Synthesis and Electrochromic Properties of Novel Poly(ether-imide)s Derived from a New Triphenylamine-Bis(ether anhydride) Monomer

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Introduction

A new kind of triphenylamine (TPA)-containing bis(ether anhydride), 4,4'-bis(3,4-dicarboxyphenoxy)-triphenylamine dianhydride (**5**), was synthesized successfully. A series of novel poly(ether-imide)s **7a-7d** with TPA moieties in main chain were prepared from the resulting bis(ether anhydride) monomer with various aromatic diamines (**6a-6d**) via a conventional two-step method (**Scheme 1**). The three-dimensional TPA kinked structure is certainly responsible for lowing interchain interactions, thus improving the solubility of polyimides. Physical, thermal, electrochemical, and electrochromic properties of these poly(ether-imide)s were also investigated.

Results and Discussion

As shown in **Figure 1**, poly(ether imide) **7d** exhibited an amphoteric redox behavior because of the presence of both the electron-rich TPA moiety and the electron-deficient imide ring in its repeating unit. The anodic peak at 1.14 V is ascribed to the oxidation of the TPA units, and the cathodic peak at −1.34 V can be attributed to the formation of radical anion of the imide unit. When the potential was continuously cycled, we observed a progressive growth in all peak currents (**Figure 2**). This behavior suggests that the oxidative coupling of the radical cations of TPA units in the polymer chain which might produce a crosslinked polyimide **7d'** (**Scheme 2**). The UV-vis-NIR absorption spectra and electrochromic behavior of **7d'** at various applied potentials are illustrated in **Figure 3**. The film showed a multicolored electrochromism from colorless neutral state to yellow, and then blue oxidized states. In addition, we fabricated as preliminary investigations single layer electrochromic cells based on polyimide **7d'** (**Figure 4**). The polymer film is colorless in neutral form. When the voltage was increased (to a maximum of 1.29 V), the color changed to yellowish orange and blue due to electro-oxidation, the same as was already observed for the solution spectroelectrochemistry experiments. We believe that optimization could further improve the device performance and fully explore the potential of these electrochromic polyimides.

Conclusions

A new bis(ether anhydride) monomer containing the triphenylamine group, coded as **5**, was successfully synthesized and was polymerized with aromatic diamines to a series of electroactive poly(ether-imide)s. Most of these poly(ether-imide)s were easily soluble in polar organic solvents and could afford flexible and strong films with high thermal stability. The poly(ether imide)s could be further converted into a crosslinked film via oxidative coupling of their TPA radical cations in an electrochemical cell. The corsslinked poly(ether-mide) films exhibit reversible electrochemical oxidation accompanied by strong color changes that can be switched through modulation of the applied potential. Electrochemical and spectral results showed that these polymers can be employed as potential anodically coloring materials in the development of electrochromic devices.

References

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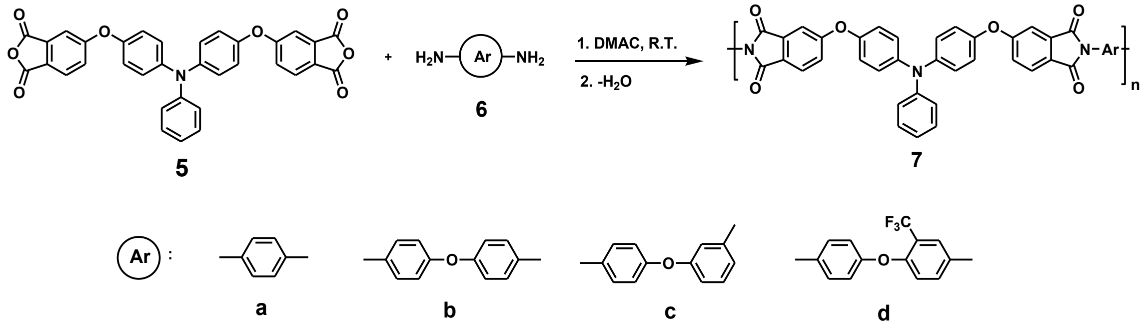


Scheme 1. Synthesis of poly(ether-imide)s

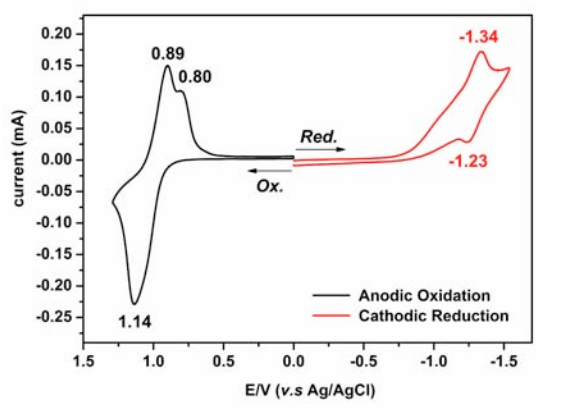


Figure 1. Cyclic voltammograms of the cast film of poly(ether-imide) **7d** on an ITO-coated glass substrate in 0.1 M Bu_4NClO_4/MeCN (for the anodic process) and DMF (for the cathodic process) solution at a scan rate of 50 and 100 mV/s, respectively.

