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Electro-optical and Electrochemical Properties of Poly(N-Benzoyl-2-ethynylpyridinium tetraphenylborate)

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A new conjugated ionic polyacetylene with bulky tetraphenylborate as counter ion was prepared by the ion-exchange reaction of poly(N-benzoyl-2-ethynylpyridium chloride) using sodium tetraphenylborate. Poly(N-benzoyl-2-ethynylpyridium chloride) was prepared in high yield by the activated polymerization of 2-ethynylpyridine with benzoyl chloride without any additional initiator or catalyst. Such instrumental methods as NMR, IR, and UV-visible spectroscopies revealed that the present polymer has a conjugated polymer backbone system having N-benzoylpyridinium tetraphenylborate as substituents. This polymer showed characteristic wide UV-visible absorption band and green PL maximum value at 620 nm, which is corresponding photon energy of 2.00 eV. The oxidation of polymer was slightly started at 0.05 V, where the vinylene unit of the conjugated polymer backbone could be oxidized in the scan and the redox process was irreversible. The kinetics of the redox process of polymer was controlled by the diffusion process.

Keywords 2-ethynylpyridine; benzoyl chloride; cyclic voltammogram; photoluminescence; polyacetylene; sodium tetraphenylborate

Introduction

The unique electronic structure of conjugated has potential to endow the polymers with such novel properties as electrical conductivity, paramagnetism, migration and transfer of energy, color, and chemical reactivity and complex formation ability [1–7].

During the past two decades, the scientific interest of polyelectrolytes have been derived from their molecular self-organization phenomena in relevance to biological macromolecular systems and to nanoscopic molecular architecture as a basis of material science [8,9]. The

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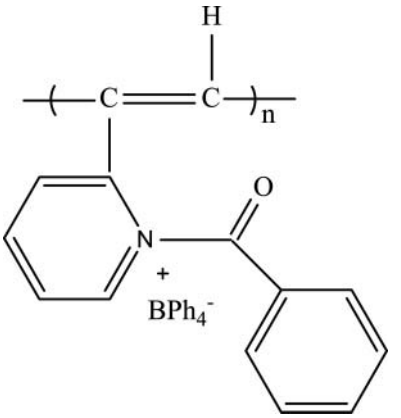

Figure 1. Chemical structure of poly(BEP-TPB).

polyelectrolytes include proteins, nucleic acids, pectins, polyacrylic acid, and polystyrene sulfonate.

A new class of ionic conjugated polymers have been prepared through the uncatalyzed polymerization of ethynylpyridines by using halogens or alkyl halides [10,11]. We have also synthesized various ionic conjugated polymers by the linear polymerization of monosubstituted acetylenes and the activated polymerization of 2-ethynylpyridine by using functional alkyl or carbonyl halides [12–21]. A new substituted polyacetylene with viologen was prepared by the reaction of 4-ethynylaniline with 1-hexyl-1′-(2,4-dinitrophenyl)-4,4′-bipyridinium dihalide [22]. Pyridine-containing ionic polyacetylenes have been used for the fabrication of intercalated nanocomposite films [23], silver-polymer nanocomposites [24], fluorescence quencher for fluorescent biotin-functionalized Lucifer Yellow dyes [25], cyclodextrin-induced fluorescence enhancement [26], hybrid polymer gels [27], and nanocrystalline CdS polymer sensitizer [28,29].

In this article, we report the synthesis of a new pyridine-containing ionic conjugated polymer with a bulky tetraphenylborate count anion, poly(N-benzoyl-2-ethynylpyridinium tetraphenylborate) [poly(BEP-TPB)] (Fig. 1), via the ion-exchange reaction of precursor poly(N-benzoyl-2-ethynylpyridinium chloride) by using sodium tetraphenylborate and the electro-optical and electrochemical properties of poly(BEP-TPB).

