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Yeong-Soon Gal [a], Tai-Long Gui [b], Sang-Yeon Shim [c], Won Seok Lyoo [d], Young-Il Park [e], Jong-Wook Park [e], Kwon Taek Lim [f] & Sung-Ho Jin [g]

[a] Polymer Chemistry Laboratory, College of Engineering, Kyungil University, Gyeongsan, 712-701, Gyeongsangbuk-Do, Korea

[b] Department of Electronic Science and Technology, Harbin University of Science and Technology, Harbin, 150080, China

[c] Department of Environ. & Applied Chem. Engineering, Kangnung-Wonju National University, Gangneung, 210-702, Korea

[d] School of Textiles, Yeungnam University, Gyeongsan, 712-749, Korea

[e] Department of Chemistry, Center for Display Research, The Catholic University of Korea, Bucheon, 420-743, Korea

[f] Division of Image and Information Engineering, Pukyong National University, Busan, 608-739, Korea

[g] Department of Chemistry Education, Pusan National University, Pusan, 609-735, Korea

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Uncatalyzed Synthesis and Properties of Polyacetylene with N-Pentylpyridinium Iodide

YEONG-SOON GAL,[1,*] TAI-LONG GUI,[2] SANG-YEON SHIM,[3] WON SEOK LYOO,[4] YOUNG-IL PARK,[5] JONG-WOOK PARK,[5] KWON TAEK LIM,[6] AND SUNG-HO JIN[7]

[1]Polymer Chemistry Laboratory, College of Engineering, Kyungil University, Gyeongsan 712–701, Gyeongsangbuk-Do, Korea
[2]Department of Electronic Science and Technology, Harbin University of Science and Technology, Harbin 150080, China
[3]Department of Environ. & Applied Chem. Engineering, Kangnung-Wonju National University, Gangneung 210–702, Korea
[4]School of Textiles, Yeungnam University, Gyeongsan 712–749, Korea
[5]Department of Chemistry, Center for Display Research, The Catholic University of Korea, Bucheon 420–743, Korea
[6]Division of Image and Information Engineering, Pukyong National University, Busan 608–739, Korea
[7]Department of Chemistry Education, Pusan National University, Pusan 609–735, Korea

Uncatalyzed synthesis of a new ionic conjugated polymer, poly(3-ethynyl-N-pentylpyridinium iodide) [P3EPPI] was performed by the activated polymerization of 3-ethynylpyridine using 1-iodopentane. The polymerization proceeded in homogeneous manner to provide a moderate yield of polymer. The polymer structure was characterized by such instrumental methods as NMR (^{1}H- and ^{13}C-), IR, and UV-visible spectroscopies to have a conjugated polymer backbone system having N-pentyl-3-pyridinium iodide as substituents. The photoluminescence maximum peak of P3EPPI was located at 534 nm, which corresponds to the photon energy of 2.32 eV. The cyclovoltamograms of polymer exhibited the electrochemically stable window at the −1.53∼1.50 V region. The kinetics of the redox process of P3EPPI was found to be mainly controlled by the reactant diffusion process from the experiment of the oxidation current density of polymer versus the scan rate.

Keywords 3-ethynylpyridine; 1-iodopentane; polyacetylene; conjugated polymer; photoluminescence; cyclic voltammogram.

Introduction

Acetylenic molecules contain a triple bond, with one more π-bond than in an olefin monomer, which can be a good candidate to introduce π-conjugated systems in organic polymers [1–5]. The backbones of acetylenic polymers are π-conjugated due to the electronic communications between their electronically unsaturated repeating units [5]. This

*Corresponding author. E-mail: ysgal@kiu.ac.kr

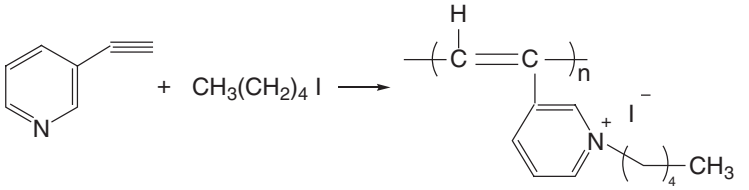
unique electronic structure has potential to endow the polymers with such novel properties as electrical conductivity, paramagnetism, migration and transfer of energy, color, and chemical reactivity and complex formation ability [1, 2, 5, 6–8]. The incorporation of various substituents to acetylene and their subsequent polymerization may lead to the conjugated organic materials with designed peculiar properties. The conjugated organic materials have potentials as materials for light-emitting diodes and photovoltaic cells [9–13].

