

Synthesis and Properties of Poly[*N*-(4-*n*-butoxybenzoyl)-2-ethynylpyridinium chloride]

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Received 26 December 2006; accepted 25 June 2007

DOI 10.1002/app.28530

Published online 10 July 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: We first synthesized a new ionic polyacetylene with benzoyl functional groups by the activation polymerization of 2-ethynylpyridine with 4-butoxybenzoyl chloride without any additional initiator or catalyst. The acetylenic triple bond of *N*-benzoyl-2-ethynylpyridinium chloride, formed in the first quaternization process, was also found to be susceptible to linear polymerization. The polymer structure was characterized by various instrumental methods to give the ideal conjugated polyene backbone structure with the designed *N*-(4-*n*-butoxybenzoyl)-2-

ethynylpyridinium) substituent and chloride counterion. The photoluminescence spectrum showed two distinguished maximum values at 575 and 630 nm, corresponding to photon energies of 2.16 and 1.97 eV, respectively. The electrochemical properties of this ionic polyacetylene were also measured and are discussed. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 719–724, 2008

Key words: conducting polymers; electrochemistry; FTIR; heteroatom-containing polymers; luminescence

INTRODUCTION

Polyacetylene (PA) and its derivatives are well-known conjugated polymers and are expected to show unique properties, such as electrical conductivity, paramagnetism, migration and transfer of energy, color, photoluminescence (PL) and electroluminescence, chemical reactivity, and complex formation ability.^{1–3} Among these materials, PA is structurally the simplest one and is a prototypical conjugated polymer that exhibits a high electrical conductivity upon doping.^{4,5} This discovery led to the 2000 Nobel Prize in Chemistry awarded to Alan Heeger, Alan MacDiarmid, and Hideki Shirakawa.^{6–8} Nevertheless, some drawbacks thus far have prevented commercial applications of PA itself. PA suffers not only from its lack of processability because of its infusibility and insolubility in common organic solvents but also from its insufficient stability toward oxygen.

To improve the processability and provide interesting functionalities of PA, various substituted PAs have been prepared by the linear polymerization of the corresponding acetylene monomers.^{1–3,9–17} In the

polymerization of substituted PAs, numerous catalyst systems have been used. The catalysts have included Pd-, Pt-, Ru-, Rh-, Mo-, W-, Ta-, and Nb-based transition metal catalysts.^{1,2} In these polymerization systems, the resulting polymers may have been poisoned by the catalyst residues.

In recent years, nitrogen-containing linear polymers have received much attention in the design and preparation of electrooptical materials.¹⁸ Unlike other π -conjugated polymers, nitrogen-containing conjugated polymers contain a nitrogen heteroatom in either the main chains or the side chains, which provide the facile quaternization reaction and protonation of the cited nitrogen. In 1978, Simionescu et al.¹⁹ first reported the synthesis of anionic radical salts of 7,7,8,8-tetracyanoquinodimethane (TCNQ) with poly(vinyl pyridine) and poly(ethynyl pyridine). They prepared 2- and 3-ethynylpyridine homopolymers with methyl iodide or ethyl iodide by mixing the quaternized polymers with lithium tetracyanoquinodimethane (LiTCNQ) or TCNQ in acetonitrile and refluxing for 30 min. In 1988,²⁰ we reported the synthesis of poly(2-ethynylpyridine) by the transition-metal-catalyzed polymerization of 2-ethynylpyridine. In 1990, Blumstein and Subramanyam²¹ conducted systematic studies on the synthesis of ionic PAs through the activated polymerization of ethynylpyridines with alkyl halides without any initiator or catalysts. This polymerization system essentially prevented the poisoning of catalyst residues. They prepared new conjugated

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Contract grant sponsor: Regional Technology Innovation Program of the Ministry of Commerce, Industry and Energy; contract grant number: RTI04-01-04.

ionic polymers by the reaction of 2-ethynylpyridines with alkyl halides, methanesulfonic acids, halogens, and halogenic acids.^{22–25} The structural features of the new ionic polymers were unique with respect to their ionic nature, high degree of substitution, and extensive backbone conjugation. We also reported the synthesis of various ionic conjugated polymers with different functionalities.^{26–31} Because of their extensive conjugation and ionic nature, these ionic PAs have potential as materials for mixed ionic and electronic conductivity, energy-storage devices such as batteries, permselective membranes, and light-emitting devices.²⁴

In this article, we report the synthesis of a novel ionic PA with carbonyl moieties by the polymerization of 2-ethynylpyridine with 4-butoxybenzoyl chloride and the characterization of the polymer structure and its properties.

