



# Conjugated organic polymer-based materials from the activated polymerization of 2-ethynylpyridine using naphthoyl chlorides



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## ABSTRACT

New ionic conjugated polymers with naphthoyl functional groups, poly[2-ethynyl-*N*-(1-naphthoyl)-pyridinium chloride] (PE1NPC) and poly[2-ethynyl-*N*-(2-naphthoyl)-pyridinium chloride] (PE2NPC) were prepared via the uncatalyzed polymerization of 2-ethynylpyridine using 1- and 2-naphthoyl chlorides. The polymerization proceeded well under mild reaction conditions to provide a high yield of the polymer. The polymer structure was characterized by such instrumental methods as NMR (<sup>1</sup>H- and <sup>13</sup>C-), IR, and UV–visible spectroscopies and was shown to have a conjugated polymer backbone system having *N*-(naphthoyl)pyridinium chloride as substituents. The electrical conductivities of iodine-doped PE1NPC and PE2NPC were  $7.2 \times 10^{-3}$  S/cm and  $3.5 \times 10^{-3}$  S/cm, respectively. UV–Vis. absorption maximum values were 394, 478, 523 nm for PE1NPC and 394, 478, 527 nm for PE2NPC, respectively. Also, photoluminescence maximum peaks of PE1NPC and PE2NPC were located at 589 and 590 nm which corresponds to the photon energy of 2.1 eV. The cyclovoltammograms of two compounds exhibited the electrochemically stable window at a –1.25 to 1.75 V region. It was found out that HOMO, LUMO levels and the band gap were measured at 4.98 eV, 2.84 eV, 2.14 eV for PE1NPC, and 4.92 eV, 2.74 eV, 2.18 eV for PE2NPC, respectively.

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## 1. Introduction

Conjugated polymers have potential as materials for preparing devices based on nanoscopic molecular architectures because they exhibit electrical, electronic, magnetic, and optical properties similar to those of metals or semiconductors while maintaining the flexibility and ease of processibility of polymers [1–7]. These polymers are widely studied for applications in light-emitting devices [8,9], photovoltaic cells [10–13], nonvolatile memory devices [14], biological and chemical sensors [15–17], and field effect transistors (FETs) [18,19].

Polyacetylene is the best-known conjugated polymer, in which its doped form shows high conductivity that stands in comparison with that of copper [20]. Unfortunately, applications of this promising material have remained limited because the polymer is insoluble, infusible, and thermally unstable. In order to overcome

these problems, various substituted polyacetylenes were synthesized using various catalyst systems, including transition metal complexes and Lewis acids [1–3,21,22]. The polymers with a conjugated backbone are expected to exhibit unique properties such as electrical conductivity, paramagnetism, photoluminescence, nonlinear optical susceptibility, high gas permeability, color, chemical reactivity and complex formation ability [1,2].

Polyelectrolytes are charged macromolecules containing large numbers of ionic substituents appended to the polymer backbone [23]. Especially, ionically conducting polymers (conjugated polyelectrolytes) are of great interest because they exhibit ionic conductivity in a flexible but solid membrane. Ionic conductivity is different to the electronic conductivity of metals and conjugated polymers, since current is carried through the movements of ions. Such ionic polyacetylenes as the triethylammonium salt of poly(6-bromo-1-hexyne) [24], poly(dihexyldipropargylammonium salt)s [25,26], polyacetylene with viologen groups [27], and poly(-propargylpyridinium bromide) [28,29] had been reported. During the past two decades, a new type of ionic polyacetylenes with

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extensive conjugation has been prepared through the activated polymerization of ethynylpyridines by using bromine, FeCl<sub>3</sub>, or various alkyl halides [30–37]. This conjugation system was achieved by introducing one or two ionic charges into each repeating unit, thus endowing such conjugated polymers with some of the highest charge densities known. We have reported the synthesis and characterization of self-doped ionic conjugated polymers, poly(2-ethynylpyridinium-*N*-benzoylsulfonate) and poly[2-ethynyl-*N*-(propanesulfonate)pyridinium betaine]. These materials were prepared via the activated polymerization of 2-ethynylpyridine with the ring-opening of 2-sulfobenzoic acid cyclic anhydride and 1,3-propanediol cyclic sulfate, respectively [38,39]. Pyridine-containing ionic polyacetylenes have been used for the fabrication of fluorescence quenchers for fluorescent biotin-functionalized Lucifer Yellow dyes [40], intercalated nanocomposite films [41], hybrid polymer gels [42], nanocrystalline CdS polymer sensitizer [43,44], silver-polymer nanocomposites [45], and nonvolatile memory devices [14].

Here, we report on the synthesis of new ionic conjugated polymers with two aromatic functional groups by the activated polymerization of 2-ethynylpyridine using 1- and 2-naphthoyl chlorides, including characterization for the chemical structure and the physical properties of the resulting polymer.

