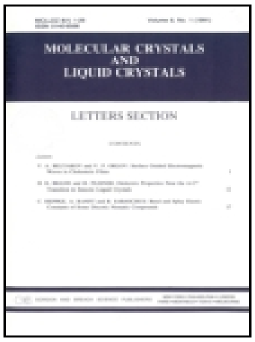

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Synthesis and Characterization of Poly [N-(4-nitrobenzenesulfonyl)-2-ethynylpyridinium chloride]

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An ionic polyacetylene with 4-nitrobenzenesulfonyl substituents was easily prepared via the non-catalyst polymerization of 2-ethynylpyridine using 4-nitrobenzenesulfonyl chloride. The polymerization proceeded in homogeneous manner to give a moderate yield of polymer (65 %). The polymer structure was characterized by such instrumental methods as IR, NMR, and UV-visible spectroscopies to have the conjugated backbone system with the designed N-(4-nitrobenzenesulfonyl)pyridinium chloride. The photoluminescence peak was observed at 584 nm corresponding to a photon energy of 2.12 eV although it is weak due to nitro group. Based on absorption spectrum, band gap was 2.16 eV. The cyclic voltammograms of polymer exhibited the electrochemically stable window at the $-1.8 \sim 1.50$ *V region. Oxidation and reduction were started at 0.43 and* -0.9 *V and had stable electrochemical property up to 30 cycles.*

Keywords polyacetylene; 4-nitrobenzenesulfonyl chloride; 2-ethynylpyridine; non-catalyst polymerization; cyclic voltammogram

Introduction

Numerous experimental and theoretical studies on the conjugated polymers have been performed over past decades [1–5]. Conjugated polymers are especially attractive for electric and opto-electronic applications because of (i) electrical conductivity; (ii) fast and high nonlinear optical responses; (iii) inherent synthetic flexibility; (iv) chemical reactivity and complex formation ability; and (iv) ease of processing into ultrathin films [6–10].

These conjugated polymers are of high interest due to their potential as promising materials for photovoltaics, displays, lasers, nonlinear optical materials, membranes for gas separation and for liquid-mixture separation, and chemical sensors [2, 3, 11–13].

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The thermal polymerization of 2-ethynylpyridine yielded the corresponding polymer with low molecular weight in low yield [14]. 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 [15]. 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 [16–18], which is similar to the polymer formation from 4-vinylpyridine including cation radical [19, 20]. We have also reported on the preparation of various pyridine-based conjugated polymers having different functionalities [21–25].

The pyridine-based ionic conjugated polymers have been used as material candidates for the fabrication of ultrathin amphiphilic films [26, 27], cationic polyacetylene-silica nanohybrids [28], hybrid polymer gels [29], nanocrystalline CdS polymer sensitizer [30, 31], SERS (surface-enhanced Raman spectroscopy) active π-conjugated polymer-Ag nanocomposites [32], unipolar write-once-read-many-times (WORM) memory devices [33],

To date, the functional sulfonyl chlorides had never used as the activating reactant for the polymerization of ethynylpyridines. Here, we report the synthesis of a new ionic polyacetylene with 4-nitrobenzenesulfonyl substituents via the non-catalyst polymerization of 2-ethynylpyridine using 4-nitrobenzenesulfonyl chloride and the characterization of the resulting poly[N-(4-nitrobenzenesulfonyl)-2-ethynylpyridinium chloride] (PNBSEPC).

Experimental

4-Nitrobenzenesulfonyl chloride (Aldrich Chemicals, 97%) was used as received. 2-Ethynylpyridine (Aldrich Chemicals, 98%) was vacuum distilled after drying with CaH_2 (85 °C/12 mmHg) [34]. The solvents were analytical grade materials. They were dried with an appropriate drying agent and distilled.

