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Electrochemical Properties of a Self-Dopable Ionic Conjugated Polymer: Poly[2-ethynyl-N-(4-sulfobutyl)pyridinium betaine]

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The electrochemical properties of a self-dopable conjugated polymer, poly[2-ethynyl-N-(4-sulfobutyl)pyridinium betaine] (PESPB) were studied. PESPB was prepared by the polymerization of 2-ethynylpyridine with the ring-opening of 1,4-butanesultone in high yield. The cyclovoltamograms of this polymer exhibited reversible electrochemical behaviors between the doping and undoping peaks. The kinetics of the redox process of this polymer was found that it is almost controlled by the diffusion process from the experiment of the oxidation current density of polymer versus the scan rate. The photoluminescence (PL) spectra of polymer showed that the photoluminescence peak is located at 511 nm, corresponding to a photon energy of 2.43 eV.

Keywords: 2-ethynylpyridine; conjugated polymer; cyclic voltammogram; ion-exchange reaction; photoluminescence; polyacetylene

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INTRODUCTION

The polymers having a conjugated backbone shows such unique properties as electrical conductivity, paramagnetism, migration and transfer of energy, color, and chemical reactivity and complex formation ability [1–5].

The driving force on self-doped polymeric materials has been to improve the processibility in aqueous media, to increase the speed of electrochromic switching, and to achieve the increased charge storage performance of polymer-based batteries [6]. The concept of self-doping in conjugated polymers was introduced by Wudl *et al.* [7]. In self-n-doped polymers, cationic sites acts as dopant and are incorporated into the polymer, where the monomer contained a covalently attached ionizable, negatively charged, functional group acting as s stable/immobile dopant anion [6,7]. The cyclopolymerization of dipropargyl monomers carrying an ionic nature is a facile synthesis method of self-doped conjugated ionic polymers. A number of dipropargyl quaternary ammonium salt was polymerized to yield the unusual conjugated polymeric materials [8–10]. The potential counterions are ionically bound to the polymer. Dihexyldipropargylammonium salts were firstly polymerized by $MoCl_5$-$EtAlCl_2$ catalyst systems to give the corresponding conjugated polymers in high yields [8]. A similar water-soluble conjugated polymer from the polymer reaction of poly(N-hexyldipropargylamine) by using methyl trifluoromethanesulfonate was reported at the same time [7]. The precursor polymer, poly(dipropargylhexylamine), was obtained via a ring-forming polymerization of the corresponding monomer using a Schrock catalyst. Treatment of this polymer with methyl trifluoromethanesulfonate in methylene chloride affords the poly(dipropargyl-N-hexyl-N-methylammonium triflate) in 92% yield.

A new class of ionic polyacetylenes have been prepared through the activated polymerization of ethynylpyridines with alkyl halides [11–15]. In recent years, we also reported a facile synthesis of new self-dopable ionic conjugated polymer, poly[2-ethynyl-N-(4-sulfobutyl)-pyridinium betains] [PESPB], by the activation polymerization of 2-ethynylpyridine with the ring-opening of 1,4-butanesultone [16].

In this paper, we report the electrochemical properties of a self-dopable conjugated polymer (PESPB). And also we deal with the optical absorption and photoluminescence properties of PESPB.

EXPERIMENTAL

2-Ethynylpyridine (Aldrich Chemicals, 98%) was vacuum distilled after drying with CaH_2 (85°C/12 mmHg). 1,4-Butane sultone (Aldrich

Chemicals, 99+%) was used as received. The analytical grade solvents were dried with an appropriate drying agent and distilled. PESPB was prepared by the direct polymerization of 2-ethynylpyridine with 1,4-butanesultone without any additional initiator or catalyst in 82% yield [16]. 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, the polymer solution was prepared and the electrochemical measurements were performed under 0.1 M tetrabutylammonium tetrafluoroborate solution containing DMF. ITO, $Ag/AgNO_3$ and platinum wire were used as a working, reference and counter electrode, respectively.

RESULTS AND DISCUSSION

In order to synthesize an ionic conjugated polymer with sulfobetaine moieties, we used the Blumstein method, a very facile synthetic method of conjugated ionic polymer by using ethynylpyridines and alkyl halides [12,13]. The activated acetylenic groups of N-substituted-2-ethynylpyridinium salt were found to be susceptible to the linear polymerization, yielding the ionic conjugated polymer systems [13]. PESPB was prepared by the activated polymerization of 2-ethynylpyridine by using 1,4-butanesultone in DMF without any additional initiator or catalyst.

