

Synthesis, Structural and Spectral Properties of an Ionic Polyacetylene: Poly[*N*-(5-nitro-2-furanmethylene)-2-ethynylpyridinium bromide]

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ABSTRACT: A new ionic polyacetylene was prepared by the activation polymerization of 2-ethynylpyridine with 2-(bromomethyl)-5-nitrofurane in high yield without any additional initiator or catalyst. This polymerization proceeded well in a homogeneous manner to give a high yield of the polymer (92%). The activated acetylenic triple bond of *N*-(5-nitro-2-furanmethylene)-2-ethynylpyridinium bromide, formed in the first quaternization process, was found to be susceptible to linear polymerization. This polymer was completely soluble in such polar organic solvents as dimethylformamide, dimethyl sulfoxide, and *N,N*-dimethylacetamide. The inherent viscosities of the resulting polymers were in the range 0.12–

0.19 dL/g, and X-ray diffraction analysis data indicated that this polymer was mostly amorphous. The polymer structure was characterized by various instrumental methods to have a polyacetylene backbone structure with the designed substituent. The photoluminescence peak was observed at 593 nm; this corresponded to a photon energy of 2.09 eV. The polymer exhibited irreversible electrochemical behaviors between the doping and undoping peaks. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 987–992, 2011

Key words: conjugated polymers; FT-IR; luminescence; synthesis; UV-vis spectroscopy

INTRODUCTION

π -Conjugated polymers have great potential in the fields of electronic and photonic devices, such as in polymer light-emitting diodes, organic photovoltaic cells, and organic thin film transistors.^{1–5} The presence of carbon–carbon alternating double bonds in the polymer main chains endows such unique properties as conductivity, nonlinear optical properties, magnetic properties, image patterning, chemical sensing, gas permeability, photoluminescence (PL), and electroluminescence.^{6–12}

Various types of conjugated polymers, such as polyacetylenes, polypyrroles, polythiophenes, poly(phenylene vinylene)s, and poly(9,9-dialkylfluorene)s, have been designed and prepared.^{6–12}

The structurally simplest conjugated polymer, polyacetylene, is a prototypical conjugated material, which exhibits metallic conductivity upon chemical doping.¹³ This finding has spawned an exciting area of research on synthetic metals. Nevertheless, some drawbacks (e.g., lack of processability, insufficient stability toward oxygen) thus far have prevented commercial applications of polyacetylene itself. Many research groups have worked on the synthesis of substituted polyacetylenes to explore their potential in the creation of functional polymers.

The great progress of various transition-metal-based polymerization catalysts has enabled the synthesis of a wide variety of polymers from substituted acetylenic monomers, including monosubstituted and disubstituted acetylenes,^{6,12} and nonconjugated diynes.^{8,11,14,15} Various catalyst systems based on groups 5 and 6 transition-metal halides and various organometallic cocatalysts have been developed for the polymerization of a broad range of acetylenic monomers with different functionalities.^{6,8,10,16} We

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have also prepared monosubstituted functional polyacetylenes from the polymerization of corresponding monomers with groups 5 and 6 transition-metal halides and various organometallic cocatalysts.^{8,11,15}

Natural polyelectrolytes have been used in water-cleaning processes for centuries. The very building blocks of life, the nucleic acids and proteins, are polyelectrolytes. Synthetic polyelectrolytes have been and continue to be a very active area of scientific research and commercial growth. Conjugated polyelectrolytes are charged conducting macromolecules containing a large number of ionizable or ionic groups.^{17,18} Various substituted ionic polyacetylenes have been prepared by the linear polymerization of the corresponding acetylene monomers.¹⁹ Notably, 2-ethynylpyridine was first thermally polymerized to give a low yield of polymer with a low molecular weight.²⁰ For 2-ethynylpyridine or 3-ethynylpyridine homopolymers with methyl iodide or ethyl iodide, the mixture of the quaternized polymers with lithium tetracyanoquinodimethane or tetracyanoquinodimethane in acetonitrile and refluxing for 30 min yielded a new type of conjugated polymer.²¹

