

# 염화 철(III)을 이용한 2-에티닐피리딘의 *in-situ* 4차염화중합을 통한 이온형 폴리아세틸렌 복합체의 합성과 특성

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## Synthesis and Properties of Ionic Polyacetylene Composite from the *In-situ* Quaternization Polymerization of 2-Ethynylpyridine Using Iron (III) Chloride

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### 초 록

염화 철(III)을 이용한 2-에티닐피리딘의 *in-situ* 4차염화 중합을 통하여 이온성 폴리아세틸렌-염화 철(III) 복합체를 용이하게 합성하였다. 합성한 폴리아세틸렌-염화 철(III) 복합체의 구조를 여러 가지 분석장비를 통해 확인한 결과 설계한 염화 철(III)-피리디늄 치환기를 갖는 공액구조 고분자가 생성되었음을 확인할 수 있었다. 본 중합의 메커니즘은 첫 번째 단계에서 형성된 에티닐피리디늄 염의 중합반응이 개시되고 전파되는 것으로 분석되었다. P2EP-FeCl<sub>3</sub> 복합체의 전기 광학 및 전기화학적 특성을 연구하였다. P2EP-FeCl<sub>3</sub> 복합체의 UV-visible 스펙트럼에서 흡수 최대값은 480 nm 및 533 nm이었고 PL 최대값은 598 nm로 나타났다. P2EP-FeCl<sub>3</sub> 복합체의 순환 전압전류 특성 측정결과 산화 피크와 환원 피크가 비가역적인 전기화학적 거동을 보였으며, 복합체의 산화 환원 과정의 동역학은 스캔 속도 대비 산화 전류 값의 도표부터 확산 제어 프로세스에 가까운 것으로 확인되었다.

### Abstract

An ionic conjugated polymer-iron (III) chloride composite was prepared via *in-situ* quaternization polymerization of 2-ethynylpyridine (2EP) using iron (III) chloride. Various instrumental methods revealed that the chemical structure of the resulting conjugated polymer (P2EP)-iron (III) chloride composite has the conjugated backbone system having the designed pyridinium ferric chloride complexes. The polymerization mechanism was assumed to be that the activated triple bond of 2-ethynylpyridinium salt, formed at the first reaction step, is easily susceptible to the step-wise polymerization, followed by the same propagation step that contains the propagating macroanion and monomeric 2-ethynylpyridinium salts. The electro-optical and electrochemical properties of the P2EP-FeCl<sub>3</sub> composite were studied. In the UV-visible spectra of P2EP-FeCl<sub>3</sub> composite, the absorption maximum values were 480 nm and 533 nm, and the PL maximum value was 598 nm. The cyclic voltammograms of the P2EP-FeCl<sub>3</sub> composite exhibited irreversible electrochemical behavior between the oxidation and reduction peaks. The kinetics of the redox process of composites were found to be very close to a diffusion-controlled process from the plot of the oxidation current density versus the scan rate.

**Keywords:** Conjugated polymer, 2-ethynylpyridine, Iron (III) chloride, Photoluminescence, Cyclic voltammogram

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## 1. Introduction

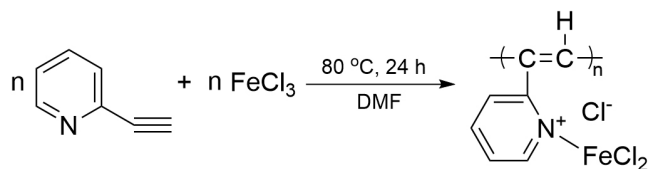
Conjugated organic polymers with alternating  $\pi$ -bonds in their backbone are worth mentioning because they can exhibit unique properties like semiconductivity, photoconductivity, paramagnetism, helix formation, optical nonlinearity, photo- and electroluminescence, and electrochromism[1-10]. The enormous advancement in the knowledge of the chemical and physical properties of organic semiconductors in the last four decades motivates the development of materials for low-cost electro-optical applications such as organic photovoltaic cells (OPVCs)[11-13], organic light emitting devices (OLEDs)[9,14], organic field-effect transistors (OFETs)[15], radio frequency identification (RF-ID) tags[16], nonvolatile memory devices[17], biological and chemical sensors[18,19], and photosensing devices[20].

