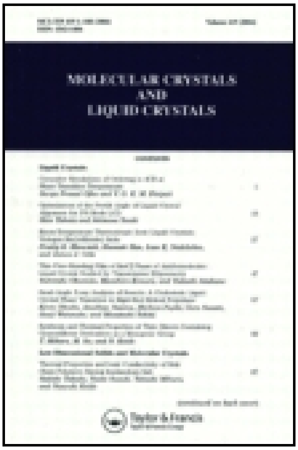

Molecular Crystals and Liquid Crystals

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Electro-Optical and Electrochemical Properties of Poly(2-ethynylpyridine)

Yeong-Soon Gal [a], Han-Na Suh [a], Won-Chul Lee [a], Sung-Ho Jin [b], Jong-Wook Park [c], Won Seok Lyoo [d], Sang-Yeon Shim [e] & Kwon Taek Lim [f]

[a] Polymer Chemistry Laboratory, College of Engineering, Kyungil University, Kyungsan, Korea

[b] Department of Chemistry Education, Pusan National University, Pusan, Korea

[c] Department of Chemistry and Center for Nanotech. Res., The Catholic University, Bucheon, Korea

[d] School of Textiles, Yeungnam University, Gyungsan, Korea

[e] Department of Environmental and Applied Chemical Engineering, Kangneung National University, Gangneung, Korea

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

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Electro-Optical and Electrochemical Properties of Poly(2-ethynylpyridine)

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[1]Polymer Chemistry Laboratory, College of Engineering, Kyungil University, Kyungsan, Korea
[2]Department of Chemistry Education, Pusan National University, Pusan, Korea
[3]Department of Chemistry and Center for Nanotech. Res., The Catholic University, Bucheon, Korea
[4]School of Textiles, Yeungnam University, Gyungsan, Korea
[5]Department of Environmental and Applied Chemical Engineering, Kangneung National University, Gangneung, Korea
[6]Division of Image and Information Engineering, Pukyong National University, Busan, Korea

The electro-optical and electrochemical properties of poly(2-ethynylpyridine) was studied and discussed. Poly(2-ethynylpyridine) was prepared by the polymerization of 2-ethynylpyridine by using the catalyst of WCl_6*-*$EtAlCl_2$*. The photoluminescence (PL) spectra of the polymer showed that the photoluminescence peak is located at 581 nm, corresponding to a photon energy of 2.14 eV. The cyclic voltamograms of polymer exhibited reversible electrochemical behaviors between the doped and undoped peaks. The kinetics of the redox process of polymer was controlled by the diffusion process from the experiment plotting the oxidation current density of polymer versus the scan rate.*

Keywords: 2-ethynylpyridine; catalyst; conjugated polymer; cyclovoltamogram; electro-optical; polyacetylene

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Address correspondence to Prof. Yeong-Soon Gal, Polymer Chemistry Laboratory, College of Engineering, Kyungil University, Hayang 712-701, Kyungsangbuk-Do, Korea. E-mail: ysgal@kiu.ac.kr

1. INTRODUCTION

For many years, considerable research efforts have been dedicated to various types of conjugated polymers because of their extraordinary electronic and optical properties [1–3]. Recently examined applications of conjugated polymers include organic light-emitting diodes (OLEDs), chemical sensors, photovoltaic cells, field-effect transistors, and so on [4–7]. The acetylenic triple bonds have rich π-electrons, which can be polymerized to yield the linear conjugated polymer systems [8]. Polyacetylene (PA), the simplest conjugated polymer, consists of a backbone of carbon atoms, each bonded to one hydrogen atom and connected together by alternating single and double bonds. It can be made free-standing thin film by using Shirakawa catalysts [$Ti(OC_4H_9)_4$-$Al(C_2H_5)_3$] [9]. However, the drawbacks are that this material is thermally unstable and insoluble, making it unsuitable for general use.

More processable conjugated polymers can be prepared by the linear polymerization of substituted acetylenic monomers and by the cyclopolymerization of nonconjugated diynes [8,10–16]. Nitrogen-containing polymers have received unabated attention in the design and synthesis of multifunctional polymers [8,10]. Unlike other π-conjugated polymers, they contain nitrogen heteroatom either in the main chains or in the side chains that provide facile quaternarization reaction and protonation of the nitrogen sites [8,10,17]. In recent years, we reported the studies on the synthesis and characterization of new conjugated cyclopolymer by the cyclopolymerization of dipropargylamine derivative [14].