EXPERIMENTAL

2-Ethynylpyridine (Aldrich Chemicals, 98%) was vacuum-distilled after it was dried with CaH₂ (85°C/12 mmHg). 4-Butoxybenzoyl chloride (Aldrich Chemicals, 99%) and analytical-grade solvents were dried with an appropriate drying agent and distilled. Poly[*N*-(4-butoxybenzoyl)-2-ethynylpyridinium chloride] (PBEC) was prepared by the activated polymerization reaction of 2-ethynylpyridine with 4-butoxybenzoyl chloride without any additional initiator or catalyst in dimethylformamide (DMF) solvent as follows. A 1 : 1 mixture of 2-ethynylpyridine (1.0 g, 9.70 mmol) and 4-butoxybenzoyl chloride (2.06 g, 9.70 mmol) in DMF solvent (3 mL) was stirred for 24 h at 100°C under a nitrogen atmosphere. As the reaction proceeded, the color of the reaction mixture changed from the light brown of the initial mixture to a dark red. The resulting polymer solution was diluted by 10 mL of DMF and precipitated into a large excess of ethyl ether. The precipitated polymer was filtered and dried *in vacuo* at 40°C for 24 h. The polymer yield was 83%.

Fourier transform infrared (FTIR) spectra were obtained with a Bruker EQUINOX 55 spectrometer with a KBr pellet. NMR (¹H- and ¹³C-) spectra were recorded on a Varian 500-MHz Fourier transform NMR spectrometer (model Unity INOVA) in dimethyl sulfoxide (DMSO)-*d*₆, and the chemical shifts are reported in parts per million with tetramethylsilane as an internal standard.

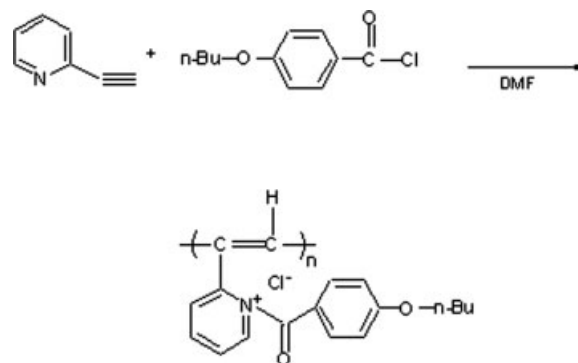
The optical absorption spectra were measured by an HP 8453 ultraviolet–visible (UV–vis) spectrophotometer. The PL spectra were obtained on a PerkinElmer LS55 luminescence spectrometer (Xenon flash tube). Electrochemical measurements were carried out with a potentiostat/galvanostat model 273A (Princeton Applied Research). To examine the elec-

trochemical properties, the polymer solution was prepared, and the electrochemical measurements were performed under 0.1M tetrabutylammonium tetrafluoroborate solution containing acetonitrile. Indium tin oxide (ITO), Ag/AgNO₃, and platinum wire were used as working, reference, and counter electrodes, respectively.

