

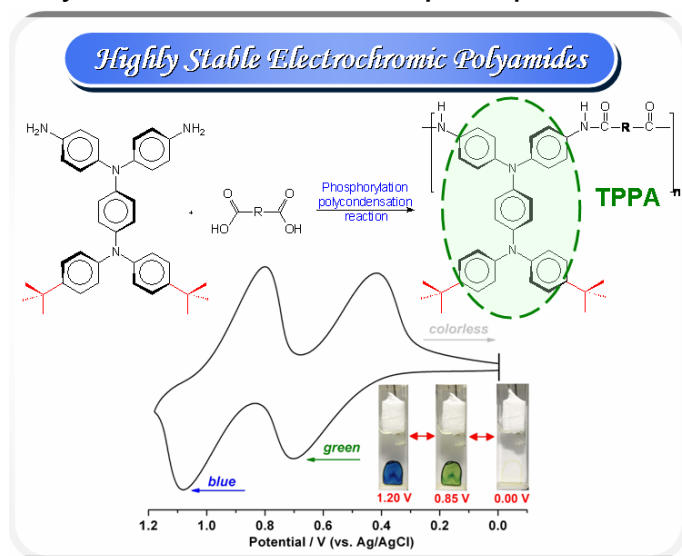
Electrochromically stable polyamides with *tert*-butyl-blocked *N,N,N',N'*-tetraphenyl-1,4-phenylenediamine units

Hui-Ming Wang,^a Sheng-Huei Hsiao,^{a*} Guey-Sheng Liou^b

^a Department of Chemical Engineering and Biotechnology, National Taipei University of Technology, 1 Chunghsiao East Road, Section 3, Taipei 10608, Taiwan;

^b Institute of Polymer Science and Engineering, National Taiwan University, 1 Roosevelt Road, Section 4, Taipei 10617, Taiwan
email: shhsiao@ntut.edu.tw

The redox property, electron-transfer process, and multi-coloring electrochromic behavior of the polymers bearing *N,N,N',N'*-tetraphenyl-1,4-phenylenediamine (TPPA) segments are interesting for opto-electronic applications.¹⁻⁴ A new triphenylamine-containing aromatic diamine monomer, *N,N*-bis(4-aminophenyl)-*N',N'*-bis(4-*tert*-butylphenyl)-1,4-phenylenediamine, was synthesized by a well-established synthetic procedure from readily available reagents. A novel family of electroactive polyamides with di-*tert*-butyl-substituted TPPA units was prepared *via* the phosphorylation polyamidation reactions of the newly synthesized diamine monomer with various aromatic or aliphatic dicarboxylic acids. All the polymers were amorphous with good solubility in many organic solvents, such as *N*-methyl-2-pyrrolidinone (NMP) and *N,N*-dimethylacetamide (DMAc), and could be solution-cast into tough and flexible polymer films. Cyclic voltammograms of the polyamide films cast onto an indium-tin oxide (ITO)-coated glass substrate exhibited two reversible oxidation redox couples at 0.57–0.60 V and 0.95–0.98 V *versus* Ag/AgCl in acetonitrile solution. Introduction of bulky *tert*-butyl substituents at the *para*-positions of pendent phenyl rings of the TPPA unit not only stabilizes arylaminium cation radicals and dications but also leads to good solubility and film-forming properties of the polyamides. After over 500 cyclic switches, the polymer films still exhibited excellent redox stability. The oxidation process was accompanied by coloration changes from a colorless or very slight yellow neutral state to a green semi-oxidized state and a blue fully oxidized state.



