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Electrochemical Characterization, Electrochroism, and Voltage-Dependent Fluorescence of Novel Perylene-Containing Polyimides

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ABSTRACT: Electrochemical and electrochromic properties of a series of cathodically coloring copolyimides containing a perylene diimide moiety are reported. Well-defined redox responses were obtained in solutions containing large cation electrolytes that can interact well with the reduced intermediates of perylene diimide. Reversible switch between red, blue, and violet colors corresponded well to the three redox states—neutral, radical anion, and dianion forms—of perylene diimide. The fluorescence intensity of these polyimides gradually decreased from the neutral state to the final reduced state.

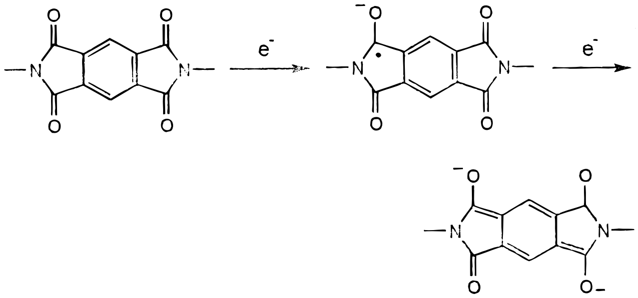
Introduction

Perylene derivatives, with their promising electroactive and photoactive properties, have attracted much attention for potential applications in organic molecular electronics.[1−3] Of particular interest is their use as light-emitting materials for the fabrication of electroluminescent display devices.[4−7] However, little attention was paid to the potential applications as electrochromic materials.

On the other hand, since the initial work by Haushalter and Krause,[8] the redox properties of some common imide compounds and polyimides have been described.[9,10] Owing to their electron affinity, imides can undergo electrochemical reduction. The redox mechanism associated with the reduction of pyromellitic diimide has been proposed (Scheme 1).[9a] The first redox couple corresponds to reduction of the neutral form to the radical anion, and the second redox couple relates to further reduction of the radical anion to the dianion state. It is known that the redox potentials can be greatly influenced by the aromatic imide structures.[10a] The potential of the first reduction shifts anodically as the π-conjugation between two imide groups increases, as seen for naphthalene, perylene, terrylene, and quaterrylene diimides.[11] Radical anions generated from naphthalene diimides are also shown to form p-stacked dimers and oligomers.[11b,c]

We previously reported the synthesis, characterization, and xerographic electrical properties of perylene-containing polyimides.[12] Recent studies on these polyimides have revealed that they are electrochromic, and their fluorescence properties are also electrochemically dependent. In this work, electrochemical and electrochromic properties of perylene-containing copolyimides are studied in detail.

Scheme 1



Experimental Section

Materials. Model perylene diimide and copolyimides (**a**−**d**) were synthesized as reported previously (Figure 1).[12] Dichloromethane, *m*-cresol, benzonitrile (PhCN), acetonitrile (MeCN), tetrahydrofuran (THF), *N*,*N*′-dimethylformamide (DMF), and pyridine (py) were purchased from Aldrich and used as received. Supporting electrolytes, lithium perchloride ($LiClO_4$), sodium perchloride ($NaClO_4$), potassium perchloride ($KClO_4$), tetra-*n*-butylammonium perchloride (n-Bu_4NClO_4), and tetraethylammonium perchloride (Et_4NClO_4) were obtained from Fluka, Aldrich, and Sigma and used without further purification. All chemicals were reagent grade unless otherwise stated.

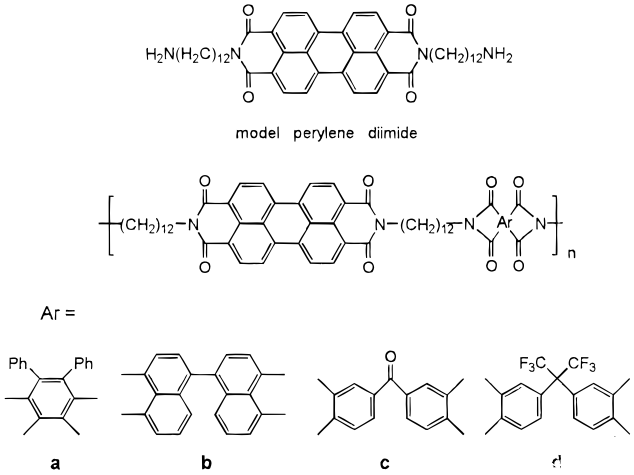


Figure 1. Structures of model perylene diimide and copolyimides **a**−**d**.