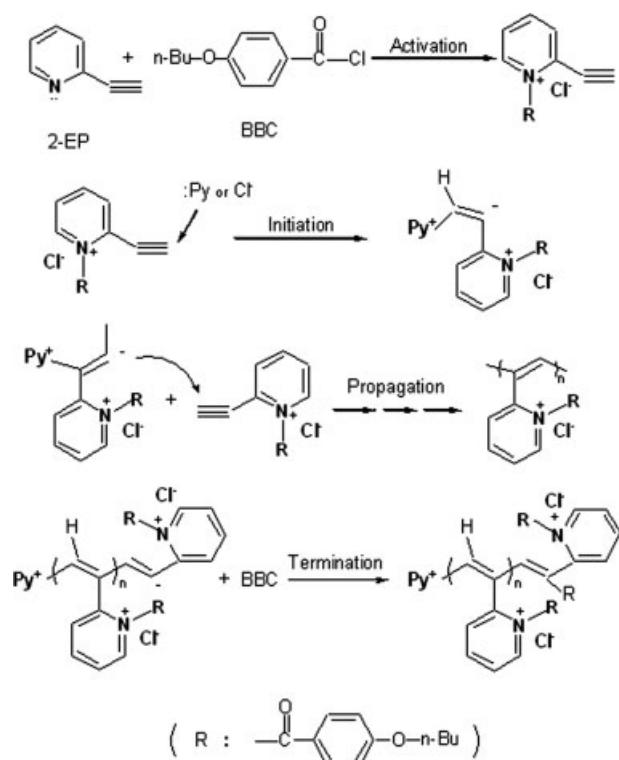
RESULTS AND DISCUSSION

There are many known examples of ionic conjugated polymers from ethynylpyridines and simple alkyl halides.^{21–25} The Blumstein method is a very facile synthetic method for the synthesis of conjugated ionic polymers.²¹ The activated acetylenic groups of *N*-substituted-2-ethynylpyridinium halides were found to be susceptible to the linear polymerization and to yield ionic conjugated polymer systems.^{23,32} However, there have been no reports on the polymerization reaction with acid chlorides. Here, we performed the activated polymerization of 2-ethynylpyridine with 4-butoxybenzoyl chloride in DMF without any additional initiator or catalyst (Scheme 1).

The polymerization reaction of the reaction mixture of 2-ethynylpyridine (2-EP) and 4-butoxybenzoyl chloride was performed at 100°C. As the reaction proceeded, the color of reaction mixture was changed from the light brown of the initial mixture into a viscous dark red solution. After precipitation and drying, a black polymer powder was obtained at 83% yield. The inherent viscosity of PBEC was 0.18 dL/g. The polymerization behaviors were found to be very similar to those of the polymerization reaction of 2-ethynylpyridine with 1-bromohexane.³³ It was also found that this polymerization was not influenced by the presence of oxygen or strong acidic cocatalysts. Thus, we ruled out the possibility of a free-radical mechanism for the formation of conjugated PAs. Katritzky et al.³⁴ succeeded in isolating the quaternarized acetylenic pyridinium salts in the reactions of propargyl



Scheme 1 Synthesis of PBEC.



Scheme 2 Proposed polymerization mechanism. BBC, 4-butoxybenzoyl chloride.

bromide and propargyl chloride with pyridine. They found that the polymerization could be initiated in these species by the addition of nucleophiles, such as pyridines and tertiary amines. This polymerization seemed to proceed with an anionic mechanism (Scheme 2). It contained the first quaternarization of 2-ethynylpyridine by 4-butoxybenzoyl chloride. The activated acetylenic triple bond of *N*-(4-butoxybenzoyl)-2-ethynylpyridinium chloride formed at the initial reaction time was susceptible to the linear polymerization. The quaternarized monomeric species could be initiated by the nonbonding electron pair of 2-ethynylpyridine and/or the chloride counteranion.

The molecular structure of the polymer was characterized by NMR, IR, and UV-vis spectroscopy. Figure 1 shows the FTIR spectra of 2-ethynylpyridine [Fig. 1(A)], 4-butoxybenzoyl chloride [Fig. 1(B)], and the polymer [PBEC, Fig. 1(C)] in KBr pellets. The FTIR spectrum of the polymer did not show the acetylenic C≡C bond stretching (2110 cm^{-1}) and acetylenic ≡C—H bond stretching (3293 cm^{-1}) frequencies of 2-ethynylpyridine. Instead, the C=C stretching frequency peaks of the conjugated polymer backbone and aromatic substituents (pyridyl and 4-butoxybenzoyl) were observed around 1600 cm^{-1} ; these became more intense than those of the C=C and C=N stretching frequencies of 2-ethynylpyridine itself. The strong carbonyl C=O stretching

peak of 4-butoxybenzoyl chloride [Fig. 1(B)] at 1770 cm^{-1} was also smaller at 1724 cm^{-1} in the IR spectrum of the polymer. The C—O—C antisymmetric stretching peak of the polymer was observed at 1248 cm^{-1} .