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Electrochromically Stable Polyamides with *tert*-Butyl-blocked *N,N,N',N'*-tetraphenyl-1,4-phenylenediamine Units

Hui-Ming Wang,^a Sheng-Huei Hsiao,^{a*} Guey-Sheng Liou^b

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E-mail: shhsiao@ntut.edu.tw



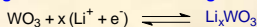
ABSTRACT

The redox property, electron-transfer process, and multi-coloring electrochromic behavior of the polymers bearing *N,N,N',N'*-tetraphenyl-1,4-phenylenediamine (TPPA) segments are interesting for optoelectronic applications.¹⁻⁴ A new triphenylamine-containing aromatic diamine monomer, *N,N*-bis(4-aminophenyl)-*N',N'*-bis(4-*tert*-butylphenyl)-1,4-phenylenediamine, was synthesized by a well-established synthetic procedure from readily available reagents. A novel family of electroactive polyamides with di-*tert*-butyl-substituted TPPA units was prepared via the phosphorylation/polyamidation reactions of the newly synthesized diamine monomer with various aromatic or aliphatic dicarboxylic acids. All the polymers were amorphous with good solubility in many organic solvents, such as *N*-methyl-2-pyrrolidone (NMP) and *N,N*-dimethylacetamide (DMAc), and could be solution-cast into tough and flexible polymer films. Cyclic voltammograms of the polyamide films cast onto an indium-tin oxide (ITO)-coated glass substrate exhibited two reversible oxidation redox couples at 0.57–0.60 V and 0.95–0.98 V versus Ag/AgCl in acetonitrile solution. Introduction of bulky *tert*-butyl substituents at the *para*-positions of pendent phenyl rings of the TPPA unit not only stabilizes arylaminium cation radicals and dication but also leads to good solubility and film-forming properties of the polyamides. After over 500 cyclic switches, the polymer films still exhibited excellent redox stability. The oxidation process was accompanied by coloration changes from a colorless or very slight yellow neutral state to a green semi-oxidized state and a blue fully oxidized state.

INTRODUCTION

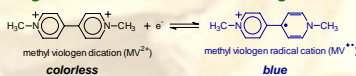
An electrochromic material is one where a reversible color change takes place upon reduction (gain of electrons) or oxidation (loss of electrons), on passage of electrical current after the application of an appropriate electrode potential.^{5,6}

