

## Electrosynthesis and Properties of Novel Electroactive Polymers from the Diamide or Diimide Derivatives with Terminal Triphenylamino Groups

Hui-Min Wang, Jun-Wen Lin, Sheng-Huei Hsiao\*

Department of Chemical Engineering and Biotechnology, National Taipei University of Technology

E-mail: [shhsiao@ntut.edu.tw](mailto:shhsiao@ntut.edu.tw)

### Introduction

Two diamide compounds TPABP-DA and TPASO2-DA and two diimide compounds TPA6F-DI and TPASO2-DI (Scheme 1) with triphenylamino end groups were synthesized. The imide ring-containing compounds can be electropolymerized into polymer films on the electrode surface in an electrolyte solution via the coupling reactions between TPA radical cations. In contrast, electro-oxidation of the diamide analogs produced stable TPA radical cations that did not undergo electropolymerization reactions. The electrochemical and electrochromic properties of the electrogenerated films from the diimide compounds are also investigated.

### Results and Discussion

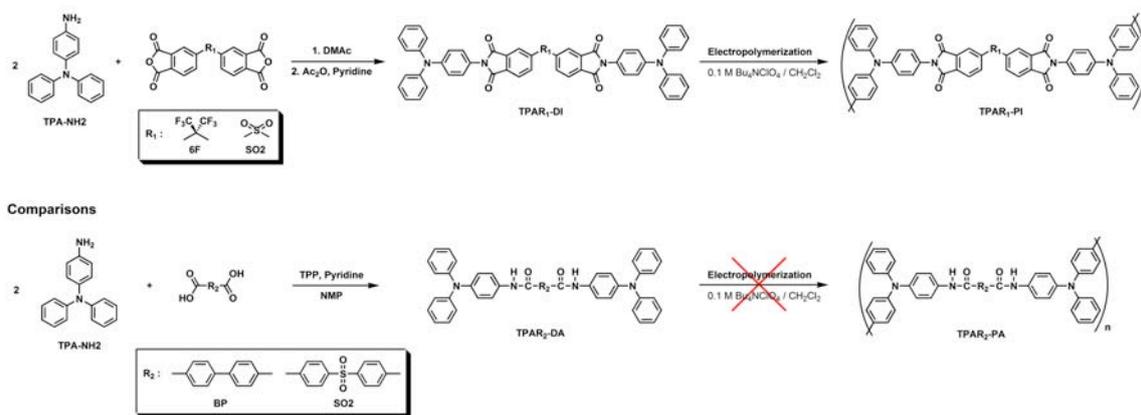
Figure 1 displays the successive cyclic voltammograms (CV) of 0.003 M TPA6F-DI and TPASO2-DI in 0.1 M Bu<sub>4</sub>NClO<sub>4</sub>/CH<sub>2</sub>Cl<sub>2</sub> solutions between 0 and 1.8 V at a potential scan rate of 150 mV/s. As the CV scan continued, polymer film was formed on the working electrode surface. The increase in the redox wave current densities implied that the amount of conducting polymers deposited on the electrode was increasing. The electrochemical properties of the analogues TPASO2-DA and TPABP-DA are completely different. Figure 2 displays their reversible electrochemical behavior, which indicates that the intermediates produced in the oxidation processes of these two compounds are stable on the time scale of the CV scan. Repetitive scans between 0 and 1.25 V produced almost the same patterns as those observed in the first scan, and no new peaks were detected under these experimental conditions. This reversible process suggests that the radical cations of the diamide compounds are more stable than those produced from the oxidation of the diimide analogues. Therefore, no polymer films were built on the electrode surface. As shown in Figure 3, the electrogenerated polymer film of TPASO2-DI showed only one oxidation peak, although two oxidation processes of the TBP moiety were expected. The half-wave potential ( $E_{1/2}$ ) of TPASO2-PI was read at 0.96 V. Furthermore, irreversible reduction waves for the formation of radical anions and dianions of the imide units in TPASO2-PI was observed in the negative side of the voltammograms at peak potentials  $E_{pc} = -1.54$  V. The typical UV-vis-NIR absorption spectra and electrochromic behavior of TPASO2-PI at various applied potentials are illustrated in Figure 4. The observed electronic absorption changes in the film of polymers at various potentials are fully reversible and are associated with strong color change; indeed, they even can be seen readily by the naked eye. Its color changes from pale yellowish (neutral state) to orange (semi-oxidized state) and blue (fully oxidized state). As a typical example, an electrochromic device based on polymer TPASO2-PI was fabricated. The spectral and color changes of the electrochromic device of polymer TPASO2-PI upon oxidation are illustrated in Figure 5. By the application of voltage to 1.9 V, the absorption bands at 487 and 717 nm gradually increased in intensity. Upon further oxidation at applied voltages to 2.1 V, a broadband at about 717 nm grew up continuously. When the voltage applied was increased (to a maximum of 2.4 V), the color changed from colorless (neutral) to orange (semi-oxidized) and blue (fully oxidized).