Polymers possessing both charges and hydrophobes along or pendant to the polymer backbone are one of the most important classes of polyelectrolytes. 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 [14, 15].

A new class of ionic conjugated polymers have been prepared through the activated polymerization of ethynylpyridines by using halogens or alkyl halides [16–19]. 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 [20–29]. The activated polymerization of ethynylpyridines by using functional alkyl or carbonyl halides can essentially prevent the contamination of polymer sample by the catalyst or initiator used. And also, this method enables the synthesis of some ionic conjugated polymers, which the synthesis had been very difficult by classical transition metal catalysts.

Yamaguchi et al. reported a new substituted polyacetylene with viologen (1,1′-disubstituted 4,4′-bipyridinium dications) side groups, which can exhibit electrochromism and self-doping behavior, by the reaction of 4-ethynylaniline with 1-hexyl-1′-(2,4-dinitrophenyl)-4,4′-bipyridinium dihalide [30].

In this article, we report the uncatalyzed synthesis of a pyridine-containing ionic conjugated polymer via the activated polymerization of 3-ethynylpyridine using 1-iodopentane (Scheme 1) and the polymer properties.



Scheme 1. Synthesis of P3EPPI.

Experimental

3-Ethynylpyridine and 1-iodopentane were purchased from Sigma-Aldrich and used as received. The analytical grade solvents were dried with an appropriate drying agent and distilled. Poly(3-ethynyl-N-pentylpyridinium iodide) [P3EPPI] was prepared by the activated polymerization of 3-ethynylpyridine by using 1-iodopentane.

A typical polymerization procedure is as follows. Equal mole ratio of 3-ethynylpyridine (1.0 g, 9.70 mmol) and 1-iodopentane (1.92 g, 9.70 mmol) was placed in two-necked, round-bottomed flask equipped with a magnetic stirrer in DMF (15 mL, $[M]_0 = 0.54$ 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 red-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 P3EPPI in 65% yield.

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. Energy dispersive X-ray (EDX) analyses were performed by Hitachi JEOL system (S-4200). 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 DMF. ITO, Ag/$AgNO_3$ and platinum wire were used as a working, reference and counter electrode, respectively.

Results and Discussion

Substituted ionic polyacetylenes have been synthesized by activated polymerization of ethynylpyridines by using bromine, $FeCl_3$, alkyl halides without any additional catalyst or initiator [16–19, 23–26]. The activated acetylenic triple 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 [27]. This is a facile synthetic method for preparing ionic polyacetylenes containing long sequences of conjugated double bonds in the backbone with ionic charges adjacent to or in conjugation with them. In addition, this polymerization reactions originally eliminate impurities which may be originated by catalyst or initiator used in other polymerization sysyems.

Here, we used this activation polymerization method for the synthesis of water-soluble ionic conjugated polymer. The reaction solution of equal mole ratio of 3-ethynylpyridine and 1-iodopentane 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 [31]. The present P3EPPI was obtained in 65% yield, whereas the polymer yield was 87% when 2-ethynylpyridine was used.

The chemical structure of P3EPPI was characterized by such various instrumental methods as infrared, NMR, and UV-visible spectroscopies. FT-IR spectra of 2-ethynylpyridine, 1-iodopentane, and P3EPPI were measured and compared. FT-IR spectrum (Figure 1) of P3EPPI did not show the acetylenic C≡C bond stretching (2111 cm^{-1}) and acetylenic ≡C–H bond stretching frequencies (3292 cm^{-1}) of 3-ethynylpyridine. Instead, the C=C stretching frequency peak of conjugated polymer backbone around 1575–1662 cm^{-1} became relatively more intense than those of the C=C and C=N stretching frequencies of 3-ethynylpyridine.