The development of various effective catalysts enabled the synthesis of functional polyacetylene derivatives through the linear polymerization of monosubstituted and disubstituted acetylenes[21,22] and non-conjugated diynes[23,24]. Catalyst systems composed of group 5 and group 6 transition metal halides and organometallic cocatalysts were successfully applied for the synthesis of various polyacetylenes with different functionalities[21,22]. We also prepared monosubstituted polyacetylenes through the polymerization of the corresponding monomers using W- and Mo-based transition metal chlorides and organometallic cocatalysts[23,25-27].

Organic polyelectrolytes are linear or branched biopolymers in which a substantial portion of the constituent units are ionic or ionizable groups[28]. For centuries, natural polyelectrolytes have attracted attention as thickeners, gums, hydrogels, hydrocolloids, coagulant aid, etc. The building blocks of life, like the nucleic acids and proteins, are polyelectrolytes[29]. Synthetic polyelectrolytes have been also used as thickeners, conditioners, clarifying agents, emulsifiers, and even drag reducers[30-32]. They have been and continue to remain an important topic in scientific research and commercial applications.

Conjugated polyelectrolytes are charged conjugated macromolecules with a large number of ionic groups[28,33]. Various polyacetylene-based polyelectrolytes with ionic substituents have been synthesized via the linear polymerization of the corresponding substituted acetylene[34,35]. The anionic radical TCNQ salt-like complex of the ethynylpyridine polymer was first reported in 1978. The N-methyl or N-ethyl substituted 2- or 3-ethynylpyridinium homopolymers were prepared by the reaction of the corresponding ethynylpyridine with methyl iodide or ethyl iodide, followed by mixing of the quaternized polymers with LiTCNQ or TCNQ in acetonitrile to yield a new type of conjugated polymer[36]. Blumstein et al. reported well-defined polyacetylenes with pyridinium salts. They used quaternizing agents such as alkyl halides, halogens, methanesulfonic acids, and halogenic acids for the polymerization of ethynylpyridines[37,38]. These polyenes contained pyridinium ring substituents associated with halide, methanesulfonate, or trifluoromethanesulfonate counterions.

We reported the synthesis of new self-doped conjugated polyelectrolytes by the uncatalyzed polymerization of 2-EP using cyclic compounds such as 2-sulfobenzoic acid cyclic anhydride and 1,4-buta-



Scheme 1. *In-situ* synthesis of P2EP-iron(III) chloride composite.

nesultone, and propiolactone[39-41]. In addition, we synthesized various conjugated polyelectrolytes with functional pyridinium substituents and determined their properties[42-45].

Polyacetylenes with functional pyridinium substituents have been used for preparing intercalated nanocomposite films[46], hybrid polymer gels[47], nanocrystalline CdS polymer sensitizers[48], silver-polymer nanocomposites[49], nonvolatile memory devices[17], and electrolytes and cathode interfacial layers for organic solar cells[50,51].

To date, the quaternization reactants for the polymerization of ethynylpyridines have mostly been halogens, haloalkanes, carbonyl chlorides, etc. We have become interested in the quaternization polymerization of ethynylpyridines using inorganic Lewis acid forms. Herein, we report the facile *in situ* synthesis of a conjugated polymer composite through the polymerization of 2-EP using iron (III) chloride (Scheme 1). The chemical structure and physical properties of the resulting conjugated polymer-iron (III) chloride composite are measured and discussed.

## 2. Experimental

### 2.1. Materials and instruments

2-EP was obtained from Sigma-Aldrich and vacuum distilled after drying with  $\text{CaH}_2$  (85 °C/12 mmHg) before use[52]. Iron (III) chloride (Aldrich Chemicals., anhydrous powder, 99.99+%) was used as received. The other chemicals, unless otherwise stated, were obtained from commercial sources and used as received.

$^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra were obtained using a Varian 500 MHz FT-NMR spectrometer (Model: Unity INOVA) in  $\text{DMSO-d}_6$  (dimethyl sulfoxide- $\text{d}_6$ ) solutions at room temperature and the chemical shifts are recorded in ppm units with internal tetramethylsilane standard. The infrared spectra of samples were recorded in KBr pellets with the half of a Bruker EQUINOX 55 Fourier transform infrared spectrophotometer. The inherent viscosity measurements of polymers were made in anhydrous DMF (dimethylformamide) at 30 °C with a concentration of 0.5 g/dL. X-ray diffraction patterns of composites were obtained with a PHILLIPS X-ray diffractometer (Model: XPert-APD) using Ni-filtered  $\text{Cu } \alpha$  radiation. The SEM/EDX studies were performed with the Hitachi JEOL system (S-4200). The electrical conductivity of polymer composite was determined by using a standard four-point probe measurement of the sample pellets with a Hewlett-Packard 3490 multimeter and a Keithley 616 Digital Electrometer. UV-visible absorption spectra were obtained by a HP 8453 UV-visible spectrophotometer in DMF. The photoluminescence spectra of poly-