The initial mixture of 2-ethynylpyridine and 1,4-butanesultone was heated at the elevated temperature (130°C). As the reaction proceeded, the color of reaction mixture was changed from the light brown of the initial mixture into viscous dark red solution. After the precipitation and drying, the black polymer powder was obtained in 82% yield. The inherent viscosity of PESPB was 0.13 dL/g. The polymerization behaviors were found to be very similar with that of the polymerization reaction of 2-ethynylpyridine by using 2-sulfobenzoic acid cyclic anhydride [17].

The chemical structure of PESPB is depicted in Figure 1.

The electro-optical and electrochemical properties of PESPB were studied by UV-visible and photoluminescence (PL) spectroscopies and cyclic voltammograms (CV). Figure 2 shows the UV-visible and photoluminescence spectra of PESPB solution (0.1 wt.%, DMF). In our previous papers [18,19], we had reported PL spectra of poly(2-ethynyl-N-propagyl-pyridinium bromide) and poly(2-ethynylpyridinium bromide) having a simple N-hexyl side chain, they showed 708 and 603 nm PL maximum

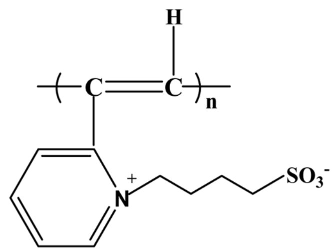


FIGURE 1 The polymer structure of PESPB.

values at each excitation wavelength of UV maximum value. We believe that the bulkiness of substituent causes some effect to electro-optical property of conjugated polyene. PESPB showed characteristic UV-visible absorption maximum value at 389 nm and green PL spectrum at 511 nm, corresponding to a photon energy of 2.43 eV. The chemical structure of PESPB is similar with that of poly(2-ethynylpyridinium bromide) having a simple N-hexyl side chain, but it showed blue-shifted PL maximum value such as from 603 to 511 nm. It accounts that the anion of SO_3^- in polymer side chain seems to restrict the π–π^* interband transition, which may be due to the steric hinderance between the bulky pendant molecular groups in the present polymer.

As shown in Figure 3, we investigated the electrochemical kinetic behavior through the cyclic voltammograms of PESPB solution with

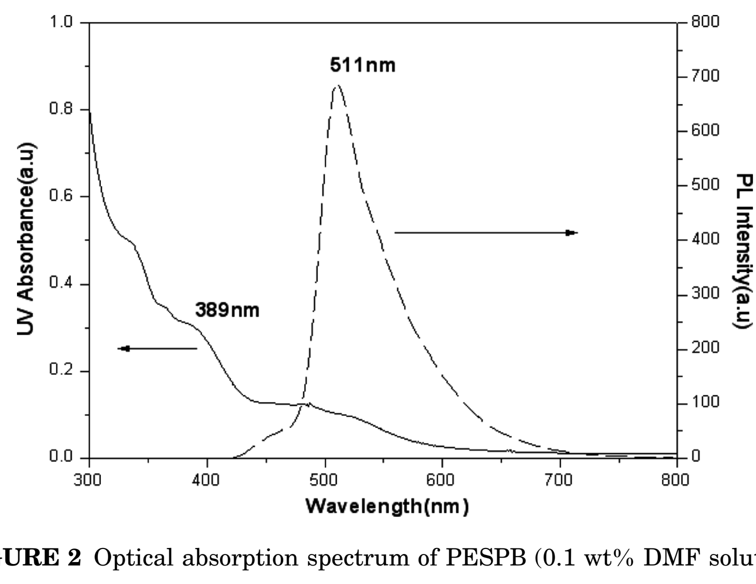
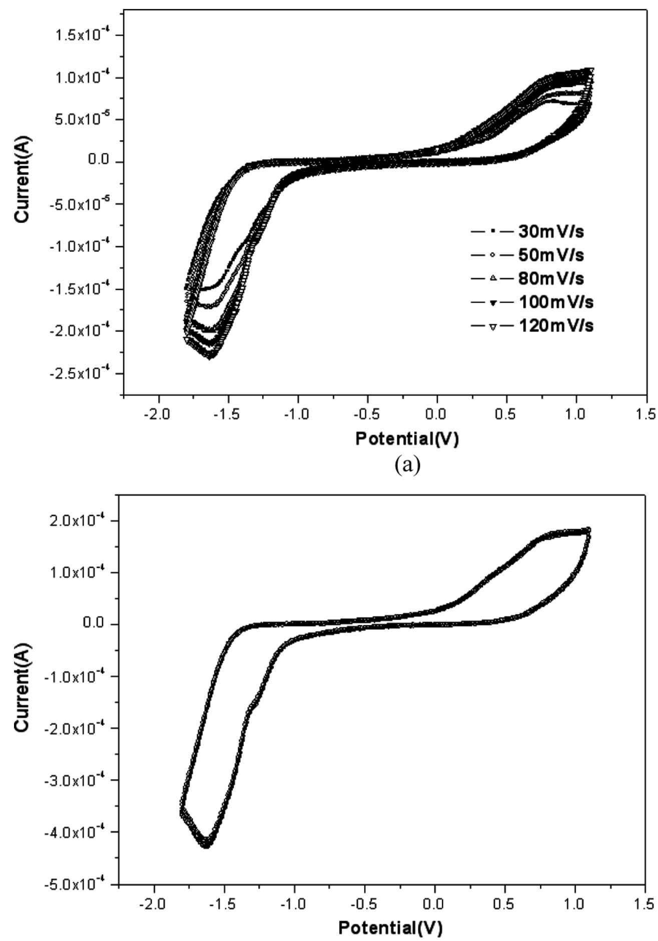