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Preparation of Polymer-Coated Electrodes. Model compound or copolyimide was added into *m*-cresol with stirring and heating at 80 °C, to give a solution of the concentration of 25 mg/mL. The solution was cast onto a working electrode, which was then baked at 100 °C for 10 min.

Instrumentation and Measurements. Electrochemical measurements were performed using a BAS 100B/W electrochemical workstation interfaced and monitored with a PC computer. The three-electrode system was employed throughout this work, which consists of a working electrode, a silver wire reference electrode, and a platinum wire auxiliary electrode. The BAS Pt disk electrode ($S = 0.018$ cm^2) as a working electrode, ITO glass electrode (0.5×2.5 cm^2), and gold mesh electrode (0.3×1.2 cm^2, 200 wires/cm, 80% transmittance) were used for cyclic voltammetry, UV–vis spectrophotometry and spectrofluorophotometry, and IR spectrophotometry, respectively. In all cases, the electrolyte solutions were deoxygenated with nitrogen for 10 min prior to use.

Spectroelectrochemical measurements were carried out by combining the electrochemical workstation with an appropriate spectrophotometer. UV–vis spectra were recorded on a Cary 3 Varian spectrophotometer using a quartz cuvette cell containing an ITO working electrode, a platinum auxiliary electrode, and a silver reference electrode. A blank ITO glass electrode with the electrolyte solution was used as reference. Infrared spectra were obtained on a Bomen Micheison 120 spectrophotometer using an optically transparent thin-layer electrochemical (OTTLE) cell as described elsewhere,[13] which consists of a transparent gold mesh working electrode, a platinum auxiliary electrode, and a silver reference electrode. Two pieces of NaCl plates were used as OTTLE cell windows. Before measuring, the background was recorded using the cell with electrolyte solution so that the results obtained for samples can be presented as transmittance difference spectra. Fluorescence emission spectra of polymer-coated ITO electrodes at different oxidation states were carried out using a Shimadzu RF-1501 spectrofluorophotometer. Similar to the cell setup as described elsewhere,[14] a four-face quartz cuvette was employed for the emission spectra. The polymer-coated ITO electrode was placed at an angle of 45° facing the incoming beam.

Results and Discussion

As shown in Figure 1, each copolyimide contains two different types of the imide units in the main chain. One is a perylene diimide, and the other is either a phthalimide or naphthalimide. A model compound is derived from perylenetetracarboxylic dianhydride.

Electrochemical Characterization. Cyclic voltammograms (CV) of the electrodes coated with model perylene diimide and perylene-containing copolyimides **a**–**d** were obtained in the electrolyte solution of 0.1 M Bu_4NClO_4 in acetonitrile. For comparison, the CV responses of model perylene diimide and copolyimide **a** are shown in Figure 2. The electrochemical data for all the copolyimides are summarized in Table 1. Polymers **a**–**d** are all electroactive. At the potential less negative than −0.90 V, two pairs of stable and reversible reduction/oxidation peaks, which are associated with the conjugated imide structures,[8–11] were obtained for model compound and all the four polymers. The similar peak position among the model and the polymers proves that the perylene imide group in the polymers is responsible for the electrochemical activity. The perylene imide is more easily reduced electrochemically than other non-perylene imides such as phthalimide. As shown in Figure 2A, the two pairs of redox peaks of the model compound are very close. However, for copolyimides **a**–**d** having a non-perylene imide group in the main chain, the difference between the two reduction peaks was enlarged significantly (Table 1). A similar observation was previously found for the polyimides derived from pyromellitic dianhydride (PMDA) and diamines,[9] where the diamine unit can affect the reduction potentials (especially the first reduction). The second reduction couple was around −0.70 V for the model compound and polymers **a**–**d**, while the first couple for these copolyimides shifted to more positive potential region. Among them, the first couple of copolyimide **a** shifted most anodically ($Ep_1 = -0.58$ V). Therefore, the best peak difference between two redox processes was obtained for copolyimide **a** ($Epc_1 - Epc_2 = 120$ mV). In addition, copolyimide **a** showed the best reversibility for both redox couples ($\Delta Ep_1 = 20$ mV, $\Delta Ep_2 = 40$ mV).

