., Kim, D. M., & Ree, M. (2011). *Polymer* 52, 2170.