Inorganic Electrochromes: Tungsten-oxide

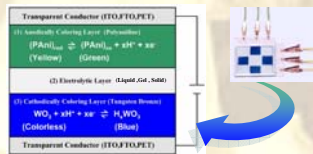


colorless blue

Organic Electrochromes: The Viologens

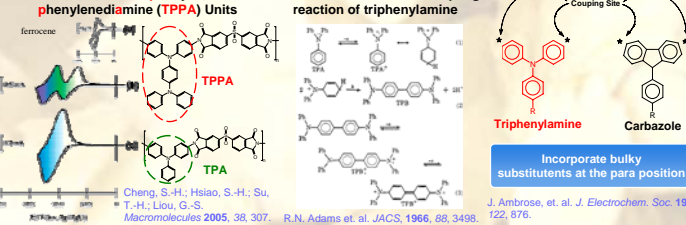


Electrochromic Devices

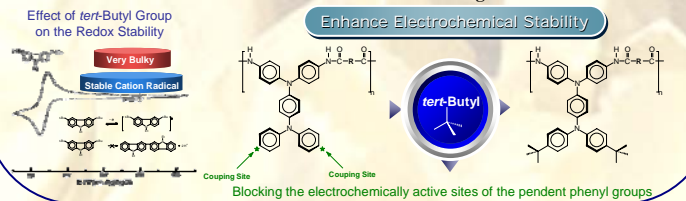


Literature Discussion

Mechanism of tail-to-tail coupling reaction of triphenylamine

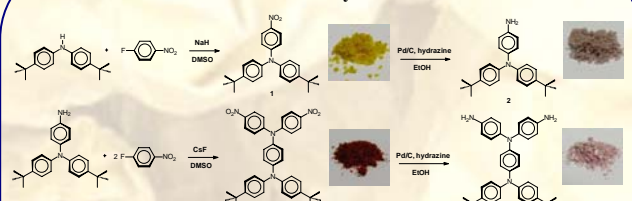


Motivation and Molecular Design

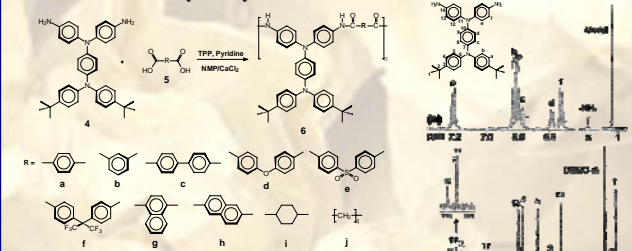


EXPERIMENTAL SECTION

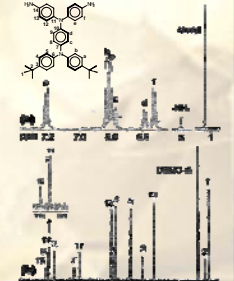
Monomer Synthesis



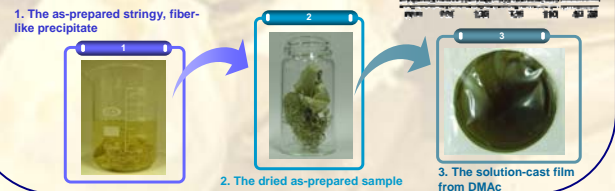
Polymer Synthesis



¹H and ¹³C NMR spectrum of diamine 4



Preparation of the Polyamide Films



RESULTS AND DISCUSSION

Inherent viscosity and Solubility of Polyamides

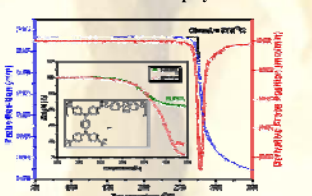
| Polymer | η_{inh}^a (dL/g) | Solubility in Various Solvents ^b | | | | | | |
|---------|-----------------------|---|------|-----|------|-----------------|-----|--|
| | | NMP | DMAc | DMF | DMSO | <i>m</i> -resol | THF | |
| 6a | 0.71 | ++ | ++ | ++ | ± | ++ | ± | |
| 6b | 0.35 | ++ | ++ | ++ | ± | ++ | ++ | |
| 6c | 0.71 | ++ | ++ | ++ | ± | ++ | ± | |
| 6d | 0.63 | ++ | ++ | ++ | ± | ++ | ± | |
| 6e | 0.48 | ++ | ++ | ++ | ± | ++ | ++ | |
| 6f | 0.51 | ++ | ++ | ++ | ± | ++ | ++ | |
| 6g | 0.29 | ++ | ++ | ++ | ± | ++ | ± | |
| 6h | 0.56 | ++ | ++ | ++ | ± | ++ | ± | |
| 6i | 0.60 | ++ | ++ | ++ | ± | ++ | ± | |
| 6j | 0.45 | ++ | ++ | ++ | ± | ++ | ± | |

Thermal properties of Polyamides^a

| Polymer | T_g at 5% weight loss (°C) ^b | | T_d at 10% weight loss (°C) ^c | | char yield (%) ^d | | |
|---------|---|-----|--|-----|-----------------------------|-----|----|
| | N_2 | Air | N_2 | Air | | | |
| 6a | 287 | 273 | 508 | 471 | 569 | 524 | 71 |
| 6b | 279 | 273 | 531 | 461 | 569 | 518 | 66 |
| 6c | 296 | 283 | 485 | 460 | 545 | 517 | 71 |
| 6d | 269 | 264 | 500 | 483 | 548 | 542 | 68 |
| 6e | 296 | 280 | 511 | 475 | 544 | 517 | 62 |
| 6f | 287 | 272 | 522 | 502 | 564 | 560 | 64 |
| 6g | 282 | 260 | 517 | 495 | 552 | 553 | 65 |
| 6h | 285 | 267 | 488 | 473 | 548 | 533 | 72 |
| 6i | 253 | 250 | 440 | 421 | 462 | 471 | 30 |
| 6j | 207 | 198 | 404 | 405 | 425 | 445 | 25 |

^a The polymer film samples were heated at 300 °C for 30 min before all the thermal analyses.^b Midpoint temperature of the baseline shift on the second DSC heating trace (rate = 20 °C/min) of the sample after quenching from 400 to 50 °C (rate = 200 °C/min) in nitrogen.^c Softening temperature measured by TMA with a constant applied load of 10 mN at a heating rate of 10 °C/min.^d Decomposition temperature at which a 5% or 10% weight loss was recorded by TGA at a heating rate of 20 °C/min and a gas flow rate of 20 mL/min. Residual weight percentage at 800 °C in nitrogen.