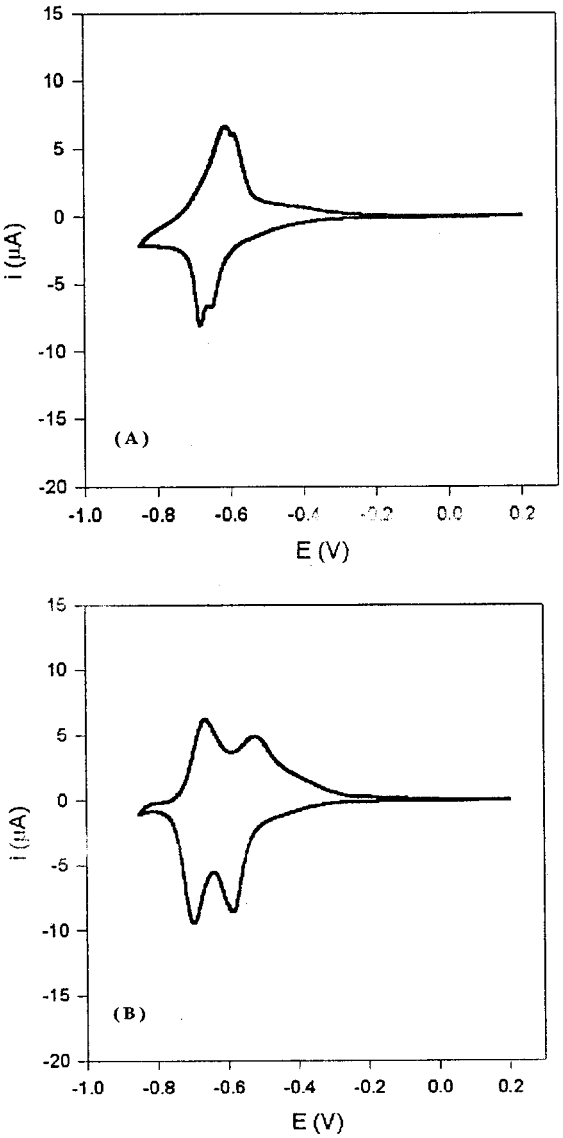

Figure 2. Cyclic voltammograms of model perylene diimide (A) and copolyimide **a** (B) coated on Pt electrode, in acetonitrile containing 0.1 M Bu_4NClO_4. Scan rate: 50 mV/s.

On further scanning the potential more negatively to −1.80 V, additional electrochemical reduction responses were observed for all the polymers (Table 1). This response could be contributed by the reduction of other non-perylene imides in the copolyimide. As expected, the model perylene diimide did not display an additional redox process at the more negative potential range, due to the absence of other imide groups. The redox responses generated in the more cathodic region are quite

Table 1. Electrochemical Data of Model Perylene Diimide and Copolyimides a−d

polymer	Epc_1/Epa_1 (V)	ΔEp_1 (mV)	Epc_2/Epa_2 (V)	ΔEp_2 (mV)	$Epc_1 - Epc_2$ (mV)	non-perylene imide Epc/Epa (V)
model	−0.64/−0.58	60	−0.68/−0.61	70	40	–
a	−0.58/−0.56	20	−0.70/−0.66	40	120	−1.49/–
b	−0.62/−0.56	60	−0.71/−0.64	70	90	−1.16/−1.11
c	−0.62/−0.58	40	−0.71/−0.64	70	90	−1.04/–; −1.41/–
d	−0.64/−0.61	30	−0.71/−0.64	70	70	−1.29/–

different for these copolyimides. In general, the phthalimide units in all cases except for copolyimide **b** produced only one irreversible reduction peak. The irreversibility is likely due to the fact that these phthalimide units lack extended π-conjugation. Copolyimide **b** displayed a reversible reduction peak at the most positive potential (−1.16 V), which is associated with the naphthalimide unit. There are two reduction peaks unrelated to the perylene imide for copolyimide **c**, due to reductions of the ketone and perylene moieties.