### Conclusions

Two series of novel TPA-encapped aromatic diamide and diimide monomers were synthesized from the condensation of 4-aminotriphenylamine with dicarboxylic acids and tetracarboxylic dianhydrides, respectively. Polymer films with tetraphenylbenzidine (TPB) segments were successfully electrodeposited onto the ITO electrode surface by electropolymerization of the diimide compounds in Bu<sub>4</sub>NClO<sub>4</sub>/CH<sub>2</sub>Cl<sub>2</sub>. However, no polymer films were built on the electrode surface using the diamide analogues. The resulting polymer films of the diimide compounds exhibited reversible oxidation redox couples due to oxidations of the TPB unit. The electrogenerated polymer films also revealed high electrochemical and electrochromic stability, with coloration change from a colorless neutral state to orange and blue oxidized forms. Thus, these film materials formed by the electrochemical polymerization of TPA-containing diimide monomers present a new entry to the polymeric electrochromics that may find potential application in the fabrication of electrochromic devices.

### References

1. P. M. S. Monk, R. J. Mortimer and D. R. Rosseinsky, *Electrochromism and Electrochromic Devices*, Cambridge University Press, Cambridge, UK, 2007.
2. E. T. Seo, R. F. Nelson, J. M. Fritsch, L. S. Marcoux, D. W. Leedy, R. N. Adams, *J. Am. Chem. Soc.*, **88**, 3498-3503(1966).
3. S.-H. Cheng, S.-H. Hsiao, T.-H. Su, G.-S. Liou, *Macromolecules*, **38**, 307-316(2005).
4. Y.-C. Kung, S.-H. Hsiao, *J. Mater. Chem.*, **21**, 1746-1754(2011).
5. H.-M. Wang, S.-H. Hsiao, *J. Polym. Sci. Part A: Polym. Chem.*, **49**, 337-351(2011).
6. H.-J. Yen, G.-S. Liou, *Polym. Chem.*, **3**, 255-264(2012).



Scheme 1. Synthesis and electropolymerization of the target monomers

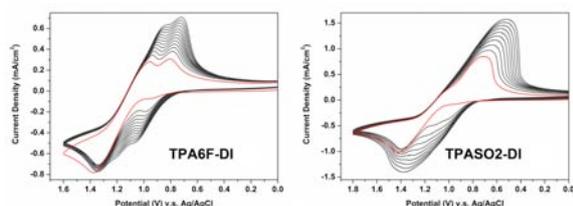


Figure 1. Repetitive cyclic voltammograms of 0.003 M TPA6F-DI and TPASO2-DI in 0.1 M Bu<sub>4</sub>NClO<sub>4</sub>/CH<sub>2</sub>Cl<sub>2</sub> solutions at a scan rate of 150 mV/s. The first CV curves were marked in red.