TMA and TGA curves of polyamide 6f

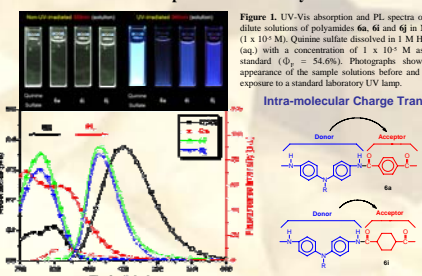


Optical and Electrochemical Properties of the Polyamides

| Polymer | In Solution | | As Film | | Oxidation Potential (V) ^b | | $E_{1/2}$ (eV) ^c | HOMO (eV) ^d | LUMO (eV) ^d | | | | |
|---------|---------------------------|------------------|---------------------------|------------------|--------------------------------------|--------|-----------------------------|------------------------|------------------------|------|------|------|------|
| | Abs. λ_{max} (nm) | Φ_{int} (%) | Abs. λ_{max} (nm) | Φ_{ext} (%) | First | Second | | | | | | | |
| 6a | 309 | 362 | 2.69 | 320 | 482 | 0.58 | 0.44 | 0.96 | 2.57 | 4.94 | 4.80 | 2.37 | 2.23 |
| 6b | 350 | 434 | 1.27 | 335 | 448 | 0.59 | 0.46 | 0.97 | 2.77 | 4.95 | 4.82 | 2.18 | 2.05 |
| 6c | 305 | 360 | 1.39 | 330 | 470 | 0.59 | 0.42 | 0.97 | 2.64 | 4.95 | 4.78 | 2.31 | 2.14 |
| 6d | 349 | 439 | 0.86 | 353 | 493 | 0.59 | 0.47 | 0.96 | 2.52 | 4.95 | 4.83 | 2.43 | 2.31 |
| 6e | 325 | 390 | 1.29 | 342 | 428 | 0.59 | 0.45 | 0.97 | 2.90 | 4.95 | 4.81 | 2.05 | 1.91 |
| 6f | 355 | 448 | 0.77 | 342 | 450 | 0.57 | 0.47 | 0.95 | 2.76 | 4.93 | 4.83 | 2.17 | 2.07 |
| 6g | 327 | 398 | 0.73 | 316 | 416 | 0.60 | 0.49 | 0.95 | 2.98 | 4.96 | 4.85 | 1.98 | 1.87 |
| 6h | 312 | 367 | 1.27 | 323 | 479 | 0.58 | 0.47 | 0.98 | 2.59 | 4.94 | 4.83 | 2.35 | 2.24 |
| 6i | 330 | 415 | 13.10 | 332 | 397 | 0.57 | 0.46 | 0.94 | 3.12 | 4.93 | 4.82 | 1.81 | 1.70 |
| 6j | 329 | 415 | 15.10 | 335 | 391 | 0.58 | 0.42 | 0.93 | 3.17 | 4.94 | 4.78 | 1.77 | 1.61 |
| 6'd | 347 | 461 | 0.28 | 347 | 415 | 0.57 | 0.44 | 0.95 | 2.99 | 4.93 | 4.80 | 1.94 | 1.81 |

^a Measured at a concentration of approximately 10⁻⁵ mol/L in NMP.^b The quantum yield in dilute solution was calculated in an integrating sphere with quartz sulfate as the standard ($\Phi_{int} = 54.6\%$).^c From cyclic voltammograms versus Ag/AgCl in CH₃CN. $E_{1/2}$: half-wave potential. ^d Energy gap = 1200 Abs. λ_{max} of the polymer film. ^e The HOMO energy levels were calculated from $E_{1/2}^{\text{ox}}$ and were referred to ferrocene (4.8 eV). ^f LUMO = HOMO - E_g .