Subramanyam and Blumstein^{22,23} prepared well-defined ionic polyacetylenes through the activated polymerization of ethynylpyridines with alkyl halides. They prepared new conjugated ionic polymers by the reaction of ethynylpyridines with alkyl halides, methanesulfonic acids, halogens, and halogenic acids. 1,4-Bis(4-benzylpyridinium)butadiyne triflate was found to be aggregated in dimethylformamide (DMF) and spontaneously converted into the 1,4-addition type of polydiacetylene.^{24–26} Recently, we synthesized self-dopable conjugated polyelectrolytes by the activated polymerization of 2-ethynylpyridine by the ring opening of 2-sulfo-benzoic acid cyclic anhydride and 1,4-butanediol without any additional initiators or catalysts.^{27,28} Also, we synthesized various pyridine-based conjugated polymers having different functionalities and characterized their polymer properties.^{29–35}

Because of their extensive conjugation and ionic nature, these ionic polyacetylenes have potential as materials for mixed ionic and electronic conductivity energy-storage devices, such as batteries, permselective membranes, and light-emitting devices.^{23,25,26}

In this study, we synthesized a new ionic polyacetylene with *N*-(5-nitro-2-furanmethylene)-2-ethynylpyridinium bromide by the activated polymerization of 2-ethynylpyridine by using 2-(bromomethyl)-5-nitro-furan and characterized the polymer structure and properties.

EXPERIMENTAL

2-Vinylpyridine (Aldrich Chemicals, 97%), bromine (Aldrich Chemicals, American Chemical Society

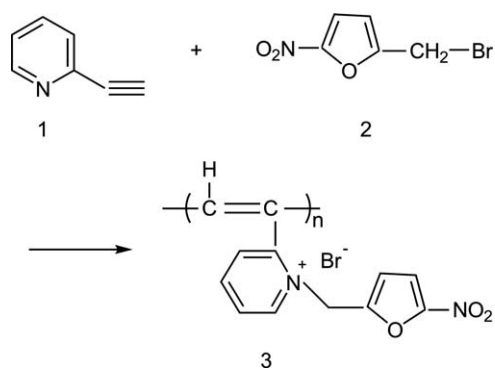
reagent, >99.5%), and sodium amide (Aldrich Chemicals, technical grade, 90%) were used as received. 2-(Bromomethyl)-5-nitro-furan (Aldrich Chemicals, 97%) was also used as received. The solvents were analytical-grade materials. They were dried with an appropriate drying agent and fractionally distilled. 2-Ethynylpyridine was prepared by the bromination of 2-vinylpyridine and a consecutive dehydrobromination reaction according to the literature method.³⁶ 2-Ethynylpyridine was vacuum-distilled after it was dried with CaH₂ (85°C/12 mmHg).

A typical synthetic procedure for poly[*N*-(5-nitro-2-furanmethylene)-2-ethynylpyridinium bromide] (PNFMEPB) is as follows. A 1 : 1 mixture of 2-ethynylpyridine (1.0 g, 9.70 mmol) and 2-(bromomethyl)-5-nitro-furan (2.0 g, 9.70 mmol) in DMF solvent (7.0 mL, initial monomer concentration = 0.97M) was stirred for 24 h at 90°C under a dry nitrogen atmosphere. As the reaction proceeded, the color of the reaction mixture changed from the light brown of the initial mixture to black. The resulting polymer solution was diluted by 10 mL of DMF and precipitated into a large excess of ethyl ether. The precipitated polymer was filtered and dried *in vacuo* at 40°C for 24 h. The black polymer powder was obtained in a 92% yield.