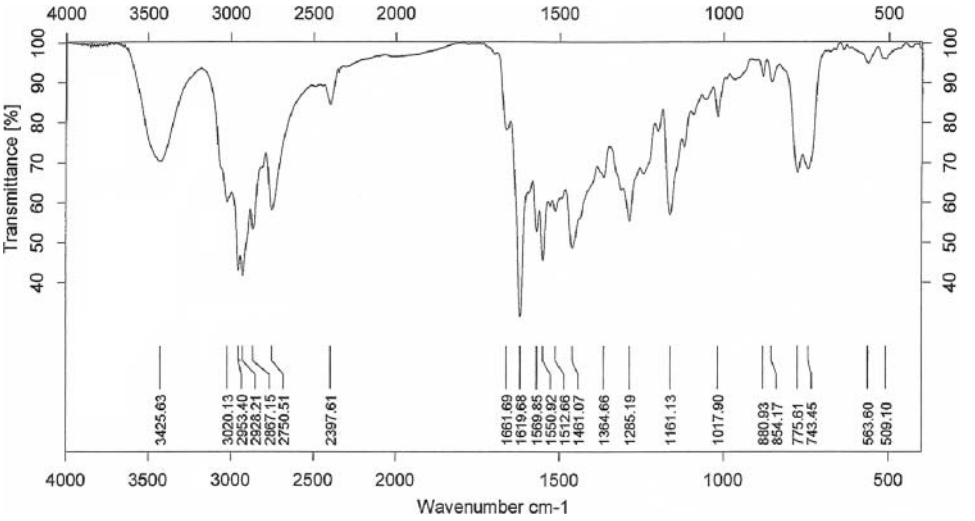


Figure 1. IR spectrum of P3EPPI in KBr pellet.

The ^{1}H-NMR spectrum of P3EPPI showed the aromatic protons of pyridyl moieties and the vinyl protons of the conjugated polymer backbone broadly at 6.3–9.7 ppm. The methyl and methylene proton peaks of pentyl substituents are observed at 0.2–2.0 ppm, whereas the proton peaks of methylene groups adjacent to nitrogen atom of pyridine moieties were seen at 3.8–5.0 ppm. The ^{13}C-NMR spectrum (Figure 2) of P3EPPI showed the aromatic carbon

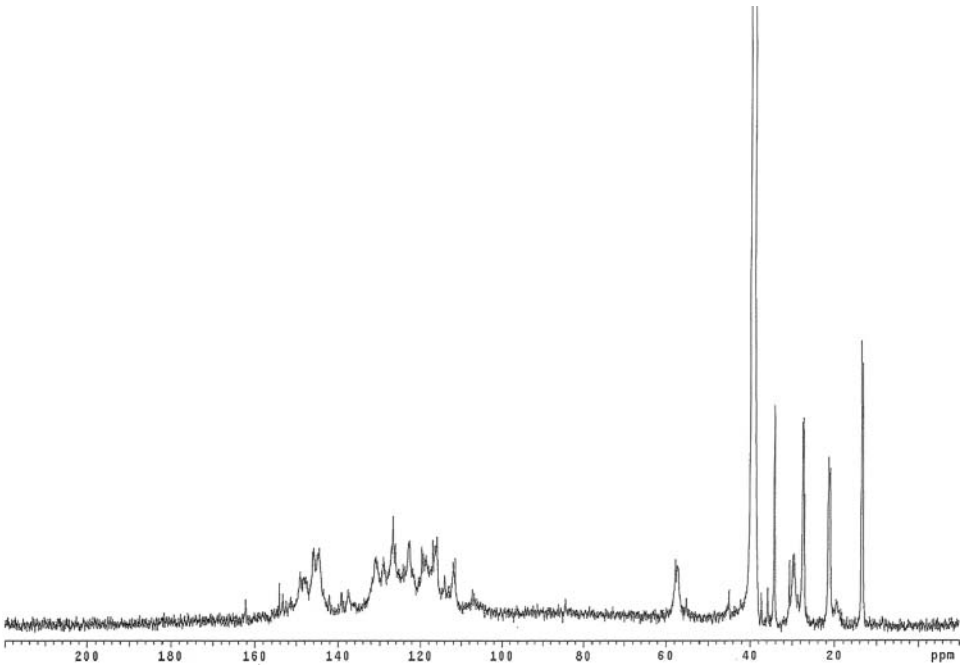


Figure 2. ^{13}C-NMR spectrum of P3EPPI in DMSO-d_6.