The $^1\text{H-NMR}$ spectrum of the polymer showed the aromatic protons of pyridyl moieties and the vinyl protons of the conjugated polymer backbone at 5.9–9.8 ppm. The methylene proton peaks adjacent to the oxygen atom were observed at 3.6–4.3 ppm. The peaks of the methyl and two internal methylene protons of butoxy substituents were observed at 0.5–1.9 ppm. Figure 2 shows the $^{13}\text{C-NMR}$ spectrum of PBEC in $\text{DMSO-}d_6$. The $^{13}\text{C-NMR}$ spectrum of the polymer showed multiple and complicated peaks in the region 110–153 ppm, which originated from the aromatic carbons of the pyridyl and 4-butoxybenzoyl moieties and the vinyl carbons of the conjugated polymer backbone. The methyl and two internal methylene carbon peaks of the butoxy substituents were observed at 14, 19, and 31 ppm. The methylene carbon peaks adjacent to the oxygen atom of the pyridyl moieties were observed at 67 ppm, and the carbonyl carbon peak of the polymer was observed at 162 ppm.

From these analytical data, we concluded that this polymer had an ionic conjugated polymer system bearing *N*-(4-butoxybenzoyl)pyridinium chloride.

PBEC was completely soluble in such organic solvents as DMF, DMSO, and NMP. In the X-ray diffractogram of PBEC powder, because the peaks in the diffraction pattern were broad and the ratio of the half-height width to the diffraction angle ($\Delta 2\theta/$

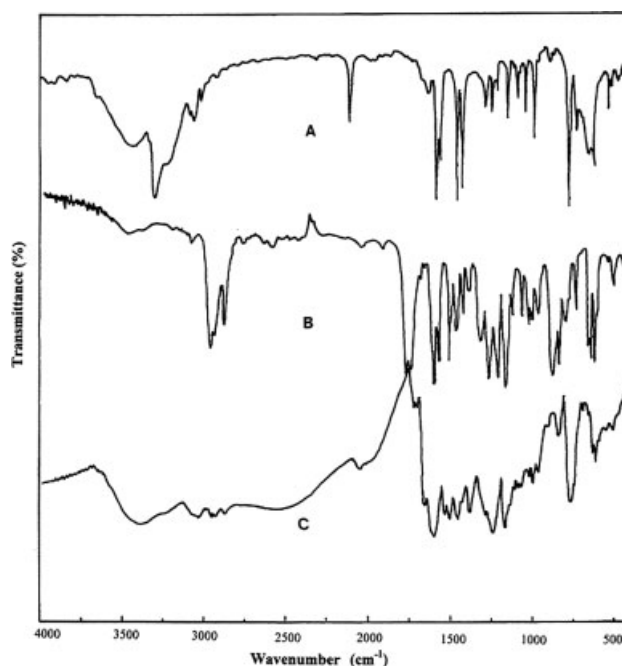


Figure 1 FTIR spectra of (A) 2-ethynylpyridine, (B) 4-butoxybenzoyl chloride, and (C) PBEC in KBr pellets.

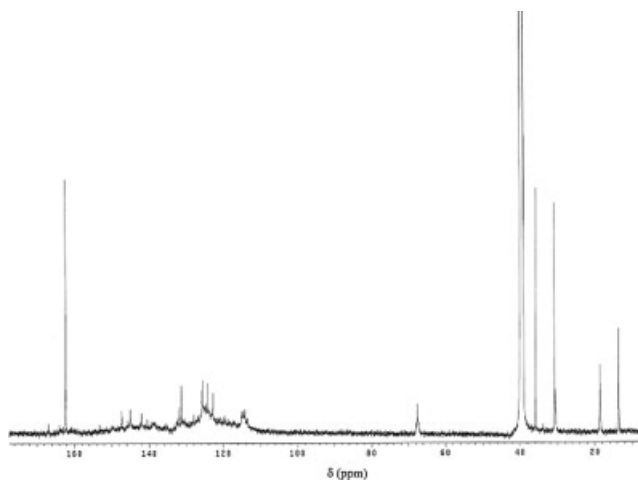


Figure 2 ^{13}C -NMR spectrum of PBEC in $\text{DMSO-}d_6$.