Experimental

2-Ethynylpyridine was prepared by the bromination of 2-vinylpyridine and the consecutive dehydrobromination reaction according to the literature method [30] and vacuum distilled after drying with CaH_2 (85°C/12 mmHg). Benzoyl chloride (Aldrich Chemicals., ACS reagent, 99%) and sodium tetraphenylborate (Alidrich Chemicals., $\geq$99.5%) were used as received. The analytical grade solvents were dried with an appropriate drying agent and distilled. The precursive poly(N-benzoyl-2-ethynylpyridinium chloride) was prepared by the uncatalyzed polymerization of 2-ethynylpyridine by using benzoyl chloride under mild reaction conditions [19]. Poly(N-benzoyl-2-ethynylpyridinium tetraphenylborate) [Poly(BEP-TPB)] was prepared by the ion-exchange reaction of precursive poly(N-benzoyl-2-ethynylpyridinium chloride) using sodium tetraphenylborate.

A typical reaction procedure is as follows. Equal mole ratio of 2-ethynylpyridine (1.0 g, 9.70 mmol) and benzoyl chloride (1.37 g, 9.70 mmol) was placed in two-necked, round-bottomed flask equipped with a magnetic stirrer in DMF (10.6 mL, $[M]_0 = 0.75$ M). The reaction solution was warmed to 80 °C and stirring was continued at this temperature for 24 h under nitrogen atmosphere. During this time the color of reaction mixture changed from the light brown of the initial mixture into dark brown. Upon completion of the polymerization reaction, the contents of the reaction mixture were allowed to cool down to room temperature. And the resulting polymer solution diluted with additional 10 mL DMF was precipitated into an excess amount of ethyl ether, followed by filtration. The collected powder was dried under vacuum overnight at 40°C for 24 h to afford poly(N-benzoyl-2-ethynylpyridinium chloride) in 89% yield. In the following ion-exchange reaction, the 50 mL methanol solution of sodium tetraphenylborate (2.11 g, 6.16 mmol) was dropped with stirring into 30 mL methanol solution of poly(N-benzoyl-2-ethynylpyridinium chloride) [1.0 g, 4.10 mmol as monomeric unit]. As soon as the two homogeneous solutions contact each other, the brown product was precipitated into the bottom. The precipitated product was filtered and dried under vacuum at 40°C for 24 hrs. 1.85 g of poly(BEP-TPB) was obtained in light-brown powder.

The ^{1}H- and ^{13}C-NMR spectra were recorded with a Varian 500 MHz FT-NMR spectrometer (Model: Unity INOVA) at room temperature. Polymer solutions were prepared by dissolving 35–40 mg of polymer per mL of DMSO-d_6. The chemical shifts are reported in ppm units with tetramethylsilane as an internal standard. FT-IR spectra were obtained with a Bruker EQUINOX 55 spectrometer using a KBr pellet. The inherent viscosities of polymers were determined at a concentration of 0.5 g/dL in DMF at 30°C. 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). The polymer solution was prepared and the electrochemical measurements were performed under 0.1 M tetrabutylammonium perchlorate(TBAP) solution containing acetonitrile. ITO, $Ag/AgNO_3$ and platinum wire were used as a working, reference and counter electrode, respectively.

Results and Discussion

A new class of ionic conjugated polymers has been synthesized by the uncatalyzed polymerization of ethynylpyridines by using bromine, $FeCl_3$, alkyl halides [11–13]. The acetylenic bond that was bonded to the N-substituted pyridinium ring caused anionic polymerization, initiated by a nucleophilic attack by the nitrogen atom of the unreacted ethynylpyridines and/or the halide anion [31]. This polymerization reactions originally eliminate impurities which may be originated by catalyst or initiator used in other polymerization systems.