Fourier transform infrared (FTIR) spectra were obtained with a Bruker Equinox 55 spectrometer with KBr pellets. ¹H-NMR and ¹³C-NMR spectra were recorded on a Varian 500-MHz FT-NMR spectrometer (Unity Inova) in hexadeuterated dimethyl sulfoxide (DMSO-*d*₆), and the chemical shifts are reported in parts per million units with tetramethylsilane as an internal standard. Thermogravimetry was performed under a nitrogen atmosphere at a heating rate of 10°C/min with a DuPont 2200 thermogravimetric analyzer. The dilute solution viscosity measurements were made at 30°C with a Lauda viscometer at a concentration of 0.5 g/dL in DMF. The optical absorption spectra were measured by an HP 8453 ultraviolet-visible (UV-vis) spectrophotometer. The PL spectra were obtained by a PerkinElmer luminescence spectrometer LS55 (Xenon flash tube). Electrochemical measurements were carried out with a WBCS 3000 system. To examine the electrochemical properties, the polymer solution was prepared, and electrochemical measurements were performed under a 0.1M tetrabutylammonium perchlorate (TBAP) solution containing DMF. Indium tin oxide, Ag/AgNO₃, and platinum wire were used as a working, reference and a counter electrode, respectively. The reprecipitated polymer was used in the experiment.

RESULTS AND DISCUSSION

Acetylenic pyridine compounds, such as ethynylpyridine, dipyritylacetylene, and dipyrityldiacetylene



Scheme 1 Synthesis of PNFMEPB: (1) 2-ethynylpyridine, (2) 2-(bromomethyl)-5-nitrofuran, and (3) PNFMEPB.

are 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 cationic radicals.²³ The activated acetylenic groups of *N*-substituted 2-ethynylpyridinium halides were found to be susceptible to linear polymerization, yielding the ionic conjugated polymer systems.^{24–26} First, this polymerization process involved the quaternization of the pyridine nitrogen in ethynylpyridine monomer. In general, these polymerizations proceeded well without any additional catalyst or initiator to give highly conjugated, charged polyacetylenes. Thus, this method could essentially eliminate impurities that may have originated from the catalyst or initiator used during the polymerization. We prepared a new ionic polyacetylene from the activated polymerization of 2-ethynylpyridine with 2-(bromomethyl)-5-nitrofuran (Scheme 1).

Table I shows the results of the polymerization of 2-ethynylpyridine with 2-(bromomethyl)-5-nitrofuran without any additional catalyst or initiator. Although the monomeric salt, *N*-(5-nitro-2-furanmethylene)-2-ethynylpyridinium bromide, formed in the first quaternization process, had a highly bulky sub-

TABLE I
Polymerization of 2-Ethynylpyridine
with 2-(Bromomethyl)-5-nitrofuran

Experiment	Solvent	Temperature (°C)	Polymer yield (%) ^a	Inherent viscosity ^b
1	DMF	65	76	0.13
2	DMF	80	89	0.15
3	DMF	90	92	0.19
4	DMSO	90	88	0.15
5	NMP	90	83	0.12

^aPolymerization was carried out without any additional catalysts or initiators. The initial monomer concentration was 0.97M.

^bEthyl ether insoluble polymer.

^cMeasured at a concentration of 0.5 g/dL in DMF at 30°C.

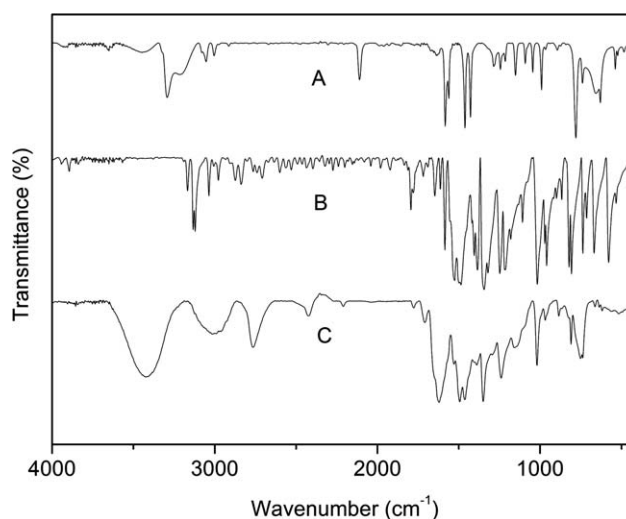


Figure 1 FTIR spectra of (A) 2-ethynylpyridine, (B) 2-(bromomethyl)-5-nitrofuran, and (C) PNFMEPB (measured in KBr pellets).