20) was greater than 0.35, this polymer was amorphous.¹

The electrooptical and electrochemical properties of PBEC were studied by UV-vis absorption and PL spectroscopy and cyclic voltammograms. Figure 3 shows the UV-vis and PL spectra of the PBEC solution (0.1 wt %, DMF). PBEC showed a broad UV-vis absorption band around 476 nm and a yellow orange PL spectrum. This PL spectrum was excited by light 476 nm in wavelength and was cut off below 515 nm by a light filter for the purpose of removing the residue of excitation light.

The PL spectrum showed two distinguished maximum values at 575 and 630 nm, which corresponded to photon energies of 2.16 and 1.97 eV. This might be explained by that there were several factors, including the molecular weight, conjugation length of the conjugated polyene, and side chain size. In

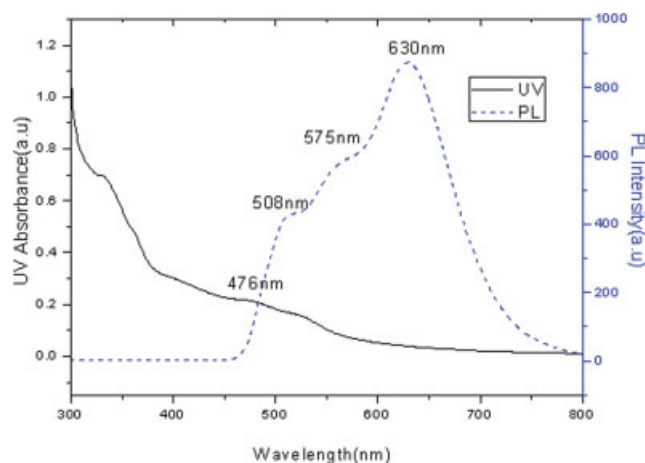


Figure 3 Optical absorption and PL spectra of the PBEC polymer solution. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

our previous article,³³ we reported the PL spectrum of poly(2-ethynylpyridinium bromide) with simple *N*-hexyl side chains; it showed a 603-nm PL maximum value at an excitation wavelength of 598 nm. Also, we believe that bulkiness of hexyl groups had some effect on the electrooptical properties of the conjugated polyene. However, there was no clear explanation for the 508-nm PL shoulder wavelength, although we cut the light at less than 515 nm.

The energy band gap of PBEC was estimated to be 2.22 eV from the analysis of the absorption edge with a plot of $h(C/\lambda)$ versus $(\alpha h(C/\lambda))^2$, where α , h , and (C/λ) are the absorbance, Planck's constant, and the frequency of light, respectively.^{35,36}

As shown in Figure 4, we investigated the electrochemical kinetic behavior by through cyclic