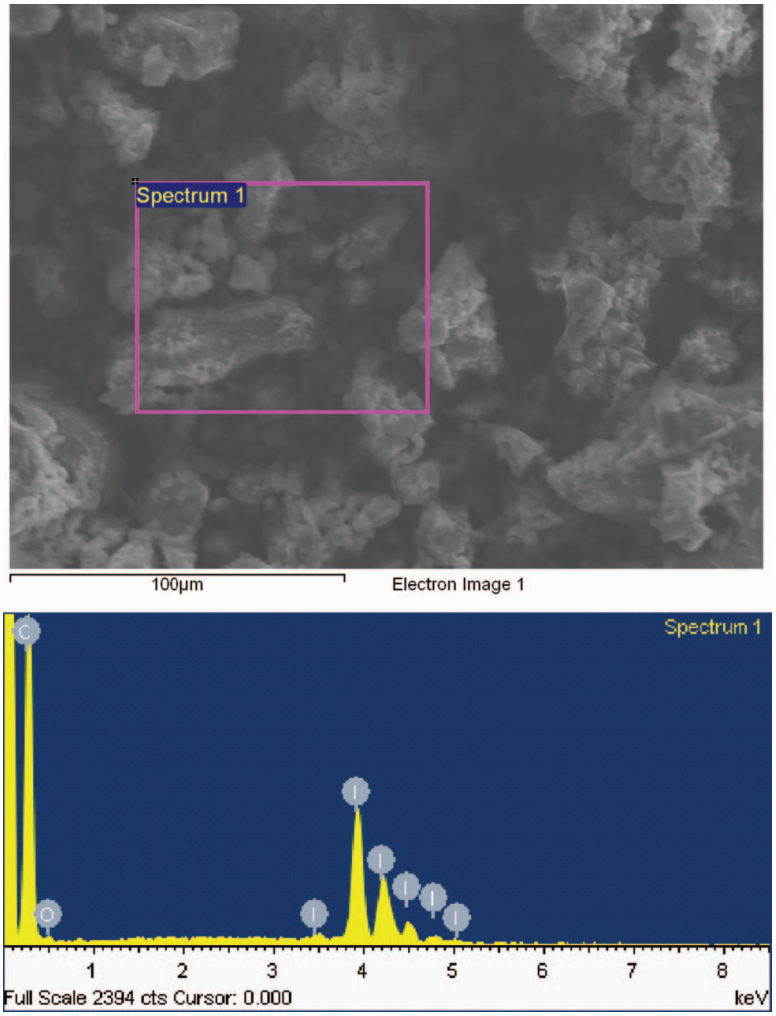


Figure 3. EDX spectrum of P3EPPI powder.

peaks of pyridyl moieties and the vinyl carbons of conjugated polymer backbone at the range of 105–155 ppm. The five carbon peaks of n-pentyl substituent were also observed at 13–58 ppm. The UV-visible spectrum of P3EPPI showed a characteristic absorption band in the visible region (up to 750 nm), which is strong evidence of the presence of the conjugated polyene backbone system. The results from EDX analysis (Figure 3) confirmed the presence of C and I atoms. The multiple peaks of iodine atom means that the iodide ion has different form and/or different environments although now we can not interpret the exact form of iodide atom. P3EPPI was completely soluble in water and such organic solvents as DMF, DMSO, and NMP and the inherent viscosity of P3EPPI was 0.10 dL/g.

We studied the electro-optical and electrochemical properties of P3EPPI by using UV-visible and photoluminescence (PL) spectroscopies and cyclic voltammograms (CV). Figure 4 shows the UV-visible and photoluminescence spectra of P3EPPI solution.