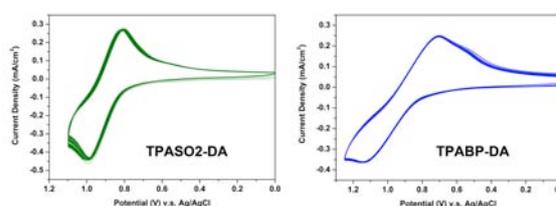


Figure 2. Repetitive cyclic voltammograms of 0.003 M TPASO2-DA and TPABP-DA in 0.1 M Bu<sub>4</sub>NClO<sub>4</sub>/CH<sub>2</sub>Cl<sub>2</sub> solutions at a scan rate of 150 mV/s.

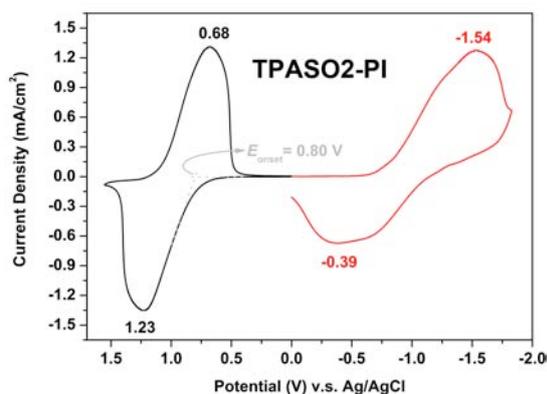


Figure 3. Cyclic voltammograms of the polymer TPASO2-PI films on the ITO-coated glass slide in 0.1 M Bu<sub>4</sub>NClO<sub>4</sub>/CH<sub>3</sub>CN (for anodic process) and DMF (for cathodic process) at a scan rate of 50 mV/s.

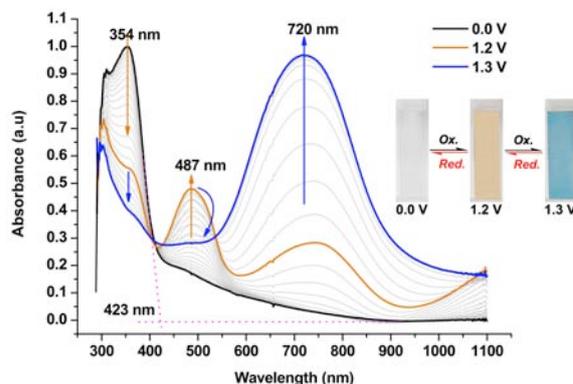


Figure 4. Spectroelectrochemistry and color changes of TPASO2-PI on an ITO-coated glass in 0.1 M Bu<sub>4</sub>NClO<sub>4</sub>/CH<sub>3</sub>CN at various applied potentials (v.s. Ag/AgCl).

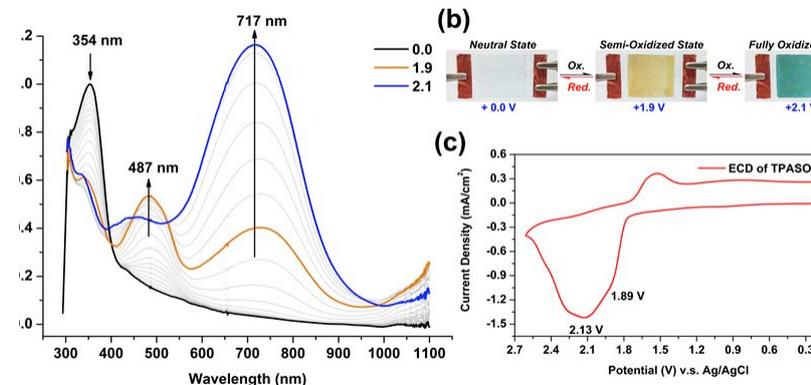


Figure 5. (a) Spectroelectrochemistry of the device, (b) photos of sandwich-type ITO-coated glass electrochromic cell, and (c) Cyclic voltammograms of polymer film in the electrochromic device based on polyimide TPASO2-PI.