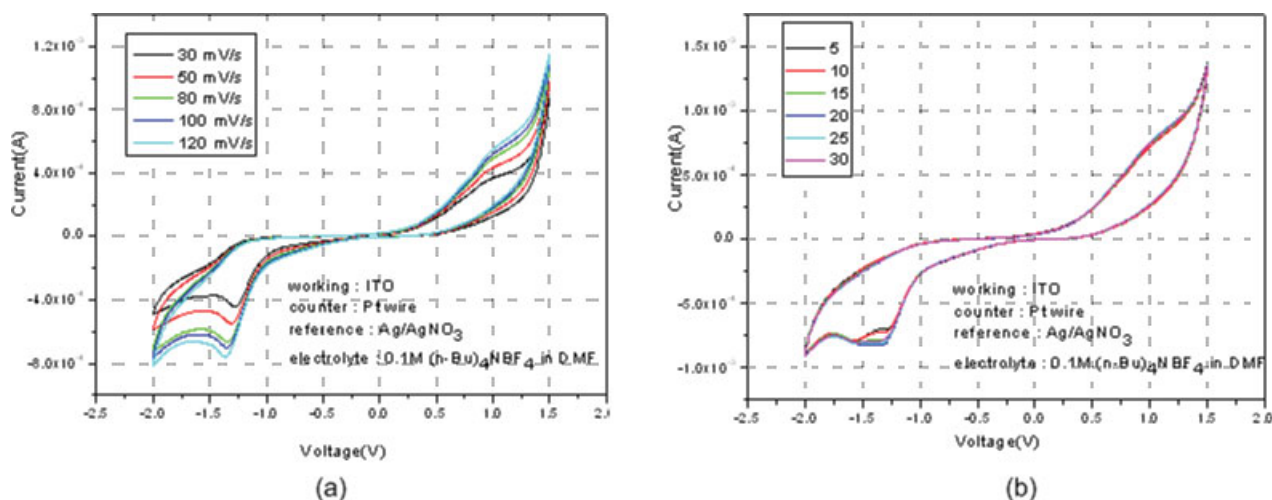


Figure 4 Cyclic voltammograms of PBEC [0.1M $(n\text{-Bu})_4\text{NBF}_4$ /acetonitrile] with various scan rates: (a) 30–120 mV/s and (b) 30 consecutive scans at 100 mV/s. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

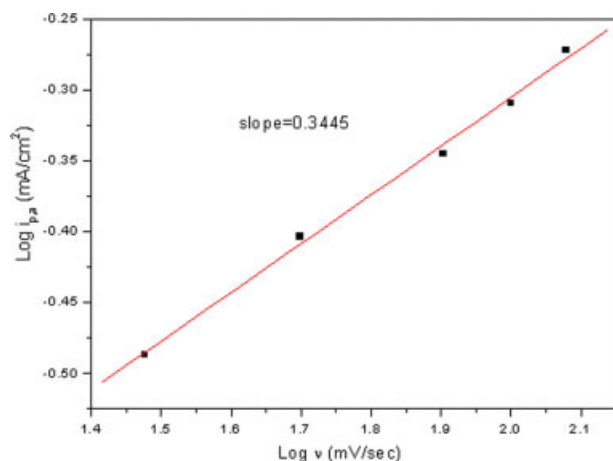


Figure 5 Plot of $\log i_{p,a}$ versus $\log v$ for PBEC. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

voltammograms of the PBEC solution with various scan rates (30–120 mV/s). The peak potentials shifted slightly to higher potentials as the scan rate was increased. In addition, we observed very stable cyclic voltammograms of PBEC from the consecutive scans (up to 30 cycles), which meant that this material had a stable redox process. As shown in Figure 5, the oxidation of PBEC occurred at 0.9 V (vs Ag/AgNO₃), where the vinylene unit of the conjugated polymer backbone could have been oxidized in the scan. PBEC also showed an irreversible reduction at −1.3 V. The redox current value gradually increased as the scan rate was increased. This result suggests that the electrochemical process of PBEC was reproducible in the potential range −2.0 to 1.5 V versus Ag/AgNO₃.

The relationship between the redox peak current and the scan rate can be expressed as a power law type as follows.^{37,38}

$$i_{p,a} = k v^x \quad (1)$$

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

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

The oxidation current density of PBEC versus the scan rate was an approximately linear relationship in the range 30–120 mV/s. When it was assumed that the electrode kinetics satisfied eq. (1), the exponent of the scan rate, the x value of PBEC, was found to be 0.34 (Fig. 5). This value means that the kinetics of the redox process were close to being controlled by the diffusion process.³⁹

CONCLUSIONS

In this study, we found that acid chlorides could be used for the activated polymerization of ethynylpyridines. A new conjugated ionic PA with *N*-(4-butoxybenzoyl)pyridinium chloride was easily prepared at 83% yield with the activated polymerization method. The reaction mechanism of this polymerization included the fact that the activated acetylenic groups of *N*-(4-butoxybenzoyl)-2-ethynylpyridinium halides were susceptible to the linear polymerization. This polymer was completely soluble in such organic solvents as DMF, DMSO, and NMP, and was mostly amorphous. The polymer structure was identified by various instrumental methods to have a conjugated backbone system with the designed substituents. The PL spectrum showed two distinguished maximum values at 575 and 630 nm, which corresponded to photon energies of 2.16 and 1.97 eV, respectively. The cyclic voltammograms of PBEC exhibited reversible electrochemical behaviors between the doped and undoped peaks. The kinetics of the redox process of the polymer were controlled by the diffusion process, as shown by the experimental plot of the oxidation current density of PBEC versus the scan rate.

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