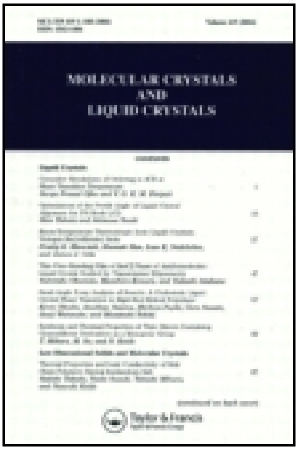

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Electrochemical Properties of Ionic Conjugated Polymer with Azobenzene Moieties

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To cite this article: Yeong-Soon Gal, Sung-Ho Jin, Kwon Taek Lim, Sung-Hoon Kim, Won Seok Lyoo, Chang-Jun Lee, Jong-Wook Park & Sang Youl Kim (2006): Electrochemical Properties of Ionic Conjugated Polymer with Azobenzene Moieties, Molecular Crystals and Liquid Crystals, 462:1, 189-195

To link to this article: http://dx.doi.org/10.1080/07370650601013153

Mol. Cryst. Liq. Cryst., Vol. 462, pp. 189–195, 2007
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/07370650601013153

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The electrochemical and electrooptical properties of an ionic conjugated polymer, poly[2-ethynyl-N-(p-cyanophenylazophenyl)oxyhexylpyridinium bromide](PCEPB) were studied. The cyclovoltamograms of this polymer exhibited the irreversible electrochemical behaviors between the doping and undoping peaks. The oxidation

This work was supported by grant No. RTI04-01-04 from the Regional Technology Innovation Program of the Ministry of Commerce, Industry and Energy (MOCIE).

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current density of PEPB versus the scan rate is approximately linear relationship in the range of $30\,mV/sec \sim 120\,mV/sec$. The exponent of scan rate, x value of PEPB, is found to be 0.6. The absorption spectrum starts around 800 nm and shows a strong absorption band at visible region due to the $\pi \rightarrow \pi^*$ interband transition of the polymer backbone, which is a characteristic peak of the conjugated polyene backbone system. The photoluminescence spectrum showed that the PL peak is located at 542 nm corresponding to the photon energy of 2.29 eV.

Keywords: conjugated polymer; cyclovoltamogram; 2-ethynylpyridine; photoluminescence; polyacetylene

INTRODUCTION

Conjugated organic materials are intensively studied mainly because of their interesting electrical and optical properties and, more importantly, their potential utility in electronic and photonic applications [1–5]. Polyelectrolytes are charged macromolecules containing a large number of ionizable or ionic groups. The polyelectrolytes include proteins, nucleic acids, pectins, polyacrylic acid, and polystyrene sulfonate. The conjugated polyacetylenic polyelectrolytes such as poly (propiolic salt)s [6], triethylammonium salt of poly(6-bromo-1-hexyne) [7], and poly(ethynylpyridine)s [8,9] were known. In 1991, Blumstein *et al.* prepared very interesting ionic polyacetylenes through the activated polymerization of ethynylpyridines with alkyl halides [10]. We have also reported the preparation of various ionic conjugated polymers having different functionalities [11–17]. Due to their extensive conjugation and ionic nature, these ionic polyacetylenes have potentials as materials for mixed ionic and electronic conductivity, energy storage devices such as batteries, permselective membrane, light-emitting devices [1,10].

Azobenzene photochemistry is a fascinating area of investigation, on one hand, because it is fairly well known [18], and on the other hand because it has produced and continues to reveal completely unexpected phenomena, some of them still explained. When the azobenzene group is incorporated into polymer, its photoisomerization can have a wide range of unexpected possible consequences [19].

In our previous paper, we reported the synthesis of a new ionic conjugated polymer with azobenzene moieties by the activated polymerization of 2-ethynylpyridine with the corresponding alkyl bromide, and the characterization of the resulting polymers [20]. Now we report on the electrochemical properties of the resulting poly[2-ethynyl-N-(*p*-cyanophenylazophenyl)oxyhexyl pyridinium bromide] (PCEPB).

EXPERIMENTAL

PCEPB was prepared by the activated polymerization of 2-ethynylpyridine with 4-[4-(6-bromohexyloxy)phenylazo]benzonitrile without any additional initiator or catalyst in DMF solvent as described elsewhere [20]. The polymer yield was 79%. This polymer was completely soluble in organic solvents such as DMF, DMSO, and NMP. The instrumental analyses on the polymer structure indicated that the present polymer have a conjugated backbone system with the designed azobenzene moieties.

