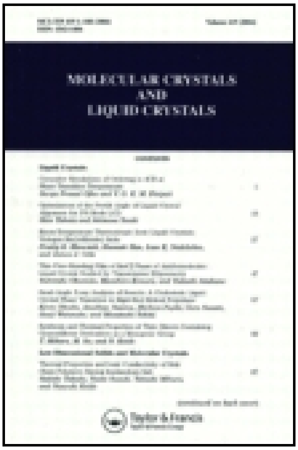

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Synthesis and Electrochemical Properties of Poly[N-(6-azidohexyl)-2-ethynylpyridinium tetraphenylborate]

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Poly[N-(6-azidohexyl)-2-ethynylpyridinium tetraphenylborate] (PAHEP-TPB) was prepared by the ion exchange reaction of the precursor polymer, poly[N-(6-azidohexyl)-2-ethynylpyridinium iodide], by using sodium tetraphenylborate in methanol. The photoluminescence (PL) spectra of polymer showed that the

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photoluminescence peak is located at 599 nm, corresponding to a photon energy of 2.07 eV. The cyclic voltamograms of the polymer exhibited reversible electrochemical behaviors between the doped and undoped peaks. It was found that the kinetics of the redox process of PAHEP-TPB is controlled by the diffusion process mixed with the electron transfer process from the experiment of the oxidation current density of polymer versus the scan rate.

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

INTRODUCTION

The polymers having a conjugated backbone are expected to show unique properties such as electrical conductivity, paramagnetism, migration and transfer of energy, color, and chemical reactivity and complex formation ability [1,2].

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 polyelectrolytes such as poly(propiolic salt)s [3], triethylammonium salt of poly(6-bromo-1-hexyne) [4], and poly (ethynylpyridine)s [5,6] were reported. Blumstein *et al.* prepared very interesting ionic polyacetylenes through the activated polymerization of ethynylpyridines with alkyl halides [7,8]. We have also prepared the pyridine-containing ionic conjugated polymers [9–14]. These ionic polyacetylenes have potentials as materials for mixed ionic and electronic conductivity, energy storage devices such as batteries, permselective membrane, light-emitting devices [15].

In synthetic organic chemistry, oganoazides have been used as a pertinent intermediates, because the azide group can subsequently be converted into several other types of substituent groups [16,17]. Azides find extensive applications in the area of lithography as the photosensitive components [18]. Aliphatic polymeric azides have been prepared by reaction of poly(vinyl chloride), poly(epichlorohydrin), halohydrins from poly(glycidyl methacrylate) and polybutadiene with sodium azide [19,20]. We had reported the synthesis of a new water-soluble conjugated polymer with a azide functional group, poly[N-(6-azidohexyl)-2-ethynylpyridinium iodide], by the activated polymerization of 2-ethynylpyridine by using 6-azidohexyl iodide [21].

In this article, we report the synthesis of PAHEP-TPB having bulky counter anions via the ion-exchange reaction of poly[N-(6-azidohexyl)-2-ethynylpyridinium iodide] by using sodium tetraphenylborate, and the electro-optical and electrochemical properties of PAHEP-TPB polymer.

EXPERIMENTAL

The synthesis of poly[N-(6-azidohexyl)-2-ethynylpyridinium iodide] was performed by the direct polymerization of 2-ethynylpyridine with 6-azidohexyl iodide without any additional initiator or catalyst in 71% yield [21]. The ion exchanged product, poly[N-(6-azidohexyl)-2-ethynylpyridinium tetraphenylborate] (PAHEP-TPB) was prepared by the ion exchange reaction of precursor polymer, poly[N-(6-azidohexyl)-2-ethynylpyridinium iodide], with sodium tetraphenylborate in methanol. The brown powders were precipitated into the reaction bottom. Then the reaction solution was filtered and washed with methanol several times in order to unreacted precursor polymer and sodium tetraphenylborates.

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 acetonitrile. ITO, $Ag/AgNO_3$ and platinum wire were used as a working, reference and counter electrode, respectively.