FIGURE 2 Optical absorption spectrum of PESPB (0.1 wt% DMF solution).



(b)

FIGURE 3 Cyclic voltammograms of PESPB [0.1 M $(n\text{-}Bu)_4NBF_4$/DMF] with various scan rates 30 ~ 120 mV/sec (a) and consecutive 30 scans under 100 mV/s (b).

various scan rates (30 ~ 120 mV/s). The peak potentials are very slightly shifted to higher potentials as the scan rate was increased. In addition, we have observed very stable cyclic voltammograms of PESPB from the consecutive scan (up to 30 cycles), which means that this material has a stable redox process. In Figure 3, the oxidation of PESPB occurred at 0.07 V (*vs* $Ag/AgNO_3$), where the vinylene unit of the conjugated polymer backbone could be oxidized in the scan. PESPB also shows irreversible reduction at −1.11 V. The redox

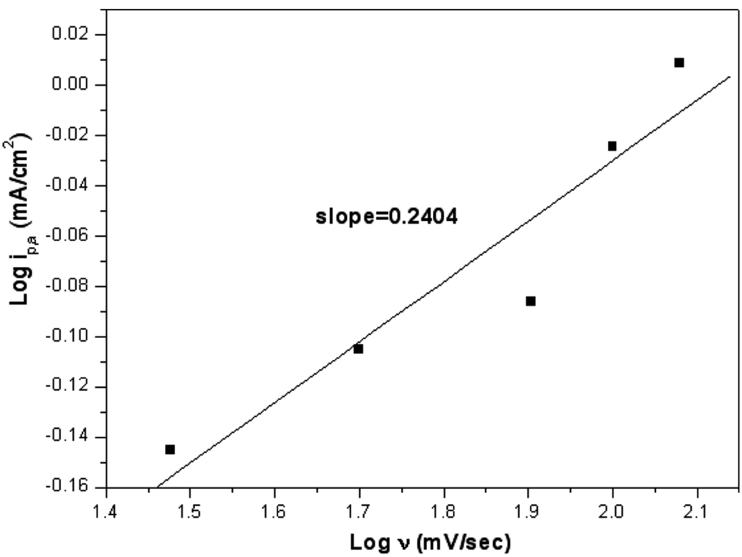


FIGURE 4 Plot of log $i_{p,a}$ *vs* log v for PESPB.

current value was gradually increased as the scan rate was increased. This result suggests that the electrochemical process of PESPB is reproducible in the potential range of $-1.80 \sim 1.1\,\mathrm{V}$ *vs* $Ag/AgNO_3$.

The relationship between the redox peak current and the scan rate can be expressed as a power law type as follows [20,21].

$$i_{p,a} = kv^x \tag{1}$$

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

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

On 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 $x = 0.5$. Relations satisfying Eq. (2) between the oxidation current density (log $i_{p,a}$) and the scan rate (log v) are shown in Figure 4. The oxidation current density of PESPB *versus* the scan rate is an approximately linear relationship in the range of $30 \sim 120\,\mathrm{mV/sec}$. The exponent of the scan rate, the x value of PESPB, is found to be 0.2404. This value means that the kinetics of the redox process is almost entirely controlled by the diffusion process [22].