In-Situ IR Study. To confirm the redox process and assign the reduction peaks, in-situ IR spectra of model perylene diimide and copolyimides were recorded at different applied potentials. As shown in Figure 3A, in the neutral state, the carbonyl peaks of model perylene diimide are at 1696 and 1655 cm^{-1}, whereas the peaks observed at 1595 and 1578 cm^{-1} are assigned to the aromatic ring stretching modes. After being reduced at −0.65 V, the carbonyl peaks shifted to 1655 and 1610 cm^{-1} and the intensity also decreased sharply. Further reduction at −0.90 V caused the peaks to shift back to the high-energy region (1675 and 1622 cm^{-1}). Upon applying the more negative potential of −1.80 V, no further change was observed. IR responses could be reversibly switched between the neutral and reduced states (0 to −0.90 V). However, after being oxidized at an extremely positive potential (e.g., +2.20 V), the redox process was switchable due to the irreversible oxidation of the perylene moiety.[15,16]

In the case of copolyimide **a** (Figure 3B), besides the carbonyl peaks of the perylene diimide moiety (1696 and 1655 cm^{-1}), two additional peaks at 1770 and 1723 cm^{-1} should be assigned to the prehnitimide moiety presented in the polymer backbone. Upon reduction at −0.65 V, the carbonyl peaks of perylene diimide decreased sharply and shifted to 1660 and 1620 cm^{-1}, which is similar to the results observed for the model compound. However, the peaks associated with the prehnitimide moiety remained, suggesting that the prehnitimide unit is more difficult to reduce. At a potential of −0.90 V, the former two peaks shifted back to a high-frequency region (1667 and 1623 cm^{-1}), while those of the prehnitimide unit still stayed unchanged. At a more negative potential of −1.80 V, the prehnitimide unit can finally be reduced as indicated by the disappearance of the original bands at 1770 and 1723 cm^{-1}.

For copolyimide **b** (Figure 3C), two broad peaks centered at 1696 and 1660 cm^{-1} were observed, due to the overlap of the two types of the imide groups (perylene dimide and naphthalimide). In comparison with the model compound and copolyimide **a**, the peak intensity did not decrease sharply upon reduction at a potential equal to or less negative than −0.90 V. Thus, only perylene diimide can be reduced at a potential less than −0.90 V. At a potential of −1.80 V, reduction of the naphthalimide moiety occurred, and both carbonyl peaks decreased dramatically.