RESULTS AND DISCUSSION

An azide group-containing conjugated ionic polymer was synthesized by the direct polymerization of 2-ethynylpyridine by using 6-azidohexyliodide at 60°C in methanol in 71% yield. The initial light-brown solution of 2-ethynylpyridine and 6-azidohexyl iodide became viscous dark-red solution as the polymerization proceeded. The resulting polymer was somewhat hygroscopic powder. In order to modify the polymer properties, we tried to exchange the iodide anion with tetraphenylborate anion. The ion-exchanged product was easily obtained by the simple mixing of the two solutions of precursor polymer and sodium tetraphenyl borate. As soon as the two solutions contact, the brown powders were precipitated into the reaction bottom. Then the reaction solution was filtered and washed with methanol several times, and dried. This polymer was insoluble

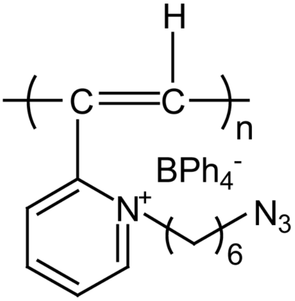

FIGURE 1 The polymer structure of PAHEP-TPB.

in water, methanol, whereas the precursor polymer was completely soluble in those solvents. The resulting polymer structure is depicted in Figure 1.

The electro-optical and electrochemical properties of PAHEP-TPB were studied by UV-visible and photoluminescence (PL) spectroscopies and cyclic voltammograms (CV). Figure 2 shows the UV-visible spectroscopy of PAHEP-TPB solution (0.1 wt.%, DMF). In our previous article [22], we had reported the PL spectrum of poly(2-ethynylpyridinium bromide) with LC moieties, it showed 454 nm PL maximum

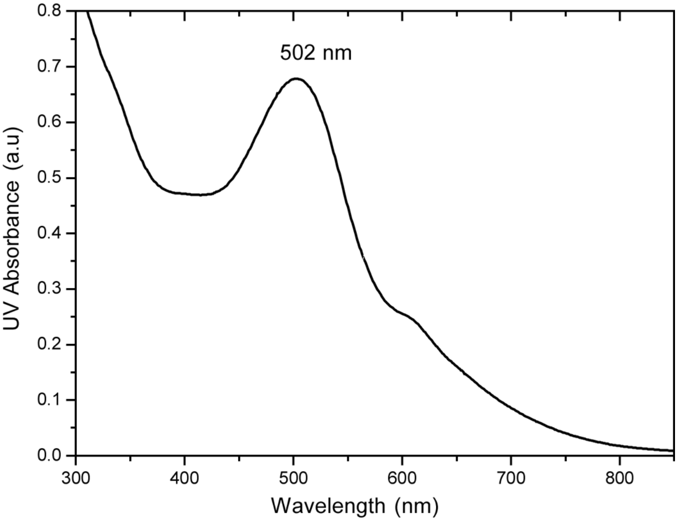

FIGURE 2 Optical absorption spectrum of PAHEP-TPB (0.1 wt% DMF solution).

value at excitation wavelength of 371 nm. PAHEP-TPB showed characteristic UV-visible absorption band at 502 nm and yellow-orange PL spectrum at 599 nm, corresponding to a photon energy of 2.07 eV. The energy band gap of PAHEP-TPB was estimated to be 1.72 eV from the analysis of the absorption edge with a plot of (hv) vs. $(\alpha hv)^2$, where α, h, and v are absorbance, Plank's constant, and the frequency of light, respectively [23,24]. The reason why PAHEP-TPB exhibited different UV-visible and PL maximum value with those of PEPB including LC moiety could be deduced that it has larger molecular weight and longer conjugation length of polymer main chain.

As shown in Figure 3, we investigated the electrochemical kinetic behavior by through the cyclic voltammograms of PAHEP-TPB solution with various scan rates (30 mV/s ~ 120 mV/s). The peak potentials are slightly shifted to higher potentials as the scan rate was increased. In addition, we have observed very stable cyclic voltammograms of PAHEP-TPB from the consecutive scan (up to 30 cycles), which means that this material has a stable redox process. In Figure 3, the oxidation of PAHEP-TPB occurred at 0.35 V (vs. $Ag/AgNO_3$), where the vinylene unit of the conjugated polymer backbone could be oxidized in the scan. PAHEP-TPB also shows irreversible reduction at -1.40 V. The redox current value gradually increased as the scan rate was increased although there was