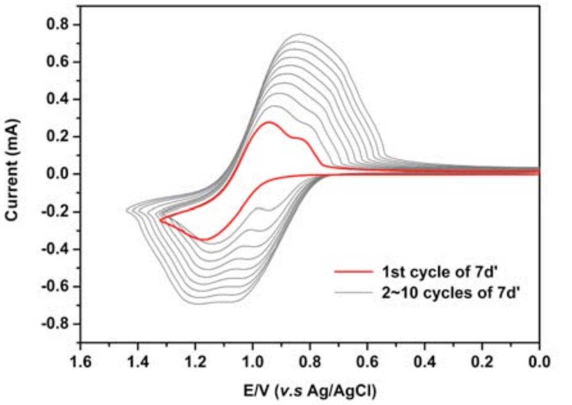
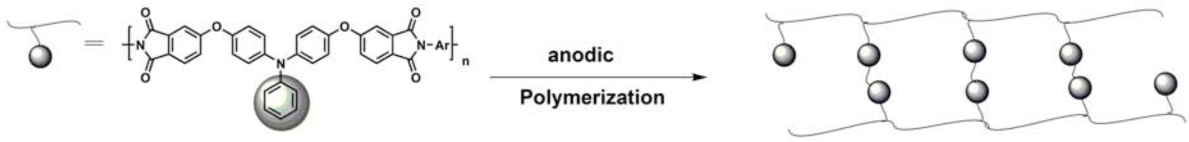


Figure 2. Repeated cyclic voltammograms of **7d** polymer between 0 and 1.45 V (form a cross-linked polymer coded with **7d'**) in 0.1 M Bu_4NClO_4/CH_2Cl_2 solution, with a scan rate of 150 mV/s.



Scheme 2. Electrochemical crosslinking of the poly(ether-imide) via the dimerization of TPA radical cations.

Table 1. Optical and electrochemical properties of polyimides

Code	Thin films (nm)		Oxidation Potential[a] (V)		Reduction Potential[b] (V)		Bandgap[c] (eV)		Energy Levels[d] (eV)	
	λ_{max}	λ_{onset}	E_{onset}	$E_{1/2}^{Ox}$	E_{onset}	$E_{1/2}^{Red}$	E_g^{opt}	E_g^{eg}	HOMO	LUMO
7a	298	557	0.89	1.01	-1.05	-1.35	2.23	2.36	5.37	3.01
7b	297	585	0.88	0.97	-1.03	-1.29	2.12	2.26	5.33	3.07
7c	302	647	0.87	0.94	-0.96	-1.28	1.92	2.22	5.30	3.08
7d	298	566	0.93	1.02	-1.03	-1.29	2.19	2.31	5.38	3.07
7'd	304	613	0.79	0.86, 0.96	-0.96	-1.24	2.79	2.20	5.32	3.12

[a] *Verus* Ag/AgCl in CH_3CN. $E_{1/2}$ = average potential of the redox couple peaks. [b] *Versus* Ag/AgCl in DMF. [c] Bandgaps calculated from absorption edge of the polymer films: $E_g^{opt} = 1{,}240 / \lambda_{onset.}, E_g^{ec}$, electrochemical band gap is derived from the difference between HOMO and LUMO values. [d] The HOMO and LUMO energy levels were calculated from $E_{1/2}^{ox}$ and $E_{1/2}^{red}$ values of CV curves and were referenced to ferrocene (4.8 eV relative to the vacuum energy level).

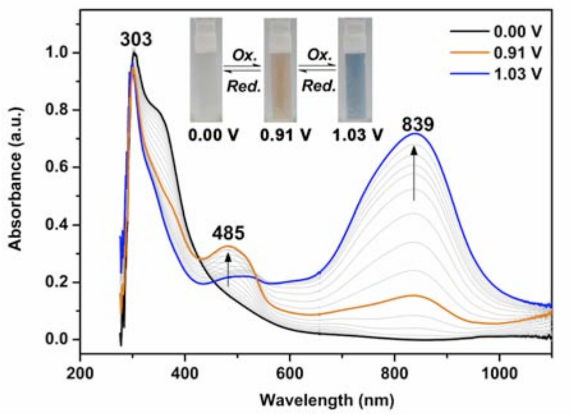


Figure 3. Spectroelectrochemistry of the polyimide **7d'** thin film on the ITO-coated glass substrate in 0.1 M Bu_4NClO_4/CH_3CN.

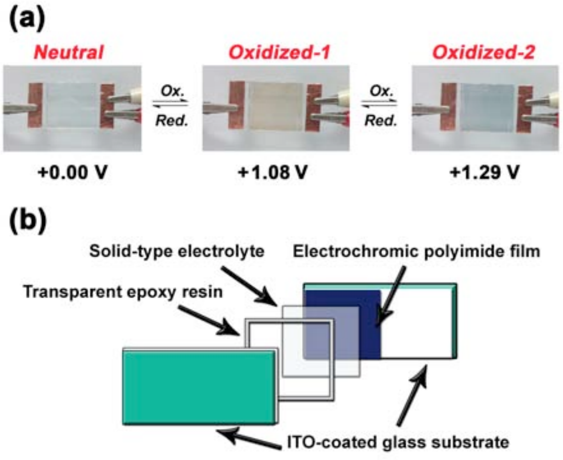


Figure 4. (a) Photos of single-layer ITO-coated glass electrochromic device, using polyimide **7d'** as active layer. (b) Schematic diagram of polyimide ECD sandwich cell.