We prepared precursor polymer, poly(N-benzoyl-2-ethynylpyridinium chloride), via the uncatalyzed polymerization method [19]. The reaction solution of equal mole ratio of 2-ethynylpyridine and benzoyl chloride in DMF solvent was exposed in heated oil bath (80 °C). As the reaction proceeded, the color of reaction mixture was changed from the light brown of the initial mixture into dark brown solution. And the viscosity of reaction solution was gradually increased. This polymerization proceeded in more mild manner than that of similar polymerization using 2-ethynylpyridine [13]. The precursor polymer was obtained in

89% yield. Poly(BEP-TPB) was prepared by the ion-exchange reaction of precursor poly(N-benzoyl-2-ethynylpyridinium chloride) by using sodium tetraphenylborate in methanol solution. The precipitated poly(BEP-TPB) was easily filtered and dried under vacuum. The brown polymer powder was obtained in high yield.

The chemical structure of poly(BEP-TPB) was characterized by such various instrumental methods as infrared, NMR, and UV-visible spectroscopies. FT-IR spectrum of poly(BEP-TPB) did not show the acetylenic C^{o}C bond stretching and acetylenic ^{o}C-H bond stretching frequencies of 2-ethynylpyridine. Instead, the C=C stretching frequency peak of conjugated polymer backbone around 1570–1663 cm^{-1} became relatively more intense than those of the C=C and C=N stretching frequencies of 2-ethynylpyridine. The carbonyl C=O stretching frequency and the olefinic =C-H stretching frequency were observed at 1734 cm^{-1} and 3053 cm^{-1}, respectively.

The ^{1}H-NMR spectrum of poly(BEP-TPB) showed the aromatic protons of pyridyl moieties and the vinyl protons of the conjugated polymer backbone broadly at 6.0–9.9 ppm. The proton peaks of tetraphenylborate are observed at 6.4–7.4 ppm. The ^{13}C-NMR spectrum of poly(BEP-TPB) showed the aromatic carbon peaks of pyridyl and tetraphenylborate moieties and the vinyl carbons of conjugated polymer backbone at the range of 106–158 ppm. The UV-visible spectrum of poly(BEP-TPB) showed a characteristic absorption band in the visible region (up to 800 nm), which is strong evidence of the presence of the conjugated polyene backbone system. The X-ray diffractogram of poly(BEP-TPB) powder was measured. The peak in the diffraction pattern is broad and the ratio of the half-height width to diffraction angle ($\Delta 2\theta/2\theta$) is greater than 0.35, indicating that the present polymer is amorphous [1,2].

The resulting poly(BEP-TPB) was completely soluble in such organic solvents as DMF, DMSO, and NMP, but insoluble in water and methanol, whereas the original poly(N-benzoyl-2-ethynylpyridinium chloride) was completely soluble in water and methanol. The inherent viscosity of poly(BEP-TPB) was 0.15 dL/g.

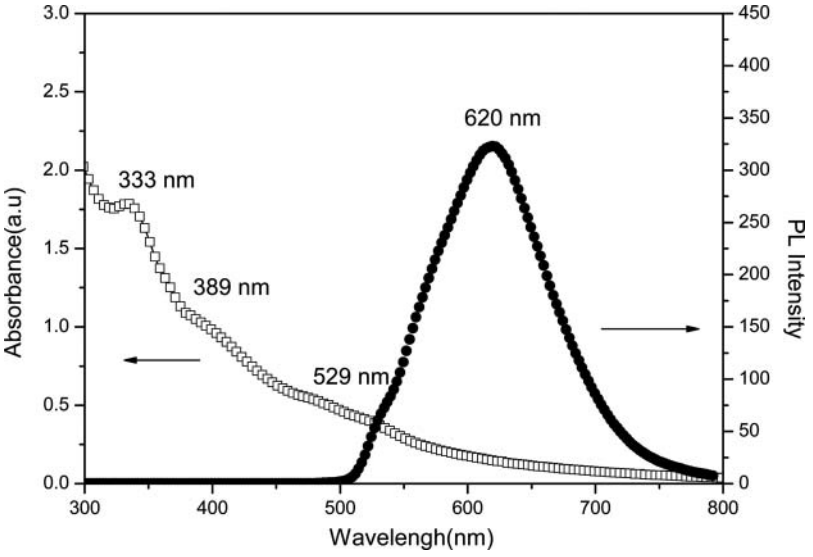

Figure 2. Optical absorption (4.5×10^{-5} wt%, DMF solution) and PL spectrum of poly(BEP-TPB) (1.44×10^{-5} wt%, DMF solution).