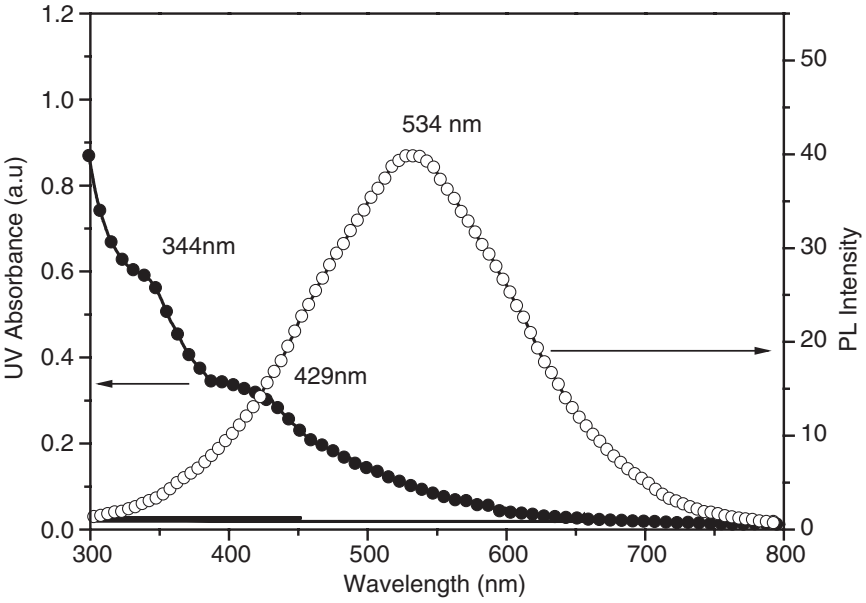
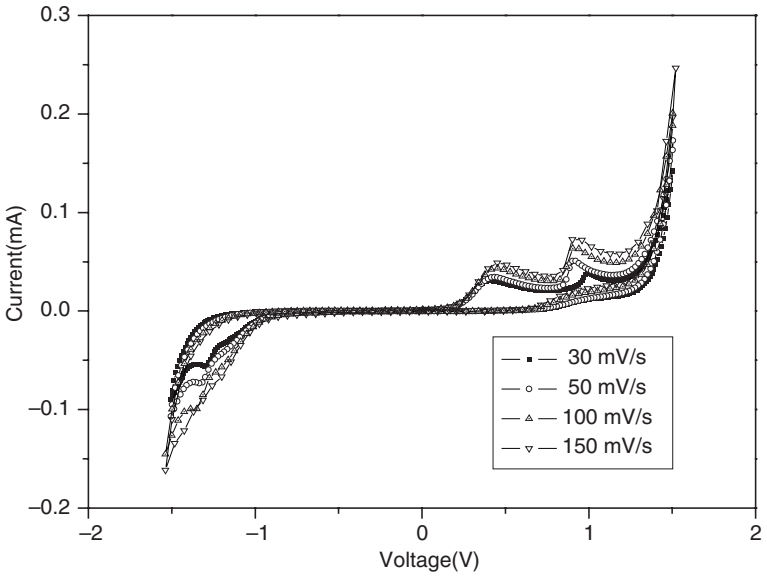


Figure 4. Optical absorption (4.5×10^{-5} wt%, DMF solution) and PL spectrum of P3EPPI (1.44×10^{-5} wt%, DMF solution, excitation wavelength: 429 nm).