stituent, this polymerization proceeded easily to give a high yield of polymer at more elevated temperatures (>65°C). The polymerization proceeded well at 90°C to give the resulting polymer in 92% yield. The polymerization proceeded well in regard to such polar organic solvents as methanol, DMF, DMSO, and *N*-methylpyrrolidone (NMP). The polymer yields according to the reaction time were checked during the polymerization in DMF. This polymerization at 90°C proceeded well within the initial 1 h (51%). The polymer yields after 3 and 6 h were 81 and 89%, respectively, and there was a plateau (92%) after 12 h.

These polymerization behaviors were very similar to those of the polymerizations of 2-ethynylpyridine with 3-(6-bromohexyloxy)methylthiophene³⁰ and 4-(methylthio)benzyl bromide.³² These polymerizations have been known to contain the first quaternization of 2-ethynylpyridine by bromoalkyl compounds.^{24,32} The initial step involves a nucleophilic attack by the nitrogen atom of unreacted 2-ethynylpyridine and/or the bromide anion on the activated electrophilic *N*-ethynyl triple bond of the quaternized acetylenic monomer.³⁴ The activated acetylenic triple bond of the monomeric species formed at the initial reaction time is susceptible to linear polymerization; this is followed by a consecutive propagation step that contains the produced macroanion and the quaternized monomeric species. Finally, this reaction is terminated by the reaction of macroanionic species with 2-(bromomethyl)-5-nitrofuran and/or other components.

The chemical structure of PNFMEPB was characterized by such instrumental methods as IR, NMR, and UV-vis spectroscopy. Figure 1 shows the FTIR spectra of 2-ethynylpyridine, 2-(bromomethyl)-5-nitrofuran,

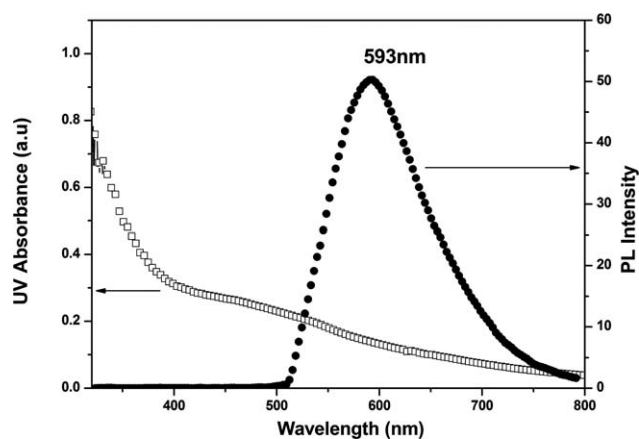


Figure 2 Optical absorption and PL spectra of the PNFMEPB polymer solutions.

and PNFMEPB, which were measured in KBr pellets. The FTIR spectrum of PNFMEPB did not show the acetylenic CC bond stretching (2110 cm^{-1}) and acetylenic C—H bond stretching (3293 cm^{-1}) frequencies of 2-ethynylpyridine monomer. The aromatic =C—H stretching vibrations of pyridine and furan moieties were found around 3014 cm^{-1} . The stretching frequencies of C=C double bonds in the polymer backbone were observed around 1620 cm^{-1} .

The $^1\text{H-NMR}$ spectrum of PNFMEPB showed the aromatic protons of pyridyl and furyl moieties and the vinyl protons of the conjugated polymer backbone at 5.6–9.8 ppm. The methylene proton peak was also observed around 4.3 ppm. The $^{13}\text{C-NMR}$ spectrum of PNFMEPB did not show the acetylenic carbon peaks. Instead, the polymer spectrum showed multiple and complicated peaks in the region 100–160 ppm, which originated from the aromatic carbons of the pyridyl and furyl moieties and the vinyl carbons of the conjugated polymer backbone. In the UV–vis spectrum of polymer, the absorption spectrum started around 800 nm and showed an absorption band in the visible region due to the $\pi\rightarrow\pi^*$ interband transition of the polymer backbone; this is a characteristic peak of the conjugated polyene backbone system. These spectral data indicated that this PNFMEPB had an ionic conjugated polymer system bearing the designed aromatic functional groups.