The electro-optical and electrochemical properties of poly(BEP-TPB) were studied by using UV-visible and photoluminescence (PL) spectroscopies and cyclic voltametry (CV). Figure 2 shows the UV-visible and photoluminescence spectra of poly(BEP-TPB) solution in DMF solution.

The absorption spectrum exhibits several absorption maximum values of 333, 389, and 529 nm. Especially, shoulder peak of 529 nm came from the $\pi \rightarrow \pi^*$ interband transition of these conjugated polymers. The photoluminescence spectra of this ionic conjugated polymer showed that the photoluminescence maximum peak is located at 620 nm corresponding to the photon energy of 2.00 eV. When PL was checked with excitation of 529 nm wavelength, excitation peak was removed by using cut-off filter in PL detection.

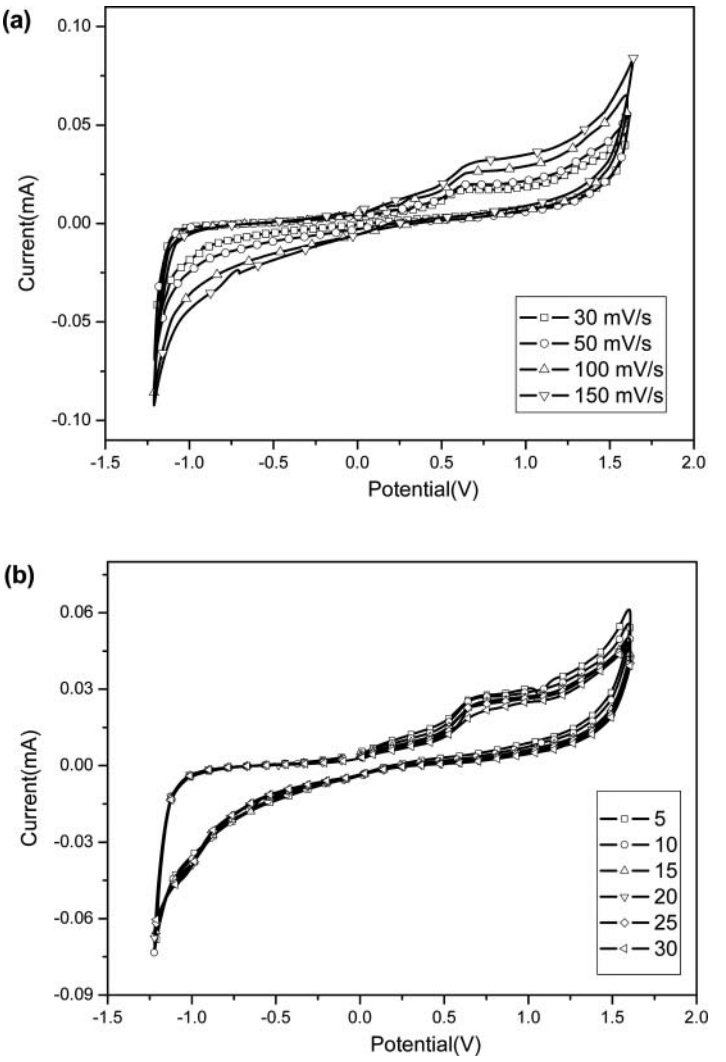

Figure 3. Cyclic voltammograms of poly(BEP-TPB) [0.1 M (n-Bu)$_4$NBF$_4$/DMF] under the various scan rates (30 mV/sec∼150 mV/sec) (a) and the consecutive scans of up to 30 cycles (b).

In our previous study, the optical properties of poly(N-benzoyl-2-ethynylpyridinium chloride), which has same side group except different counter chloride anion were reported [19]. Poly(N-benzoyl-2-ethynylpyridinium chloride) showed different UV maximum value of 500 nm and shorter shifted PL maximum values of 509 and 530 nm. Comparing the maximum wavelength values of UV and PL data in two polymers, maximum values of poly(BEP-TPB) was red-shifted compared to poly(N-benzoyl-2-ethynylpyridinium chloride). It might be mainly attributed to the bulky counter anion of tetraphenylborate although it could not be clearly explained.