PNBSEPC was synthesized by the non-catalyst polymerization of 2-ethynylpyridine by using 4-nitrobenzenesulfonyl chloride. The polymerization was carried out with oil bath. A round-bottom flask (100 mL) was equipped with magnetic stirrer. The reaction procedure was as follows. After the reactor was charged with 20.0 mL of DMF ($[M]_0 =$ 0.51 M), 2-ethynylpyridine (1.213 g, 11.76 mmol), and 4-nitrobenzenesulfonyl chloride (2.00 g, 11.76 mmol). And degassed with nitrogen for 5 min to remove the oxygen in the solution. The solution was stirred at 80 °C for 24 hrs. As the polymerization proceeded, the color of solution was gradually turned into more viscous dark brown solution, indicating the formation of conjugated backbone system. After completion of the reaction, the polymer solution diluted with additional 10 mL DMF 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 polymer powder was obtained in 65 % yield.

FT-IR spectra were obtained with a Bruker EQUINOX 55 spectrometer. The solid specimens were prepared by mixing the powders with KBr powder and then pressed into round pellets. NMR (^{1}H-and ^{13}C) spectra were obtained in DMSO-d_6 solutions at room temperature using a Varian 500 MHz FT-NMR spectrometer (Model: Unity INOVA). All chemical shifts are referenced to tetramethylsilane as an internal standard by using known shifts of residual proton or carbon solvent signals. The inherent viscosities of polymers were determined at a concentration of 0.5 g/dL in DMF at 30 °C. X-ray powder diffraction (XRD) data were obtained with a PHILLIPS X-ray diffractometer (Model: XPert-APD). The UV-visible absorption spectra were recorded on a HP 8453 UV-visible Spectrophotometer.

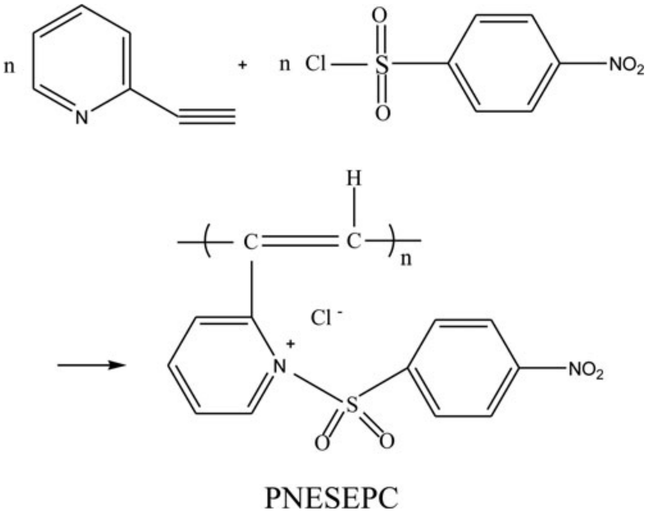
Cyclic voltammetry (CV) was carried out with a Potentionstat/Galvanostat Model 273A (Princeton Applied Research) at a scan rate of 100 mV/s. The polymer solution was prepared in DMF and the electrochemical measurements were performed under 0.1 M tetra-n-butylammonium tetrafluoroborate (TBAT) in anhydrous acetonitrile. A platinum wire was as the counter electrode and an Ag/$AgNO_3$ electrode was used as the reference electrode. All of the electrochemical experiments were performed in the open air at room temperature.

Results and Discussion

All the polymerization reactions involve the quaternization of monomeric compound containing an acetylenic triple bond that is attached either directly to or via a sequence of conjugated double bonds to a quaternizable nitrogen atom. Monomeric ethynylpyridinium species are spontaneously polymerized to form highly conjugated, charged polyacetylenes.

Here, we synthesized a new ionic polyacetylene with 4-nitrobenzenesulfonyl substituents (Scheme 1) via the non-catalyst polymerization of 2-ethynylpyridine using 4-nitrobenzenesulfonyl chloride. This non-catalyst polymerization method can essentially eliminate the impurities that may be originated from the catalyst or initiator used during the polymerization.

The mixture of 2-ethynylpyridine and 4-nitrobenzenesulfonyl chloride in DMF solvent was kept in heated oil bath (70 °C) for 24 hrs. As the reaction proceeded, the color of reaction mixture was changed from the light brown of the initial mixture into dark brown and the viscosity of reaction mixture was gradually increased. Although the monomeric salt, N-(4-nitrobenzenesulfonyl)-2-ethynylpyridinium chloride, formed at the first quaternization process, has a highly bulky substituent, the present polymerization proceeded easily in a homogeneous manner to give relatively a moderate yield of polymer (polymer yield: 65 %). The polymerization behaviors were found to be very similar with those of the similar non-catalyst polymerizations using 3-(6-bromohexyloxy)methylthiophene, 2-thiophene carbonyl chloride, 1,3-propanesultone [22, 23, 35].