## 2. Experimental

### 2.1. General information

NMR spectra were recorded at room temperature in 5–10% DMSO-*d*<sub>6</sub> solutions using a Varian 500 MHz FT-NMR spectrometer (Model: Unity INOVA), where 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. CHN analyses were carried out with a Carlo Erba model 1106 elemental analyzer. The inherent viscosities of polymers were determined at a concentration of 0.5 g/dL in DMF at 30 °C. Thermogravimetry (TG) was performed under a nitrogen atmosphere at a heating rate of 10 °C/min with a Q600 (TA Instruments) thermogravimetric analyzer. The optical absorption spectra were measured by using a HP 8453 UV–VIS–NIR spectrometer. Energy dispersive X-ray (EDX) analyses were performed by Hitachi JEOL system (S-4200). The electrical conductivity of the sample was determined by using a standard four-point probe measurement without extensive pumping of the doped pellets with a Hewlett-Packard 3490 multimeter and a Keithley 616 Digital Electrometer. Conductivity was calculated from the measured resistance of the sample [46]. The chemical composition of iodine-doped polymer samples was determined by the weight uptake method.

A Perkin Elmer luminescence spectrometer LS50 (Xenon flash tube), utilizing a lock-in amplifier system with a chopping frequency of 150 Hz, was used for photoluminescence spectroscopy. The redox potential of the polymer was determined by cyclic voltammetry (CV) using an EG&G 362 electrochemical workstation with a scanning rate of 100 mV/s or various other scan rates of 30–120 mV/s. The polymer was dissolved in acetonitrile (AN) with 0.1 M tetrabutylammonium tetrafluoroborate as an electrolyte. A platinum working electrode and saturated Ag/AgNO<sub>3</sub> reference electrode were used. Ferrocene was used for potential calibration (all reported potentials are reference against ferrocene/ferrocenium, FOC).

### 2.2. Materials

2-Vinylpyridine (Aldrich Chemicals., 97%), bromine (Aldrich Chemicals., 99.5+%), sodium amide (Aldrich Chemicals., tech., 90%),

1-naphthoyl chloride (97%) and 2-naphthoyl chloride (98%) were received from Aldrich Chemicals and used as received. 2-Ethynylpyridine was prepared by the bromination of 2-vinylpyridine and the consecutive dehydrobromination reaction according to the literature method [47].

### 2.3. Polymer synthesis

An ionic polyacetylene with the pendent *N*-naphthoyl pyridinium moieties was synthesized by the activated polymerization of 2-ethynylpyridine using naphthoyl chloride without any additional initiator or catalyst as follows. In a 100 mL two-neck flask equipped with rubber septum and purified nitrogen inlet-outlet, DMF (20 mL, [M]<sub>0</sub> = 0.75 M), 2-ethynylpyridine (2.0 g, 19.4 mmol), and 1-naphthoyl chloride (3.70 g, 19.42 mmol) were added into the reactor. The reaction was carried out at 60 °C oil bath. As the reaction proceeded, the color of reaction mixture was changed from light-brown of the initial mixture into a viscous dark red. After 24 h, the resulting polymer solution was diluted with a small amount (about 10 mL) of DMF and was precipitated into a large excess amount of ethyl ether. The precipitated polymer was collected by filtration and dried under vacuum at 40 °C for 24 h. The black polymer powder was obtained in 83% yield.

## 3. Results and discussion

The polymerization of ethynylpyridine derivatives had been performed with various transition metal catalysts [28,48]. The uncatalyzed polymerization of ethynylpyridine using bromine, FeCl<sub>3</sub>, and alkyl halides is a facile synthetic method utilized for preparing ionic polyacetylenes containing long sequences of conjugated double bonds in the backbone with ionic charges adjacent to, or in conjugation, with them [30–37]. Thus, this uncatalyzed polymerization reaction originally eliminate impurities which may originate from either the catalyst or the initiator used in other polymerization systems.

New ionic polyacetylenes (PE1NPC and PE2NPC) with pendant naphthoyl groups, were prepared through the uncatalyzed polymerization of 2-ethynylpyridine using 1-naphthoyl chloride and 2-naphthoyl chloride, respectively (Scheme 1).

The uncatalyzed polymerization of 2-ethynylpyridine using naphthoyl chloride proceeded easily in a homogeneous manner to provide the corresponding polymer in high yields (1-naphthoyl chloride: 83%, 2-naphthoyl chloride: 87%). As the reaction proceeded, the solution became viscous and the color of reaction mixture was changed from the light brown of the initial mixture into dark brown. Table 1 shows the polymerization results of 2-ethynylpyridine using 1- and 2-naphthoyl chloride. As shown in this table, the polymerization process proceeded well in regards to such polar organic solvents as DMF, DMSO, NMP, and pyridine. The polymerization behavior of 2-ethynylpyridine by using 1- and 2-naphthoyl chlorides was very similar.

This polymerization reaction involves quaternarization of pyridine nitrogen in 2-ethynylpyridine. Although the monomeric salt, 2-ethynyl-*N*-naphthoylpyridinium chloride, has a highly bulky substituent, this polymerization proceeded easily in a relatively low temperature (60 °C) similarly to those of the polymerizations by using simple alkyl halides such as propargyl bromide, bromoacetic acid, and 1-(2-bromoethyl)pyrrole [32,35,36]. It means that the acetylene functional groups in the *N*-carbonyl compounds of 2-ethynylpyridine are activated for the linear acetylene polymerization. It contains the first quaternarization of 2-ethynylpyridine by naphthoyl chlorides. The initial step involves a nucleophilic attack by the nitrogen atom of unreacted 2-ethynylpyridine and/or the chloride anion on the electrophilic *N*-ethynyl triple bond of the

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