The electrochemical kinetic behavior through the cyclic voltammograms of poly(BEP-TPB) solution with various scan rates (30 mV/s∼150 mV/s) was also investigated (Fig. 3(a)). As the scan rate was increased, the oxidation and reduction potentials are very slightly shifted to higher potentials because of higher speed of scan rate. Additionally, we have observed stable cyclic voltammograms of poly(BEP-TPB) from the consecutive scan (up to 30 cycles), which means that this material has a stable redox process in tetrabutylammonium perchlorate (TBAP)/acetonitrile electrolyte solution (Fig. 3(b)). In Fig. 3(a), the oxidation of poly(BEP-TPB) started at 0.05 and 0.43 V (*vs* $Ag/AgNO_3$), where the vinylene and pyridine units of the conjugated polymer could be oxidized in the scan. Poly(BEP-TPB) also shows reduction peak at −1.10 V. The redox current value was gradually increased as the scan rate was increased. This result suggests that the electrochemical process of poly(BEP-TPB) is reproducible in the potential range of −1.20∼1.60 V *vs* $Ag/AgNO_3$, and there are two redox peaks.

The relationship between the redox peak current and the scan rate can be expressed as a power law type as follows [15,16].

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

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

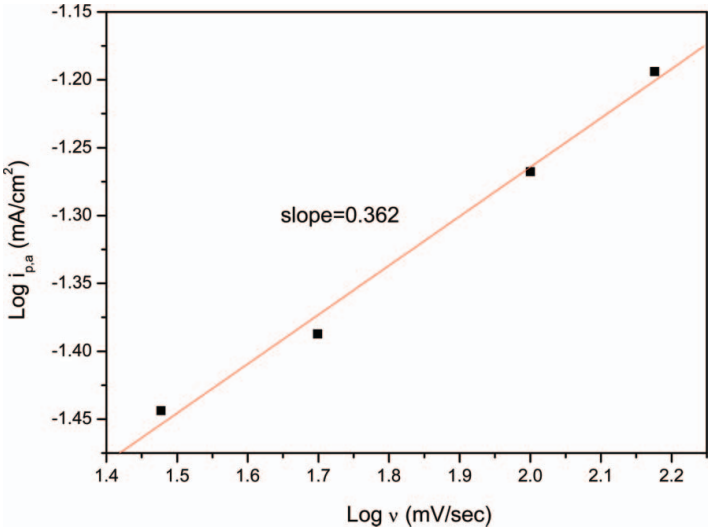

Figure 4. Plot of log $i_{p,a}$ *vs* log *v* for poly(BEP-TPB).

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 empirical 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 Fig. 4. The exponent of the scan rate, the x value of poly(BEP-TPB), is found to be 0.362. This means that the kinetics of the redox process is close to a diffusion process [32].

Conclusions

A new ionic conjugated polymer with bulky tetraphenylborate was easily prepared via the ion-exchange reaction of precursor poly(N-benzoyl-2-ethynylpyridinium chloride), which was prepared by the uncatalyzed polymerization of 2-ethynylpyridine by using benzoyl chloride. The chemical structure of poly(BEP-TPB) was characterized by various instrumental methods to have an ionic conjugated polymer system bearing the designed N-benzoylpyridinium tetraphenylborates. The photoluminescence spectra of polymer showed that the photoluminescence peak is located at 620 nm, corresponding to a photon energy of 2.00 eV. The cyclic voltammogram of poly(BEP-TPB) exhibited irreversible electrochemical behavior between the oxidation and reduction peaks, but it showed two redox peaks. The kinetics of the redox process of polymer was close to a diffusion process from the experiment plotting the oxidation current density of poly(BEP-TPB) *versus* the scan rate.

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