2-Ethynylpyridine was firstly thermally polymerized to give a low yield of polymer with low molecular weight [18]. For 2- or 3-ethynylpyridine homopolymers with MeI or EtI, mixing the quaternized polymers with LiTCNQ or TCNQ in acetonitrile and refluxing for 30 min yielded a new type of conjugated polymer [19]. Acetylenic pyridine compounds such as ethynylpyridine, dipyridylacetylene, and dipyridyl-diacetylene were known to be polymerized spontaneously by a simple alkyl halide treatment without giving the N-alkyl product, which is similar to the polymer formation from 4-vinylpyridine including cation radical [20]. We have also reported the preparation of various pyridine-based conjugated polymers having different functionalities [10,16,21,22].

In this article, we present the research results on the electro-optical and electrochemical properties of poly(2-ethynylpyridine) prepared by transition metal catalyst.

2. EXPERIMENTAL

2-Ethynylpyridine (2-EP, Aldrich Chemicals, 98%) was vacuum distilled after drying with calcium hydride. WCl_6 (Aldrich Chemicals, 99.9+%) and $EtAlCl_2$ (Aldrich Chemicals) were also used without further purification. The polymerization solvent, chlorobenzene, was dried with calcium hydride and distilled. A typical synthetic procedure of poly(2-EP) is as follows: In a 50 mL reactor equipped with rubber septum, 2.0 g (19.39 mmol) of 2-EP was added. Then the catalyst solution of 3.88 mL of 0.1 M WCl_6 in chlorobenzene and 3.88 mL of 0.1 M $EtAlCl_2$ in chlorobenzene after shaking the catalyst solution at room temperature for 15 min, was injected into the polymerization reactor. After 24 hrs at 80°C, the polymer solution diluted with 10 mL methanol was precipitated into a large excess of ethyl ether. The precipitated polymer was filtered and dried in vacuum oven at 40°C for 24 hrs. The black powder was obtained in 80% yield.

NMR (^{1}H- and ^{13}C-) spectra of polymers were recorded on a Varian 500MHz FT-NMR spectrometer (Model: Unity INOVA) in DMSO-d_6. FT-IR spectra were obtained with a Bruker EQUINOX 55 spectrometer using a KBr pellet. The optical absorption spectra were measured by a HP 8453 UV-visible Spectrophotometer. Electrochemical measurements were carried out with a Potentionstat/Galvanostat Model 273A (Princeton Applied Research). To examine electrochemical properties, 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. 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.

3. RESULTS AND DISCUSSION

We prepared a polyacetylene with pyridyl substituents by the polymerization of 2-EP by using the WCl_6-$EtAlCl_2$ catalyst system, and elucidated the polymer structure by NMR, IR, and UV-visible spectroscopies. The polymer yield and inherent viscosity were 80% and 0.16 dL/g, respectively. This polymer was completely soluble in such polar solvents as methanol, water, and DMF. In the ^{1}H-NMR spectrum of poly(2-EP), as polymerization proceeded, the acetylenic proton peaks of 2-EP at 3.2 ppm disappeared; the broad peaks due to the protons on the conjugated double bonds and aromatic pyridyl protons were observed at 5.6–9.6 ppm. Figure 1 shows ^{13}C-NMR spectrum of poly (2-EP) measured in DMSO-d_6. It showed the vinyl and aromatic pyridyl carbon peaks of polymer at 108–168 ppm. The FT-IR spectrum of poly (2-EP) did not show the acetylenic C=C bond stretching (2110 cm^{-1}) and acetylenic $\equiv C-H$ bond stretching (3293 cm^{-1}) frequencies of 2-EP.