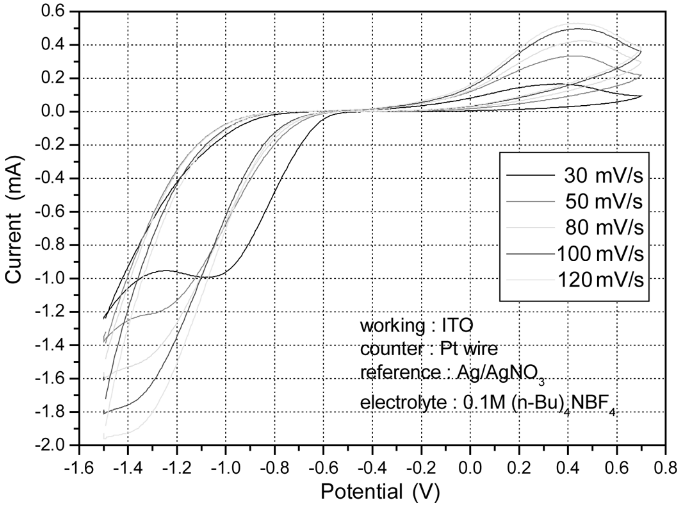

FIGURE 3 Cyclic voltammograms of PAHEP-TPB [0.1 M $(n\text{-}Bu)_4NBF_4$/acetonitrile] with various scan rates 30 mV/sec ~ 120 mV/sec.

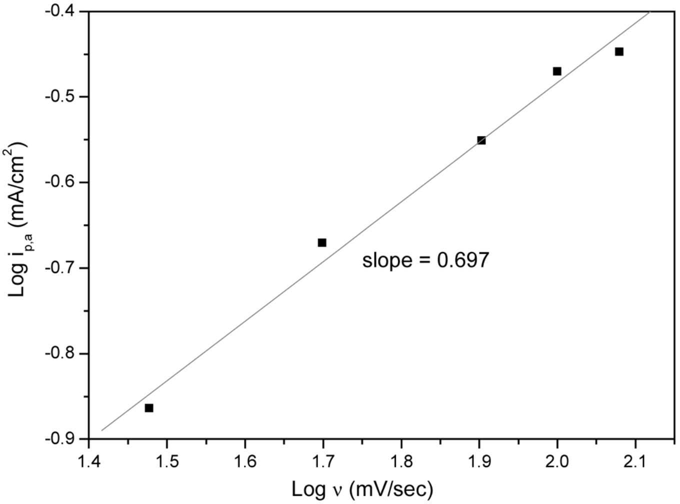

FIGURE 4 Plot of log $i_{\mathrm{p,a}}$ vs. log v for PAHEP-TPB.

unmatched reduction current at $-1.05\,\mathrm{V}$ in the first scan. This result suggests that the electrochemical process of PAHEP-TPB is reproducible in the potential range of $-1.50 \sim 0.70\,\mathrm{V}$ vs. $\mathrm{Ag/AgNO_3}$.

The relationship between the redox peak current and the scan rate can be expressed as a power law type as follows [25,26].

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

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

where $i_{\mathrm{p,a}}$ = 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 $i_{\mathrm{p,a}}$) and the scan rate (log v) are shown in Figure 4. The oxidation current density of PAHEP-TPB vs. the scan rate is an approximately linear relationship in the range of $30\,\mathrm{mV/sec} \sim 120\,\mathrm{mV/sec}$. The exponent of the scan rate, the x value of PAHEP-TPB, is found to be 0.697. This value means that the kinetics of the redox process is almost entirely controlled by the diffusion and the electron transfer process together [27].

CONCLUSIONS

The modification of the properties of conjugated ionic polymer was easily performed via the simple ion-exchange reaction of the precursor ionic polymer. The photoluminescence (PL) spectra of the polymer showed that the photoluminescence peak is located at 599 nm corresponding to the photon energy of 2.07 eV. The cyclic voltamograms of this hydrophobic ionic polymer with highly bulky substituents exhibited reversible electrochemical behaviors between the doped and undoped peaks. It was concluded that the kinetics of the redox process of polymer was controlled by the diffusion process mixed with the electron transfer process from the experiment plotting the oxidation current density of PAHEP-TPB vs. the scan rate.

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