mers were obtained by a Perkin Elmer luminescence Spectrometer LS55 (Xenon flash tube) equipped with a lock-in amplifier system in a chopping frequency of 150 Hz. Electrochemical behaviors of polymers were studied with a Potentionstat/Galvanostat Model 273A(Princeton Applied Research). The solutions of samples were prepared and the electrochemical measurements of polymer were performed under 0.1 M acetonitrile solution of tetrabutylammonium perchlorate (TBAP). ITO, Ag/AgNO<sub>3</sub>, and platinum wire were used as a working, reference and counter electrode, respectively.

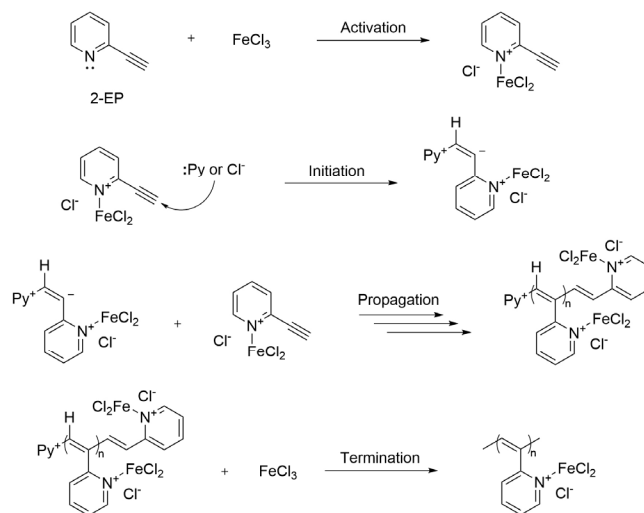
## 2.2. *In-situ* preparation of poly(2-ethynylpyridine) [P2EP]-iron(III) chloride composite

Poly(2-ethynylpyridine) [P2EP]-iron (III) chloride composite was prepared by the uncatalyzed *in-situ* quaternization polymerization of 2-EP using iron (III) chloride. The reaction was carried out in a 100 mL round-bottom flask with a magnetic stirrer as follows. After the reactor was charged with 30 mL of DMF ( $[M]_0 = 0.30$ ), 2-EP (1.0 g, 9.7 mmol), and iron (III) chloride (1.57 g, 9.7 mmol), the reaction mixture was warmed to 80 °C and stirring was continued for 24 h under nitrogen atmosphere. The color of reaction mixture was changed from the initial light brown, dark brown, and black, successively, accompanied with release of considerable heat. After polymerization time, the reaction solution was diluted with additional DMF and precipitated into an excess amount of ethyl ether, followed by filtration. The collected black products were dried overnight under vacuum oven at 40 °C. Finally, the P2EP-FeCl<sub>3</sub> composite was obtained in 93 % yield.

## 3. Results and discussion

A new family of substituted ionic conjugated polymers has been synthesized by the uncatalyzed polymerization of ethynylpyridines using quaternizing agents such as halogens, alkyl halides, methanesulfonic acids, and halogenic acids[37,38]. The acetylenic functional groups of pyridinium compounds such as ethynylpyridinium salts, dipyridinium acetylene salts, and dipyridinium diacetylene salts, which were formed by quaternization via the Menshutkin reaction or by the formation of donor-acceptor complexes with alkyl halides[38], can be activated to the nucleophilic attack of the nucleophiles produced following the linear polymerization, yielding the ionic conjugated polymers with the designed functional groups[37,43,44]. Because this polymerization reaction does not need any additional initiator or catalyst, which is commonly used in other polymerization reactions, this method can prevent sample contamination caused by such catalysts or initiators.

In this study, we used the quaternization polymerization method for preparing ionic conjugated polymer-iron (III) chloride composite. An equimolar mixture of 2-EP and iron (III) chloride in DMF was exposed to an 80 °C oil bath. The polymerization proceeded well in a homogeneous manner under this reaction condition. As the reaction proceeded, the initial light brown color of the reaction mixture successively changed into a black color, with the reaction solution becoming more viscous. The black P2EP-iron (III) chloride composite was obtained in 93% yield.



Scheme 2. Proposed polymerization mechanism.