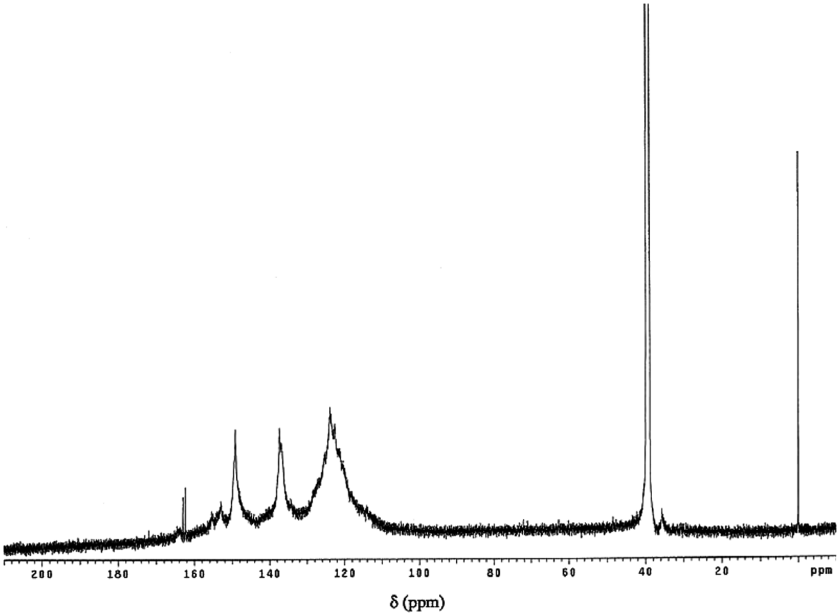

FIGURE 1 ^{13}C-NMR spectrum of poly(2-EP) in DMSO-d_6.

The absorption and photoluminescence spectra of poly(2-EP) were measured and discussed. Figure 2 shows the UV-visible and photoluminescence (PL) spectra of poly(2-EP) solution (0.1 wt%, DMF). In our previous papers [22,23], we had reported the PL spectra of poly(2-ethynyl-N-propagylpyridinium bromide) and poly(2-ethynylpyridinium bromide) having a simple N-hexyl side chain. They showed 708 nm and 603 nm PL maximum values at each excitation wavelength of UV maximum value. It may be believed that the side chain in the conjugated polymer shifts PL maximum value because it has different molecule arrangement. Poly(2-EP) also showed characteristic UV-visible absorption band at 463 nm and shoulder at 513 nm, and this polymer exhibited PL maximum peak at 581 nm corresponding to the photon energy of 2.13 eV. Polyacetylene backbone not including a pyridinium salt showed the relatively short PL maximum value.

We studied the electrochemical kinetic behavior of poly(2-EP) by using the cyclic voltameter. The measured cyclic voltammograms of poly(2-EP) with the various scan rates (30 mV/s∼150 mV/s) are shown in Figure 3(a). The peak potentials are very slightly shifted to higher potentials as the scan rate is increased. Also we have observed very stable cyclic voltammograms of poly(2-EP) from the

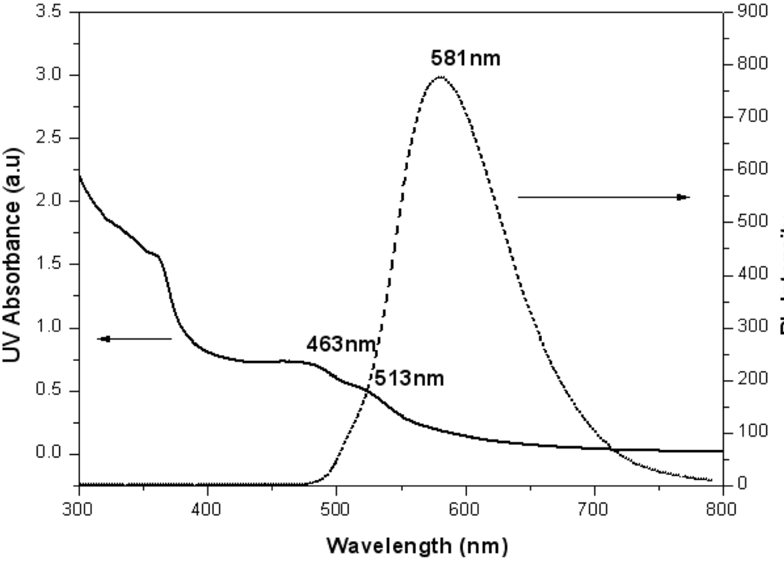

FIGURE 2 Optical absorption and photoluminescence spectra of poly(2-EP) solution.

consecutive scan (up to 30 cycles) in Figure 3(b), which means that this material has relatively stable redox process. In Figure 3, the oxidation of poly(2-EP) was occurred at 0.28 V (vs $Ag/AgNO_3$) and it also showed the irreversible reduction 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(2-EP) is reproducible in the potential range of $-2.5 \sim +1.5$ V vs $Ag/AgNO_3$.

It has been reported that the relationship between the redox peak current and the scan rate can be expressed as a power law type as follows [24,25].