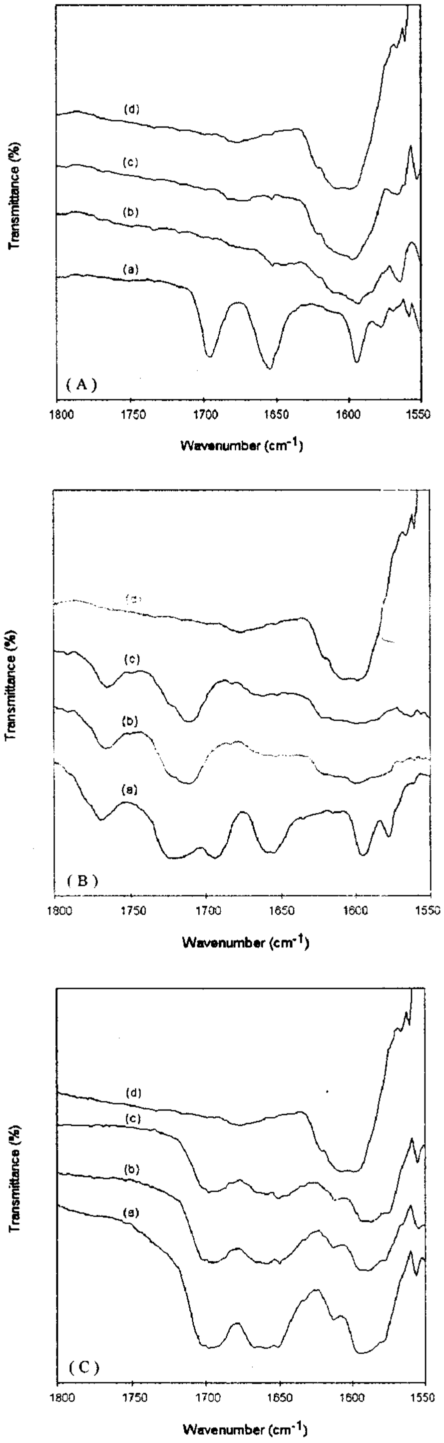

Figure 3. In situ IR spectra of model perylene diimide (A), copolyimide **a** (B), and copolyimide **b** (C) in an OTTLE cell (0.1 M Bu_4NClO_4 in acetonitrile). (a) Neutral, (b) −0.65 V, (c) −0.90 V, (d) −1.80 V.

Effect of Electrolytes and Solvents. Because of its unique electrochemical properties such as low peak potentials, large gap between two reduction peaks, and reversibility of redox process, copolyimide **a** was chosen for this study. In Bu_4NClO_4, the reduction peaks of