The optical absorption spectra were measured by a HP 8453 UV-Visible Spectrophotometer. The photoluminescence spectra were obtained by Perkin Elmer luminescence spectrometer LS55 (Xenon flash tube) utilizing a lock-in amplifier system with a chopping frequency of 150 Hz. Electrochemical measurements were carried out with a Potentionstat/Galvanostat Model 273A (Princeton Applied Research). To examine electrochemical properties, polymer solution was prepared and the electrochemical measurements were performed under 0.1 M tetrabutylammonium tetrafluoroborate solution containing acetonitrile. ITO, Ag/$AgNO_3$ and platinum wire were used as a working, reference and counter electrode, respectively.

RESULTS AND DISCUSSION

The electro-optical properties of PCEPB (Fig. 1) were measured and discussed. Figure 2 shows the UV-Visible and photoluminescence (PL) spectra of PCEPB solution (0.1 wt.%, DMF). In our previous paper [21], we had reported the PL spectrum of poly(2-ethynylpyridinium bromide) with LC moieties, it showed 542 nm PL maximum value at excitation wavelength of 470 nm. PL spectrum could be changed by excited wavelength of 365 nm because of photoisomerization, therefore we evaluated PL maximum value with excitation wavelength of 470 nm. PCEPB showed characteristic UV-Visible absorption

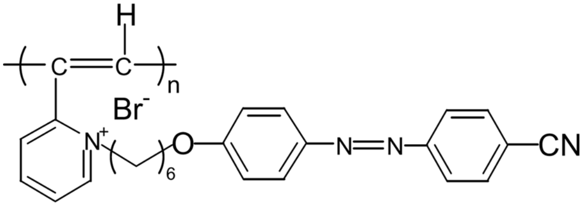


FIGURE 1 Chemical structure of PCEPB.

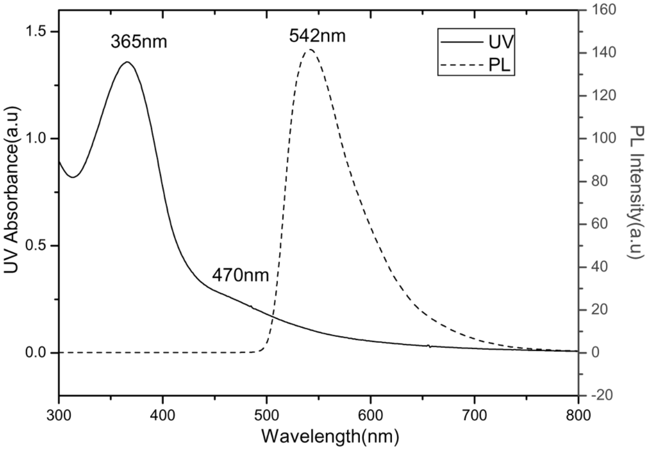


FIGURE 2 Optical absorption and photoluminescence spectra of PCEPB polymer solution.

band at 365 nm and yellowish green PL spectrum at 542 nm corresponding to the photon energy of 2.29 eV.

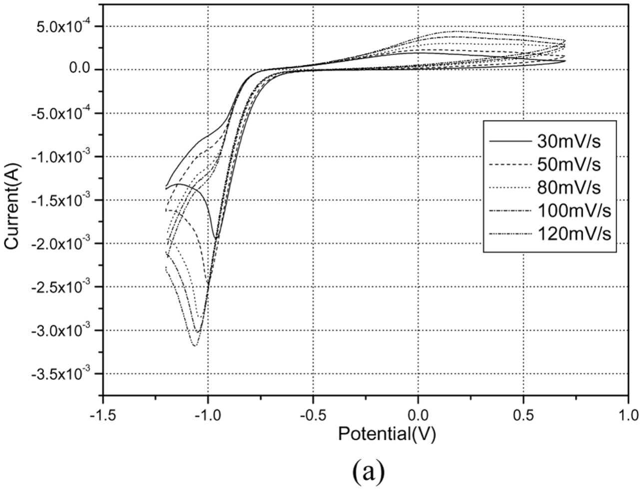
To investigate the electrochemical kinetic behavior, the measured cyclic voltammograms (CV) of PCEPB with the various scan rates (30 mV/s ~ 120 mV/s) are shown in Figure 3(a). The solution could be stirred during CV experiment for getting more accurate CV result, but we checked electrochemical property without stirring because polymer solution was well homogenized. The peak potentials are gradually shifted to higher potentials as the scan rate is increased. Also we have observed very stable cyclic voltammograms of PCEPB from the consecutive scan (up to 30 cycles) in Figure 3(b), which means that this material has relatively stable redox process.