The nature of this polymerization was very similar to that of the polymerization of 2-EP using propargyl bromide[42] and methyl iodide [54]. The quaternization polymerizations of ethynylpyridines initially involved the quaternization of 2-ethynylpyridine by alkyl halides [37,42,44]. The present *in situ* quaternization polymerization also involved the formation of 2-ethynyl-N-iron (III) dichloropyridinium chloride. The initiation step of polymerization involved a nucleophilic attack by the nitrogen atom of 2-ethynylpyridine and/or the chloride anion on the activated electrophilic acetylenic functional group of 2-ethynyl-N-iron (III) dichloropyridinium chloride[43]. The monomeric 2-ethynyl-N-iron (III) dichloropyridinium chlorides formed after the first step were susceptible to the consecutive propagation reaction. Finally, the polymerization reaction was terminated by a reaction of the propagating macroanionic ends with iron (III) chloride and/or other components. The proposed mechanism is shown in Scheme 2. The resulting conjugated polymer complex was completely soluble in water and in organic solvents such as DMF, NMP (N-methyl-2-pyrrolidone), and DMSO. The inherent viscosity of the P2EP-iron(III) chloride composite was 0.16 dL/g.

The chemical structure of the P2EP-iron (III) chloride composite was characterized by FT-IR, <sup>1</sup>H- and <sup>13</sup>C-NMR, and UV-visible spectroscopies. The <sup>1</sup>H-NMR spectrum of the P2EP-iron (III) chloride composite showed only broad proton peaks in the range of 6.3~10.1 ppm, while the corresponding <sup>13</sup>C-NMR spectrum showed aromatic pyridyl carbon peaks of the pendant groups and vinyl carbon peaks of the conjugated polymer main chain in the range of 130~200 ppm. Figure 1 shows the FT-IR spectrum of the P2EP-iron (III) chloride composite in a KBr pellet. Bands due to acetylenic ≡C-H bond stretching (3293 cm<sup>-1</sup>) and C≡C bond stretching (2110 cm<sup>-1</sup>) of 2-EP did not appear in the FT-IR spectrum. The aromatic and vinyl =C-H stretching bands were observed at 3083 cm<sup>-1</sup>. The UV-visible spectrum of the P2EP-iron (III) chloride composite showed only a broad absorption band in the visible region (up to 800 nm), indicating the formation of the conjugated backbone system. The SEM/EDX analysis (Figure 2) of

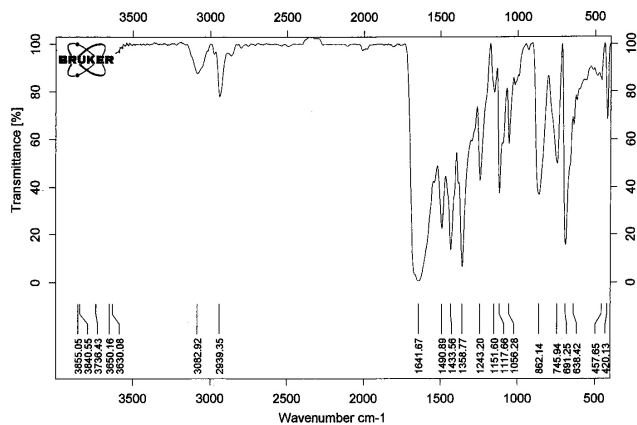


Figure 1. FT-IR spectrum of P2EP-iron(III) chloride composite in KBr pellet.