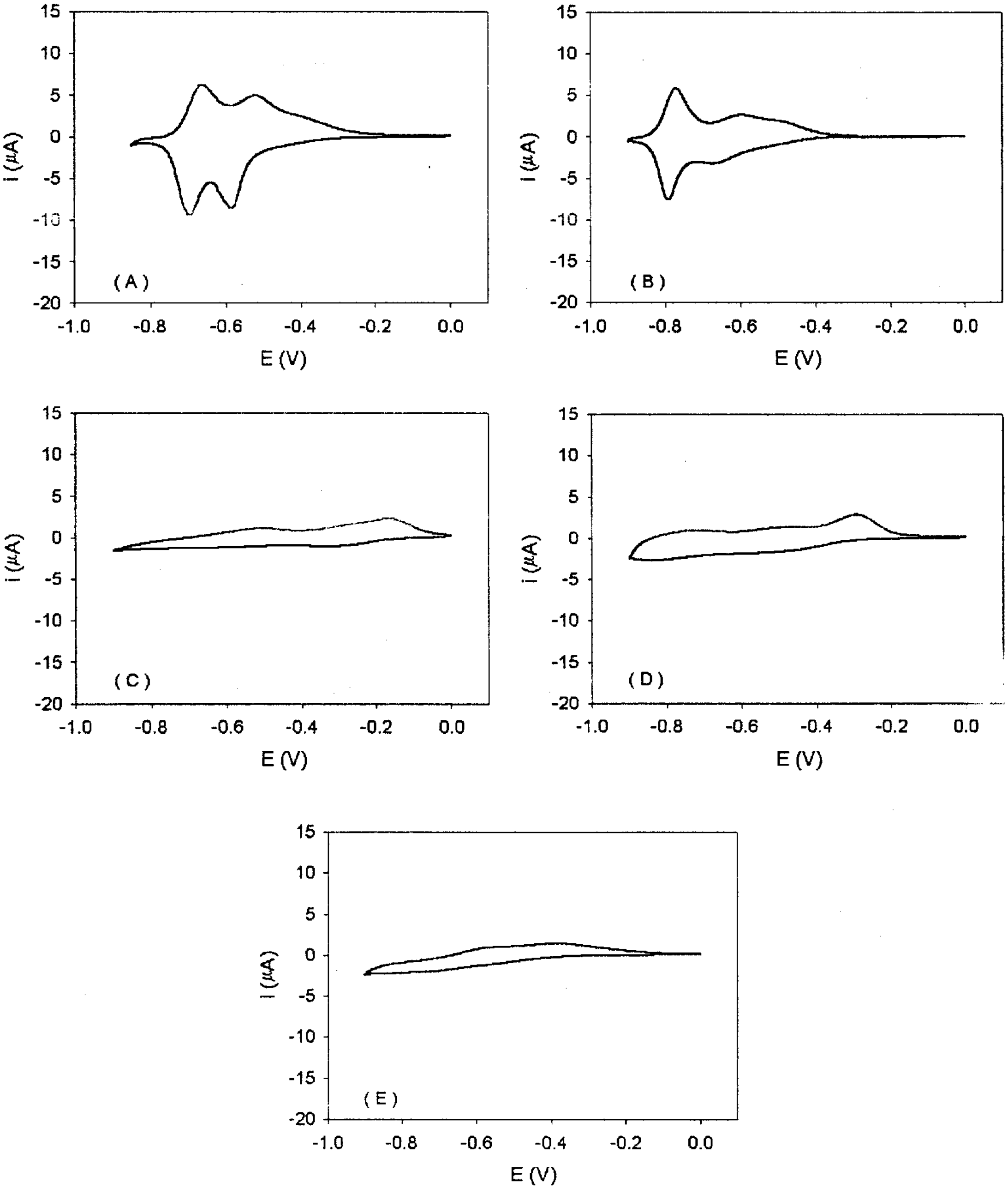

Figure 4. Cyclic voltammograms of copolyimide **a** coated on Pt electrode, in acetonitrile containing 0.1 M electrolyte. Scan rate: 50 mV/s. (A) Bu_4NClO_4, (B) Et_4NClO_4, (C) $LiClO_4$, (D) $NaClO_4$, (E) $KClO_4$.

copolyimide **a** shifted anodically with an increase of the electrolyte concentration between 0.01 and 1.0 M, indicating that a cation is inserted as a compensating counterion into the polymer film to preserve electroneutrality during the imide reduction.[17] The type of cation was found to be an important factor governing the electrochemical behavior of polymer film (Figure 4). Well-defined redox peaks were obtained in the electrolyte solutions containing organic cations (Bu_4N^+ and Et_4N^+), which indicates a stronger affinity between the cation and the reduced forms of imide. In Bu_4NClO_4 solution, the reduction peaks appeared at more positive potential (−0.68 V) than in Et_4NClO_4 (−0.81 V), whereas the responses observed in inorganic metal electrolytes such as $LiClO_4$, $NaClO_4$, and $KClO_4$ were rather ill defined. This result indicates that the solvophobic interactions between larger cations and imide anions are more dominant than the electrostatic interactions (ion pairing). Such a solvophobic interaction between larger cations and aromatic hydrocarbon radical anions[18,19] or C_{60} anions[20] has been demonstrated previously. In our case, this interaction was further confirmed by using a range of solvents with different electron-acceptor and -donor properties (Table 2).[21] Solvents with a higher donor ability should stabilize to a greater extent the imide anions, so that the imide reduction occurs at more positive potentials. Accordingly, the positive shift of the reduction peak potentials with the increase of Gutmann donor number was observed, except that the reduction potentials were more positive in THF and PhCN than in DMF and MeCN, respectively. It should be noted that polymer film coated on the electrode became soluble in PhCN, DMF, and

Table 2. Effect of Solvent on the Electrochemistry of Copolyimide a

solvent	DN[a]	AN[a]	Epc$_1$/Epa$_1$ (V)	ΔEp$_1$ (mV)	Epc$_2$/Epa$_2$ (V)	ΔEp$_2$ (mV)	Epc$_1$− Epc$_2$ (mV)
CH_2Cl_2	0.0	20.4	−0.64/−0.60	40	−0.75/−0.70	50	110
PhCN	11.9	15.5	−0.51/−0.43	80	−0.62/−0.59	30	110
MeCN	14.1	18.9	−0.58/−0.56	20	−0.70/−0.66	40	120
THF	20.0	8.0	−0.40/−0.28	120	−0.57/−0.45	120	170
DMF	26.6	16.0	−0.48/−0.40	80	−0.56/−0.54	20	80
py	33.1	14.2	−0.31/−0.26	50	−0.44/−0.41	30	130

[a] DN = Gutmann donor number. AN = Gutmann acceptor number.