CONCLUSIONS

A new self-dopable conjugated polymer was easily prepared in 82% yield by using the activated polymerization method. This polymer was completely soluble in such organic solvents as DMF, DMSO, and NMP. The photoluminescence spectra of polymer showed that the photoluminescence peak is located at 511 nm, corresponding to a photon energy of 2.43 eV. The cyclic voltamograms of PESPB exhibited reversible electrochemical behavior between the oxidation and reduction peaks. The peak potentials are very slightly shifted to higher potentials as the scan rate was increased. The kinetics of the redox process of polymer was only controlled by the diffusion process from the experiment plotting the oxidation current density of PEPSB *versus* the scan rate.

REFERENCES

[1] Masuda, T. & Higashimura, T. (1984). *Acc. Chem. Res.*, *17*, 51.
[2] Choi, S. K., Gal, Y. S., Jin, S. H., & Kim, H. K. (2000). *Chem. Rev.*, *100*, 1645.
[3] Murphy, A. R. & Frechet, J. M. J. (2007). *Chem. Rev.*, *107*, 1066.
[4] Lo, S. C. & Burn, P. L. (2007). *Chem. Rev.*, *107*, 1097.
[5] Samuel, I. D. W. & Turnbull, G. A. (2007). *Chem. Rev.*, *107*, 1272.
[6] Freund, M. S. & Deore, B. (Ed). (2007). *Self-Doped Conducting Polymers*, John Wiley & Sons Ltd., West Sussex, England.
[7] Zhang, N., Wu, R., Li, Q., Pakbaz, L., Yoon, C. O., & Wudl, F. (1993). *Chem. Mater.*, *5*, 1598.
[8] Kang, K. L., Kim, S. H., Cho, H. N., Choi, K. Y., & Choi, S. K. (1993). *Macromolecules*, *26*, 4539.
[9] Kim, S. H., Choi, S. J., Park, J. W., Cho, H. N., & Choi, S. K. (1994). *Macromolecules*, *27*, 2339.
[10] Gal, Y. S. & Choi, S. K. (1995). *Eur. Polymer J.*, *31*, 941.
[11] Simionescu, C. I., Dumitrescu, S., Percec, V., & Diaconu, I. (1978). *Materiale Plastice (Romania)*, *15*, 69.
[12] Gal, Y. S., Cho, H. N., Kwon, S. K., & Choi, S. K. (1988). *Polymer (Korea)*, *12*, 30.
[13] Blumstein, A. & Subramanyam, S. (1991). *US Patent*, 5, 037, 916.
[14] Subramanyam, S. & Blumstein, A. (1991). *Macromolecules*, *24*, 2668.
[15] Gal, Y. S., Lee, W. C., Kim, S. Y., Park, J. W., Jin, S. H., Koh, K. N., & Kim, S. H. (2001). *J. Polym. Sci.: Part A: Polym. Chem.*, *39*, 3151.
[16] Gal, Y. S., Jin, S. H., & Park, J. W. (2007). *J. Polym. Sci.: Part A: Polym. Chem.*, *45*, 5679.
[17] Gal, Y. S., Jin, S. H., Lim, K. T., Kim, S. H., & Koh, K. (2005). *Curr. Appl. Phys.*, *5*, 38.
[18] Gal, Y. S. & Jin, S. H. (2004). *Bull. Korean Chem. Soc.*, *25*, 777.
[19] Gui, T. L., Jin, S. H., Lee, W. C., Park, J. W., Koh, K., Kim, S. H., Lee, S. S., Bae, J. S., Kim, S. Y., & Gal, Y. S. (2005). *Curr. Appl. Phys.*, *5*, 23.

[20] Gal, Y. S., Jin, S. H., Gui, T. L., Park, J. W., Lee, S. S., Park, S. H., Koh, K., Kim, S. H., Jang, S. H., & Lee, W. C. (2006). *Curr. Appl. Phys.*, *6*, 675.
[21] Park, J. W., Lee, J. H., Ko, J. M., Cho, H. N., & Choi, S. K. (1994). *J. Polym. Sci.: Part A: Polym. Chem.*, *32*, 2789.
[22] Bard, A. J. & Faulker, L. R. (1980). *Electrochemical Methods*, Wiley: New York, Chapter 3, 6, and 10.