UV and PL Spectra of Some Polyamides



REFERENCES

- Cheng, S.-H.; Hsiao, S.-H.; Su, T.-H.; Liou, G.-S. *Macromolecules* 2005, 38, 307.
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- Monk, P. M. S.; Mortimer, R. J.; Rossinsky, D. R. *Electrochromism: Fundamentals and Applications*, VCH, Weinheim, Germany, 1995.
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Repeated CV Scans of Polyamides 6d & 6'd

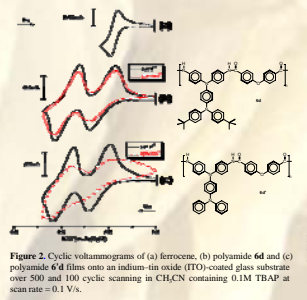


Figure 2. Cyclic voltammograms of (a) ferrocene, (b) polyamide 6d and (c) polyamide 6'd films onto an indium-tin oxide (ITO)-coated glass substrate over 500 and 100 cyclic scanning in CH₃CN containing 0.1M TBAP at scan rate = 0.1 V/s.

Spectroelectrochemistry of polyamide 6d

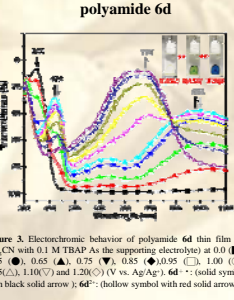
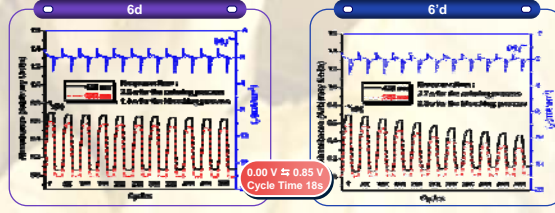


Figure 3. Electrochromic behavior of polyamide 6d thin film (on CHCN with 0.1 M TBAP as the supporting electrolyte) at 0.0 (○), 0.55 (●), 0.65 (▲), 0.75 (▼), 0.85 (◆), 0.95 (◇), 1.00 (□), 1.05(△), 1.10(▽) and 1.20(V) vs. Ag/AgCl. 6d^{•+} (solid symbol with black solid arrow); 6d²⁺ (hollow symbol with red solid arrow).

Electrochromic Stability of Polyamides 6d & 6'd



Coloration Efficiency of Polyamides 6d & 6'd

| Cycles ^a | ΔOD^b | | Q (mC/cm ²) ^c | | Decay (%) ^d | | | |
|---------------------|---------------|-------|--|------|------------------------|-----|------|-------|
| | 6d | 6'd | 6d | 6'd | 6d | 6'd | | |
| 1 | 0.581 | 0.584 | 2.69 | 2.88 | 216 | 203 | 0 | |
| 50 | 0.575 | 0.565 | 2.71 | 3.04 | 212 | 186 | 1.85 | 8.37 |
| 100 | 0.570 | 0.545 | 2.69 | 3.02 | 212 | 181 | 1.85 | 10.84 |
| 150 | 0.565 | 0.517 | 2.66 | 2.94 | 212 | 176 | 1.85 | 13.30 |
| 200 | 0.560 | 0.486 | 2.67 | 2.82 | 210 | 172 | 2.78 | 15.27 |
| 250 | 0.555 | 0.454 | 2.66 | 2.71 | 209 | 167 | 3.24 | 17.73 |
| 300 | 0.547 | 0.422 | 2.65 | 2.57 | 206 | 164 | 4.63 | 19.21 |
| 350 | 0.542 | 0.394 | 2.64 | 2.44 | 205 | 161 | 5.37 | 20.69 |
| 400 | 0.535 | 0.368 | 2.63 | 2.37 | 203 | 155 | 6.31 | 23.65 |
| 450 | 0.527 | 0.347 | 2.62 | 2.26 | 201 | 153 | 6.94 | 24.63 |
| 500 | 0.519 | 0.322 | 2.59 | 2.13 | 200 | 151 | 7.41 | 25.62 |

^a Times of cyclic scan by applying potential steps 0.00 to 0.85 V (vs. Ag/AgCl). ^b Optical density change at 983 nm for 6d and 910 nm for 6'd. ^c Integrated charge determined from the in situ experiments. ^d Coloration efficiency is derived from the equation: $\eta = \Delta OD/Q$. Decay of coloration efficiency after cyclic scans.