In Figure 3, the oxidation of PCEPB occurred at 0.086 V (vs. $Ag/AgNO_3$), where vinylene unit of conjugated polymer backbone might be oxidized in the scan. PCEPB also shows the irreversible reduction at -1.01 V. The redox current value was gradually increased as the scan rate was increased. This result suggests that the electrochemical process of PCEPB is reproducible in the potential range of $-1.2 \sim 0.7$ V vs. $Ag/AgNO_3$.

It has been reported that the relationship between the redox peak current and the scan rate can be expressed as a power law type as follows [22,23].

$$i_{\mathrm{p,a}} = k\,v^{x} \tag{1}$$

$$\mathrm{Log}\, i_{\mathrm{p,a}} = \log k + \mathrm{x} \log v \tag{2}$$



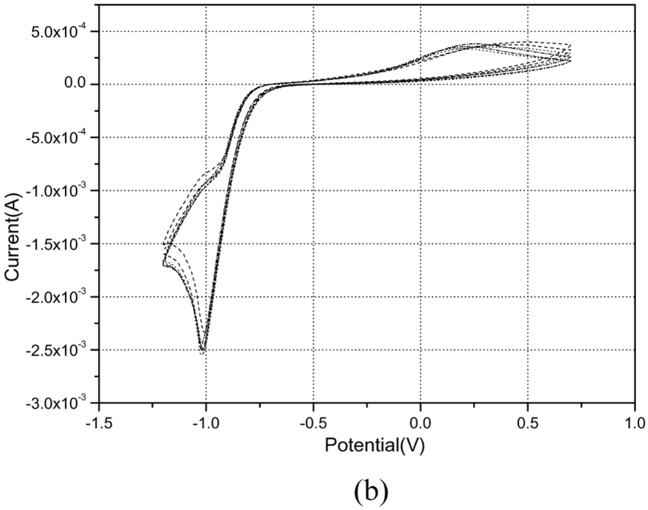


FIGURE 3 Cyclic voltammograms of PCEPB [0.1 M (n-Bu)$_4$NBF$_4$/DMF] with various scan rates (a) 30 mV/sec ~ 120 mV/sec and consecutive 30 scans (b) at 100 mV/s.

where $i_{\mathrm{p,a}}$ = oxidation peak current density, v = scan rate, k = proportional constant, and x = exponent of scan rate.

Assuming that electrode kinetics satisfies Eq. (1), the electrochemical redox reaction on the electrode is controlled by either the electron transfer process, where x = 1, or the reactant diffusion process, where x = 0.5 [20,22]. Relations satisfying Eq. (2) between the oxidation current

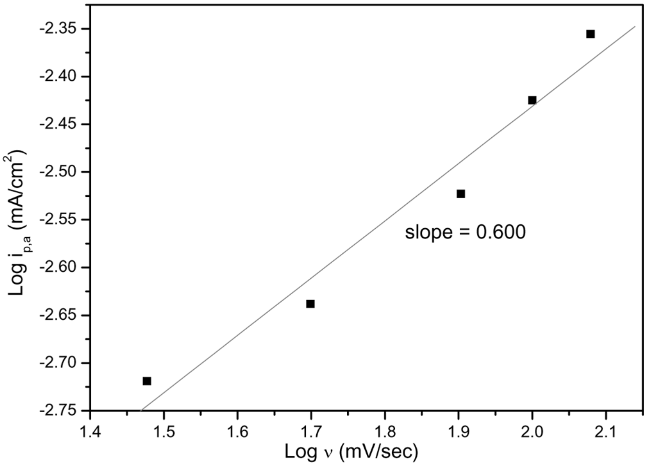


FIGURE 4 Plot of $\log i_{\mathrm{p,a}}$ vs. $\log v$ for PCEPB.

density ($\log i_{\mathrm{p,a}}$) and the scan rate ($\log v$) are shown in Figure 4. The oxidation current density of PCEPB versus the scan rate is approximately linear relationship in the range of 30 mV/sec ~ 120 mV/sec. The exponent of scan rate, x value of PEPB, is found to be 0.6. This value means that the kinetics of the redox process is almost controlled by the diffusion process [22–24].

CONCLUSIONS

The photoluminescence (PL) spectra of PCEPB showed that the photoluminescence peak is located at 542 nm corresponding to the photon energy of 2.29 eV. The cyclovoltamograms of the polymer exhibited the irreversible electrochemical behaviors between the doping and undoping peaks. It was found that the kinetics of the redox process of PCEPB is almost controlled by the diffusion process from the experiment of the oxidation current density of PCEPB versus the scan rate.

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