This polymer was completely soluble in such polar organic solvents as DMF, DMSO, and *N,N*-dimethylacetamide. The inherent viscosities of the resulting polymers were in the range 0.12–0.19 dL/g. In the X-ray diffractogram of the PNFMEPB powder, because the peak in the diffraction pattern was broad and the ratio of the half-height width to the diffraction angle ($\Delta 2\theta/2\theta$) was greater than 0.35, this polymer was amorphous.^{8,34}

The optical absorption and luminescence properties of PNFMEPB were characterized with UV–vis absorption spectroscopy and PL spectroscopy. Figure 2 shows the results of UV–vis and PL spectroscopy for the PNFMEPB solution ($1.3 \times 10^{-4}\text{ M}$ for UV–vis spectroscopy and $2.6 \times 10^{-4}\text{ M}$ for PL spectroscopy in DMF). PNFMEPB showed a very broad UV–vis absorption band ranging from 300 to 700 nm and a yellowish orange PL maximum value at 593 nm, which corresponded to a photon energy of 2.09 eV.

In our previous articles,^{30,34} we reported the UV–vis and PL properties of poly[2-ethynyl-*N*-(3-thienylmethyleneoxy)hexylpyridinium bromide] (PETHPB) and poly[2-ethynyl-*N*-(2-thiophenecarbonyl)pyridinium chloride] (PETCPC). The polymer PETHPB had the same polymer main chain and a longer methylene unit of the hexyl-oxy group between pyridinium and thiophene groups as PETCPC, which has only a carbonyl group at same position. Shorter side chain moieties in PETCPC compared to PETHPB increased the UV–vis and PL maximum values from 470 and 510 to 500 and 573 nm, respectively. This was explained by the fact that the small-sized side group did not largely affect the

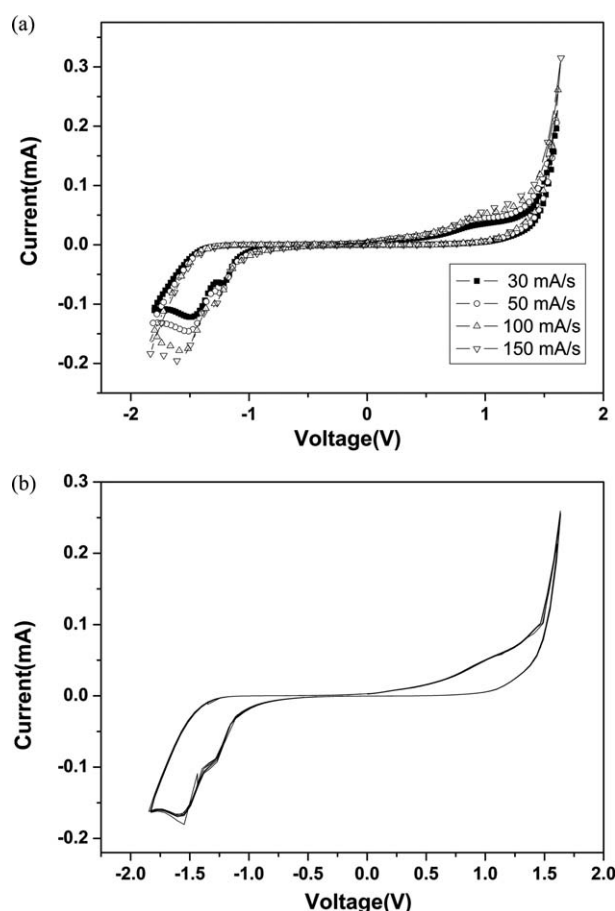


Figure 3 Cyclic voltammograms of PNFMEPB (0.1M TBAP/DMF) with (a) various scan rates (30–120 mV/s) and (b) 30 consecutive scans at 100 mV/s.