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

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

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

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 $x = 0.5$ [24,26]. Relations satisfying Eq. (2) between the oxidation current density ($\log i_{\mathrm{p,a}}$) and the scan rate ($\log v$) were obtained.

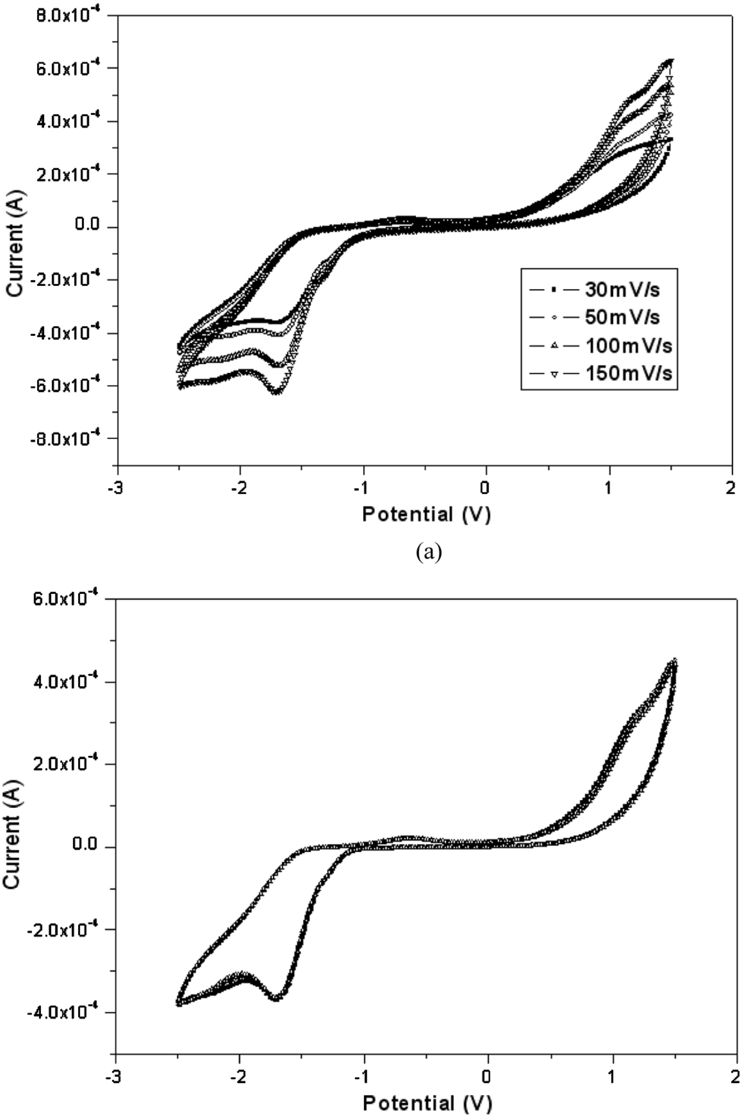

FIGURE 3 Cyclic voltammograms of poly(2-EP) [0.1 M $(n\text{-}Bu)_4NBF_4$/DMF] (a) 30 mV/sec∼150 mV/sec with various scan rates and (b) consecutive 30 scans under 100 mV/s.

The oxidation current density of poly(2-EP) versus the scan rate is approximately linear relationship in the range of 30 mV/sec~150 V/sec. The exponent of scan rate, x value of poly(2-EP), is found to be 0.378. This value means that the kinetics of the redox process may be mainly controlled by the reactant diffusion process [24–26].

4. CONCLUSIONS

In this article, we studied the electro-optical and electrochemical properties of poly(2-EP) prepared by WCl_6-$EtAlCl_2$ catalyst system. This polymer was completely soluble in organic solvents, thus well-processable. The photoluminescence (PL) spectra of poly(2-EP) indicated that the photoluminescence maximum peak is located at 581 nm, which corresponded to the photon energy of 2.13 eV. The cyclovoltamograms of poly(2-EP) exhibited the reversible electrochemical behaviors between the doping and undoping peaks. It was found that the kinetics of the redox process of poly(2-EP) might be mainly controlled by the reactant diffusion process from the experiment of the oxidation current density of poly(2-EP) versus the scan rate. Due to its good solubility and reactivity, this pyridyl-containing polyacetylene has potential as materials for mixed ionic and electronic conductivity, energy storage devices such as batteries, permselective membrane, and light-emitting devices.

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