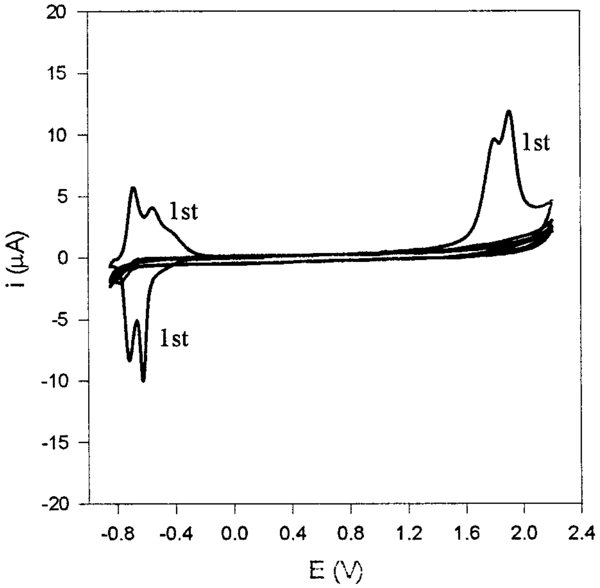

Figure 5. Continuous cyclic voltammograms of copolyimide **a** coated on Pt electrode, in acetonitrile containing 0.1 M Bu_4NClO_4. Scan rate: 50 mV/s. The first cycle started at +0.20 V cathodically.

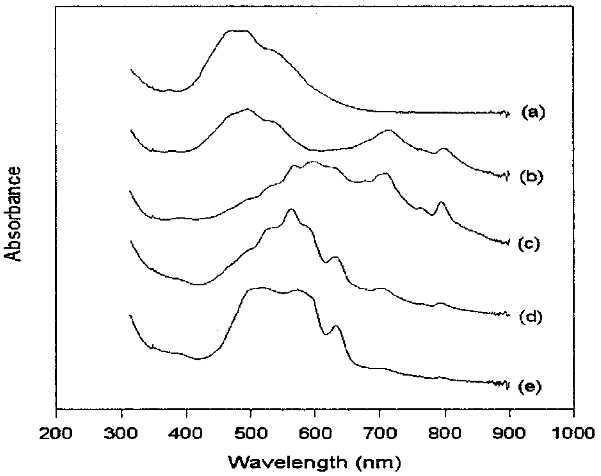

Figure 6. In-situ UV−vis spectra of copolyimide **a** coated on ITO glass electrode, in acetonitrile containing 0.1 M Bu_4NClO_4. (a) Neutral, (b) −0.55 V, (c) −0.65 V, (d) −0.90 V, (e) −1.80 V.

pyridine upon reduction. CV responses decreased sharply after the first potential scan and almost completely disappeared after four cycles. In contrast, the redox peaks are stable after many CV cycles in MeCN, CH_2Cl_2, and THF.

When the potential was scanned anodically to +2.20 V, an irreversible oxidation of the perylene moiety[15,16] was also observed for model diimide and four copolyimides. As shown in Figure 5, multiple cyclic voltammograms were run on copolyimide **a** by starting potential scan cathodically from +0.20 to −0.80 V. Then, the potential was reversed anodically to +2.20 V. The subsequent cycles were continuously performed between −0.80 and +2.20 V. In the first cycle, two pairs of reversible peaks were obtained at the negative potential range, which is the same as that shown in Figure 1. Once the potential was reversed to the positive potential range, two distinct irreversible oxidation peaks were found at +1.80 and +1.90 V. These two peaks should be attributed to the irreversible oxidation of perylene, corresponding to $Per \rightarrow Per^{+} \rightarrow Per^{2+}$.[15,16] After the perylene oxidation, the reversible reduction peaks in the negative potential region decreased gradually and disappeared finally after several cycles, suggesting that the formation of perylene cations hinders the insertion of cationic species from solution into the polymer film for the electrostatic neutralization during the reduction of imide. This phenomenon was observed for model diimide and copolyimides **a**−**d**. Keeping a potential less positive than +1.20 V can avoid the perylene oxidation and allows for reproducible and reversible redox cycles of the perylene diimide.