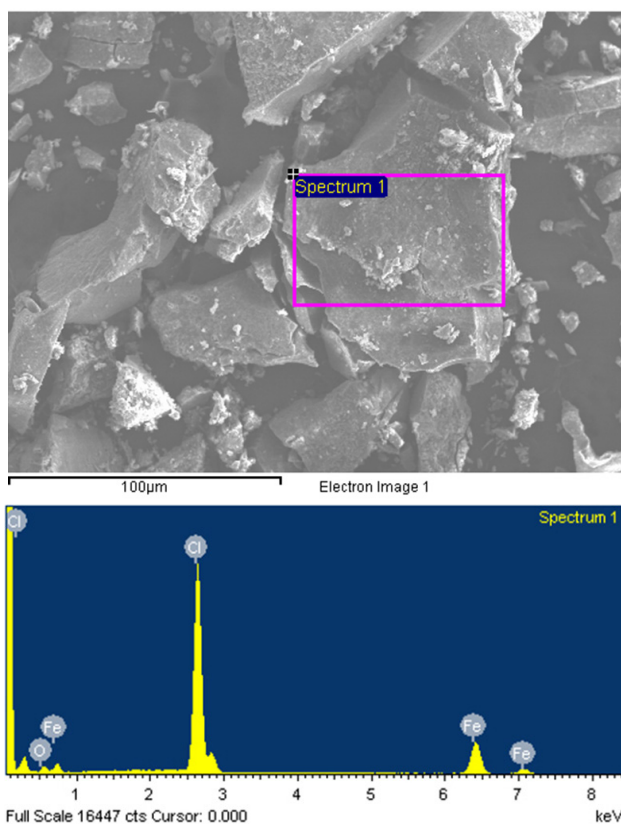


Figure 2. EDX spectrum of P2EP-iron(III) chloride composite powder.

the P2EP-iron (III) chloride composite confirmed the presence of Fe and Cl atoms in different environments.

The electrical and electro-optical properties of the P2EP-iron (III) chloride composite were measured. The electrical conductivity of the composite pellet was  $2.1 \times 10^{-3}$  S/cm. This value was very similar with that of iodine-doped poly(2-ethynylpyridine) ( $5.0 \times 10^{-3}$  S/cm)[55]. The X-ray diffraction pattern of a powdery sample of the P2EP-iron (III) chloride composite showed broad peaks, with the ratio of the half-height width to diffraction angle ( $\Delta 2\theta/2\theta$ ) being greater than 0.35[21,43]. This suggested that the material was amorphous.

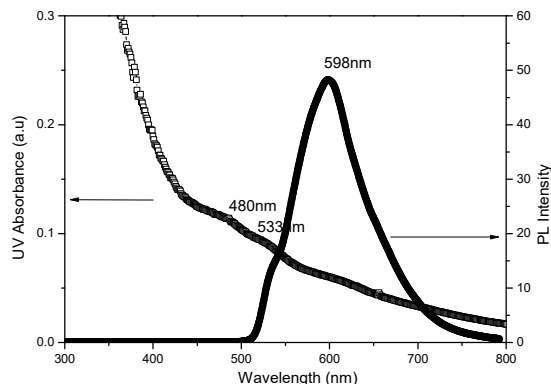


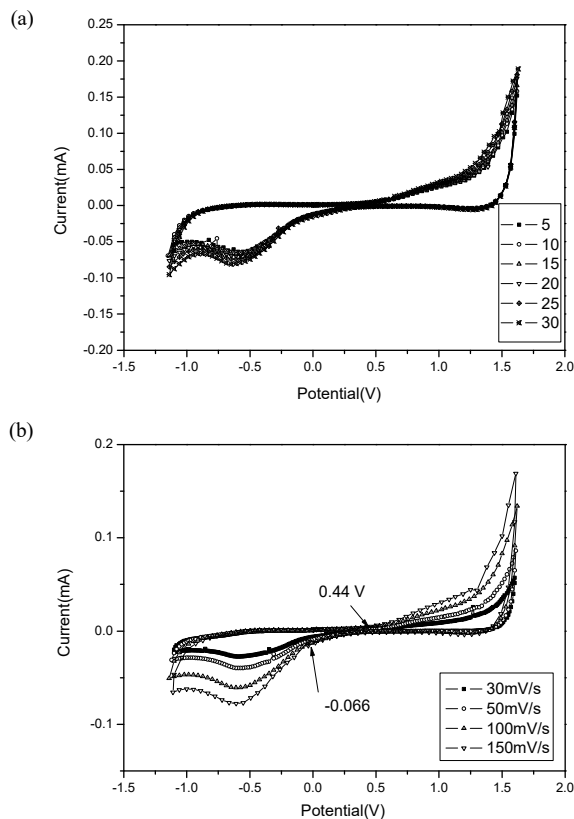
Figure 3. Optical absorption and photoluminescence spectra of P2EP-iron(III) chloride composite.

Figure 3 shows the optical absorption and photoluminescence (PL) spectra of the P2EP-iron (III) chloride composite solution (0.0038 wt. %) in DMF. In our previous study[56], we have shown that P2EP exhibits UV maxima at 463 and 513 nm and a PL maximum at 581 nm. However, as shown in Figure 3, when iron (III) chloride was incorporated in P2EP, the optical maximum values were shifted to longer wavelengths. The UV maxima shifted to 480 and 533 nm, respectively, while the PL maximum shifted to 598 nm. This shifted can be attributed to the fact that the P2EP-iron (III) chloride composite has a more extended  $\pi$ -conjugation than P2EP itself. Notably, the UV and PL maxima shifted by 17 nm.