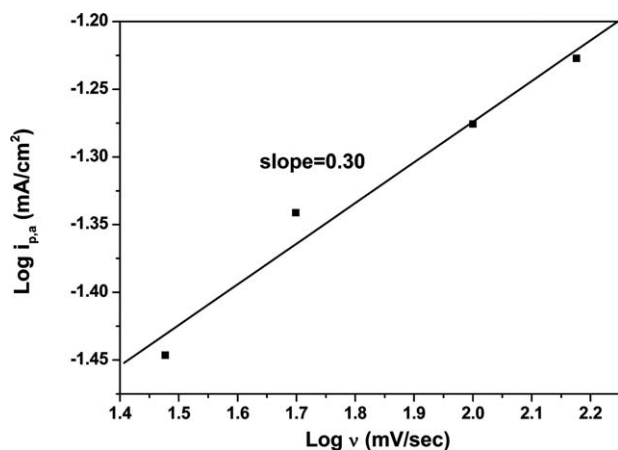


Figure 4 Plot of $\log i_{p,a}$ versus $\log v$ for PNFMEPB.

molecular planar arrangement of the main-chain backbone, such as conjugated polyene. Considering these differences, we thought that PETCPB exhibited redshifted UV-vis and PL spectra compared to PETHPB. In the case of PNFMEPB, it also had small-sized side groups, including a methyl group between the pyridinium and furyl groups. We believe that this caused more redshifted UV-vis and PL spectra.

To evaluate the electrochemical kinetic properties of PNFMEPB for electro-active applications, cyclic voltammetry (CV) was measured at various scan rates (30–150 mV/s) and in consecutive scans. As shown in Figure 3, we performed CV for of PNFMEPB solutions with various scan rates, 30–150 mV/s [Fig. 3(a)], and in consecutive scans [Fig. 3(b)] to determine the electrochemical kinetic behavior of PNFMEPB. PNFMEPB showed very stable CV behavior from the consecutive scans (up to 30 cycles), which means that this material had a stable redox process within the range –1.80 to 1.60 V. This result suggests that the electrochemical process of PNFMEPB was reproducible in the potential range of –1.80 to 1.60 V versus Ag/AgNO₃. Additionally, the oxidation of PNFMEPB was started at 0.5 V, where the vinylene unit of the conjugated polymer backbone could be oxidized in the scan and the redox process was irreversible. Interestingly, as the scan rate of CV increased, the peak potential shifted slightly to higher potentials and increased the redox current substantially.

The relationship between the redox peak current and the scan rate can be expressed as a power-law relationship:^{37–39}

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

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

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

If one assumes that the electrode kinetics satisfy 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 $x = 0.5$. The relations between $\log i_{p,a}$ and $\log v$ satisfying eq. (2) are shown in Figure 4. The oxidation current density of PNFMEPB versus the scan rate was an approximately linear relationship in the range 30–150 mV/s. The x value of PNFMEPB was found to be 0.30 in this electrochemical system. This value means that the kinetics of the redox process did not empirically reach to the ion diffusion process under these electrochemical conditions.

CONCLUSIONS

The activated polymerization method was used for the synthesis of a new conjugated ionic polyacetylene with two bulky aromatic moieties (pyridine and furan). This polymerization of 2-ethynylpyridine with 2-(bromomethyl)-5-nitrofuran proceeded well to give a high yield of polymer. The resulting polymer powder was black and was completely soluble in such organic solvents as DMF, DMSO, and DMA. The activated acetylenic triple bond of the monomeric species formed in the initial reaction time was found to be susceptible to linear polymerization. Such instrumental methods as IR, NMR, and UV-vis spectroscopy indicated that this polymer had a conjugated polymer backbone system having the designed substituents. PNFMEPB showed the characteristic wide UV-vis absorption band and a yellowish orange PL maximum value at 593 nm, which corresponded to a photon energy of 2.09 eV. The oxidation of PNFMEPB was started at 0.5 V, where the vinylene unit of the conjugated polymer backbone could be oxidized in the scan, and the redox process was irreversible.

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