Electrochromic Behavior. The electrochromic properties of model compound and copolyimides **a**−**d** were investigated by recording the UV−vis spectra in situ under potentiostatic conditions. Color changes from the original red to blue then to violet upon reduction were observed for all compounds studied. As shown in Figure 6, once reduced to the radical anion form, the red film of copolyimide **a** turned blue. The original absorbance peaks at 480 and 540 nm decreased; at the same time peaks at 610, 715, and 800 nm appeared and increased gradually. Further reduction caused a decay of the peaks at longer wavelengths and appearance of the peaks at shorter wavelengths, accompanied by a color change from blue to violet. When applying a very cathodic potential of −1.80 V where the non-perylene imide can be reduced, the violet color of the polymer film did not change (Figure 6, spectra d and e). If an extremely anodic potential of +2.20 V was applied, due to the irreversible oxidation of the perylene moiety, the polymer film remained red and could not change its color under subsequent negative potentials. This observation is in good agreement with the results of cyclic voltammetric and IR responses, which again confirms that the coloration of copolyimides studied in this work is based on the redox processes of perylene diimide rather than non-perylene imide or the oxidation of perylene unit.

Potential-Dependent Fluorescence. Perylene has been often employed as a fluorescent material in device applcations.[14,22,23] Thus, the ability of switching the fluorescent property of the perylene-based polyimide **a** was investigated. Under excitation at 480 nm, the strongest fluorescent emission was obtained at 717 nm for polyimide **a** in the neutral state (Figure 7). Its fluorescence was found to be potential dependent. Upon reduction of the perylene imide groups, the emission intensity gradually decreased under the negative po-

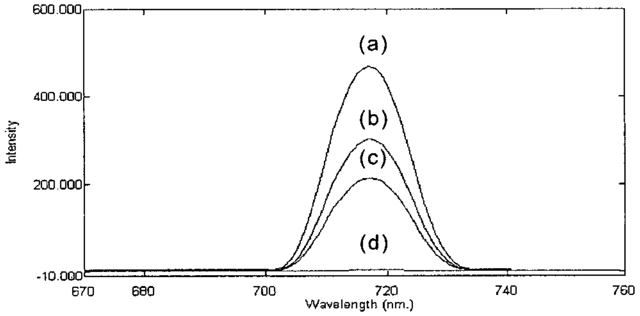

Figure 7. In-situ fluorescence spectra of copolyimide **a** coated on ITO glass electrode, in acetonitrile containing 0.1 M Bu$_4$NClO$_4$. λ_{ex} = 480 nm. (a) Neutral, (b) −0.55 V, (c) −0.65 V, (d) −0.90 V.

tentials. At a potential of −0.90 V, no emission can be seen (spectrum d, Figure 7). Thus, a reversible switch of the fluorescent emission between the two redox states of polyimide **a** can be realized. When being excited at other wavelengths (610, 715, or 800 nm) that correspond to the UV−vis absorption peaks of the reduced forms of copolyimide **a**, no apparent fluorescence was observed.

Conclusion

Novel perylene-containing polyimides are shown to be electroactive, electrochromic, and voltage-dependently fluorescent. Because of its extended π-conjugation, the perylene diimide unit behaved more electroactive and underwent an electrochemical reduction at less negative potentials, compared to the case of phthalimide and naphthalimide units. Larger electrolyte cations and good electron-donating solvents facilitate the electrochemical reduction of perylene diimide through the interactions with the reduced intermediates. The electrochromic responses relate to the reduction of perylene diimide in polyimides. The reversible color changes of polyimide films between red, blue, and violet correspond to the neutral, radical anion, and dianion forms of the perylene diimide unit. The fluorescent emission at the excitation wavelength of 480 nm can be tuned electrochemically or switched between two different redox states.

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