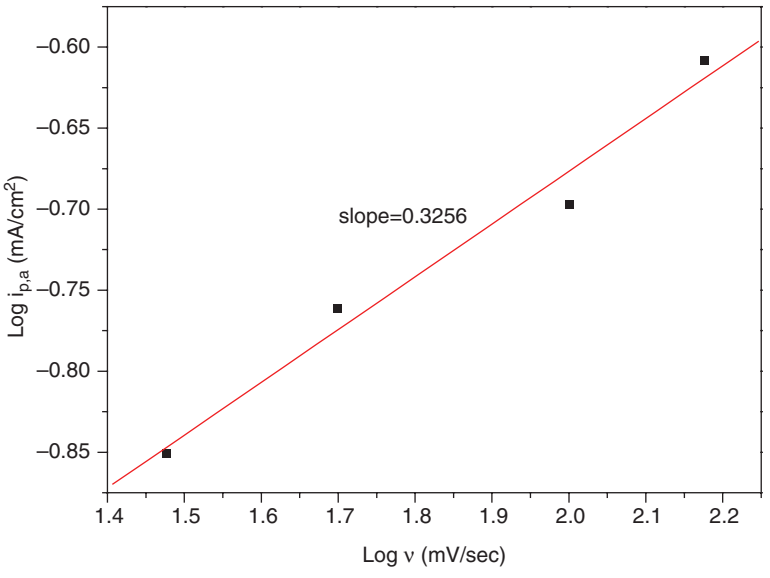
The absorption spectrum starts from 750 nm to shorter wavelength region and exhibits absorption maximum value of 429 nm, which is due to the $\pi \rightarrow \pi^*$ interband transition of these conjugated polymers. The photoluminescence spectra of this ionic conjugated polymer showed broad emission band in the range of 450 nm and 650 nm under the 429 nm excitation and the maximum peak of 534 nm corresponding to the photon energy of 2.32 eV. In our previous study [31], the optical properties of poly(2-ethynyl-N-pentylpyridinium iodide) (P2EPPI) was reported. P2EPPI had same side group, but it includes the different link position between conjugated polyene and pyridinium moiety. P2EPPI has the second carbon site from nitrogen atom in link and P3EPPI links together by the third carbon site. Thus, both of them has different electronic effect based on resonance concept. P2EPPI showed UV-Vis and PL maximum values of 515 and 583 nm and UV-Vis aborption edge of 700 nm. Comparing the maximum wavelength values of UV-Vis and PL data and aborption edge values, P3EPPI was clearly blue-shifted up to 100 nm compared to P2EPPI in all optical data. It is explained by the electronic effect of link position between conjugated polyene and pyridinium group. We believe that the link sites of P2EPPI and P3EPPI include lobe and node state in electron density distribution, respectively. Further study on the electron density calculation such as DFT method is considered.

The electrochemical kinetic behavior through the cyclic voltammograms (CVs) of P3EPPI solution with various scan rates (30 mV/s $\sim$ 150 mV/s) was also investigated as shown in Figure 5 (a). All CV data tendency of P3EPPI was similar to that of P2EPPI. The oxidation and reduction current densities were increased according to the increased scan rates. The stable cyclic voltammograms of P3EPPI from the consecutive scan (up to 30 cycles) was verified.

It means that this material has a stable redox process in TBAP/DMF electrolyte solution. Also, the oxidation of P3EPPI occurred at 0.2 and 0.81 V (*vs* $Ag/AgNO_3$) and these values



(a)



(b)

Figure 5. Cyclic voltammograms of P3EPPI in 0.1M TBAP/acetonitrile solution: (a) various scan rates of 30 mV/sec ∼ 150 mV/sec, (b) plot of log $i_{p,a}$ *vs* log *v* for P3EPPI.

were increased compared to P2EPPI. P2EPPI showed the oxidation at 0.11 and 0.63 V. It means that P3EPPI is not relatively easy oxidation and it needs higher energy to take the electron from polymer in oxidation compared to P2EPPI. It is well matched with the result of blue-shifted maximum and edge values in optical data. P3EPPI exhibited the reproducible electrochemical process in the potential range of -1.53 ∼ 1.50 V *vs* $Ag/AgNO_3$, and there

are two vivid redox peaks. Plot of log $i_{p,a}$ *vs* log *v* for P3EPPI was additionally shown in Figure 5 (b). Empirically, when the slope value is close to 0.5 or 1.0, it means that the kinetics of the redox process can be defined as a diffusion process or electron transfer process [25–27]. This polymer showed that the kinetics of the redox process is close to a diffusion process of electrolyte ion because slope value was 0.3256.

Conclusions

The non-catalyst synthesis of an ionic conjugated polymer was performed by reaction of equal mole ratio of 3-ethynylpyridine and 1-iodopentane without any additional initiator or catalyst. The polymerization of 3-ethynyl-N-pentylpyridinium iodide, monomeric unit, proceeded in mild manner to give the P3EPPI in moderate yield (65%). The activated acetylenic bond of the monomeric salt formed at the initial reaction time is susceptible to the linear polymerization. The chemical structure of P3EPPI was characterized by various instrumental methods to have an ionic conjugated polymer system bearing the designed N-pentyl-3-pyridinium substituents. The photoluminescence spectra of polymer showed that the photoluminescence peak is located at 534 nm, corresponding to a photon energy of 2.32 eV. The cyclic voltammogram of P3EPPI exhibited irreversible electrochemical behavior between the oxidation and reduction peaks, but it showed two vivid 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 P3EPPI *versus* the scan rate.

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