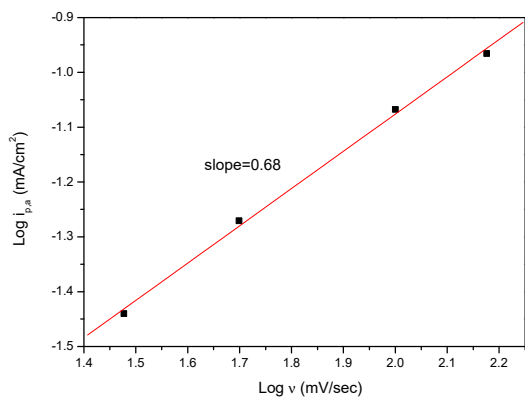
In order to characterize the electrochemical properties of the P2EP-iron (III) chloride composite, cyclic voltammograms were recorded according to the consecutive scan at various scan rates (30~150 mV/s). Figure 4 shows the cyclic voltammograms of the P2EP-iron (III) chloride composite. Typical cyclic voltammograms obtained at a scan rate of 100 mV/s are presented in Figure 4(a). It is evident that the shape of the cyclic voltammograms was almost unchanged. Thus, we concluded that the P2EP-iron (III) chloride composite was very stable and did not undergo severe degradation up to 30 consecutive scan cycles. Figure 4(a) shows that the oxidation of the P2EP-iron (III) chloride composite occurred at 0.44 V (vs. Ag/AgNO<sub>3</sub>) and the irreversible reduction of this material occurred at -0.066 V. Thus, the electrochemical process of this composite was reproducible in the potential range from -1.1 to 1.6 V vs. Ag/AgNO<sub>3</sub>. As shown in Figure 4(b), the current value increased with increasing scan rate. Comparison of the cyclic voltammogram data of P2EP-iron (III) chloride and P2EP revealed that the reduction peak potential of the composite clearly decreased to approximately -0.5 V, while the corresponding value for P2EP was more than -1.5 V[54,56]. This suggested that the iron (III) chloride facilitated the formation of a pyridinium cation in the polymer unit, unlike P2EP, and the former could easily accept electrons during the reduction scan.

The relationship between the redox peak current and scan rate can be expressed as a power law[57,58]:

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



**Figure 4.** Cyclic voltammograms of P2EP-iron(III) chloride composite in 0.1M TBPA/acetonitrile solution: (a) consecutive scans (5 cycles, 10 cycles, 15 cycles, 20 cycles, 25 cycles, 30 cycles), (b) various scan rates of 30 mV/sec ~150 mV/sec.



**Figure 5.** Plot of  $\log i_{p,a}$  vs.  $\log v$  for P2EP-iron(III) chloride composite.

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

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

Considering that the electrode kinetics satisfy Eq (1), the electrochemical redox reaction can be controlled either by the electron transfer process, where  $x = 1$ , or by the reactant diffusion process, where  $x = 0.5$ .

Figure 5 shows the plot of the oxidation current density ( $\log i_{p,a}$ ) as a function of the scan rate ( $\log v$ ) for the P2EP-iron (III) chloride composite. This plot was approximately linear in the range of 30~150 mV/s, and the exponent of the scan rate,  $x$ , was found to be 0.68. Thus, the kinetics of this redox process were very close to those of a diffusion-controlled process. Additionally, the scan rate exponent of P2EP was 0.378[56]. Thus, the P2EP-iron (III) chloride composite was relatively more active than P2EP.

## 4. Conclusions

An ionic conjugated polymer (P2EP)-iron (III) chloride composite was conveniently prepared by the *in-situ* quaternization polymerization of 2-EP using iron (III) chloride. The activated acetylenic triple bond of the monomeric pyridinium salts formed in the initial reaction step was susceptible to the consecutive propagation step. The polymerization reaction was terminated by a reaction between the macroanionic species and iron (III) chloride and/or other components. This material was completely soluble in water and in organic solvents such as DMF, NMP, and DMSO. The PL spectra of the P2EP-iron (III) chloride composite showed a PL maximum at 598 nm, which corresponded to a photon energy of 2.08 eV. Cyclic voltammograms of this composite indicated irreversible electrochemical behavior based on the oxidation and reduction peaks. The P2EP-iron (III) chloride composite was more electrochemically active than P2EP.

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