Scheme 1. Synthesis of PNESEPC

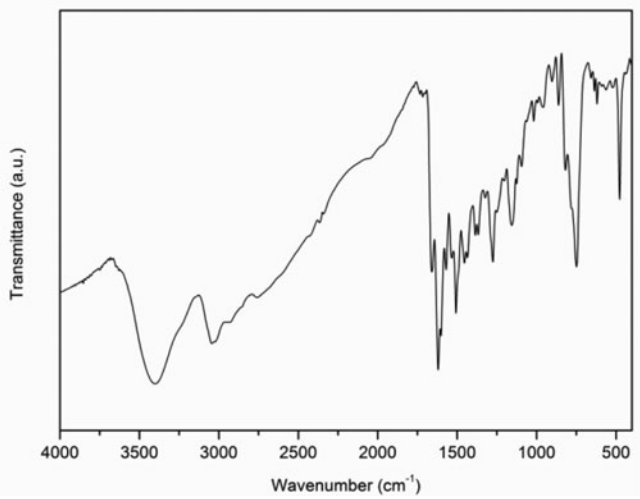


Figure 1. FT-IR spectrum of PNESEPC in KBr pellet.

The chemical structure of PNESEPC was characterized by various instrumental methods such as IR, NMR, and UV-visible spectroscopies. Figure 1 shows the FT-IR spectrum of PNESEPC measured in KBr plates. The infrared spectrum shows a broad, intense band at around 3385 cm^{-1} that arises from the vinylic =C-H stretching in the pyridinium moieties that are strongly hydrogen bonded. This broad peak is characteristic of most polymers prepared by the non-catalyst polymerization of acetylenic pyridines and is indicative of their ionic nature. The infrared spectrum of polymer did not show the acetylenic C≡C bond stretching (2110 cm^{-1}) and acetylenic ≡C-H bond stretching (3293 cm^{-1}) frequencies of 2-ethynylpyridine. Instead, the C=C stretching frequency of conjugated polymer backbone around 1625 cm^{-1} became relatively more intense than those of the C=C and C=N stretching frequencies of 2-ethynylpyridine and 4-nitrobenzenesulfonyl chloride. The strong peak at 750 cm^{-1} is due to the CH out-of-plane deformation of pyridyl moieties.

The ^{1}H-NMR spectrum of PNESEPC in DMSO-d_6 showed the aromatic pyridyl and phenylene protons and the vinylic protons of conjugated backbone in the range of 5.7-9.0 ppm. And the ^{13}C-NMR spectrum showed the aromatic carbon peaks of pyridyl and phenylene moieties and the vinyl carbons of conjugated polymer backbone showed in the range of 107-145 ppm. The UV-visible absorption spectrum of polymer showed a characteristic absorption peak in the visible region (up to 800 nm), which indicate the formation of polyene backbone system.

The morphologies of PNESEPC were also investigated by X-ray diffraction analysis. The peak in the diffraction pattern is broad and the ratio of the half-height width to diffraction angle ($\Delta 2\theta / 2\theta$) is greater than 0.35 [1, 3], indicating that the present polymer is mostly amorphous. This polymer was soluble in such organic solvents as DMF, NMP, and DMSO. The inherent viscosity of PNESEPC was 0.15 dL/g.

The electro-optical and electrochemical properties of PNESEPC were measured. Figure 2 shows UV-Visible (UV-Vis.) and photoluminescence (PL) spectra of PNESEPC solution (UV-Vis. and PL: 1.0×10^{-4} M, DMF). The absorption spectrum exhibits broad absorption band in visible wavelength region. Maximum values of 332, 400, and 500 nm were found and the absorption peaks at visible range were due to the $\pi \rightarrow \pi^*$ interband

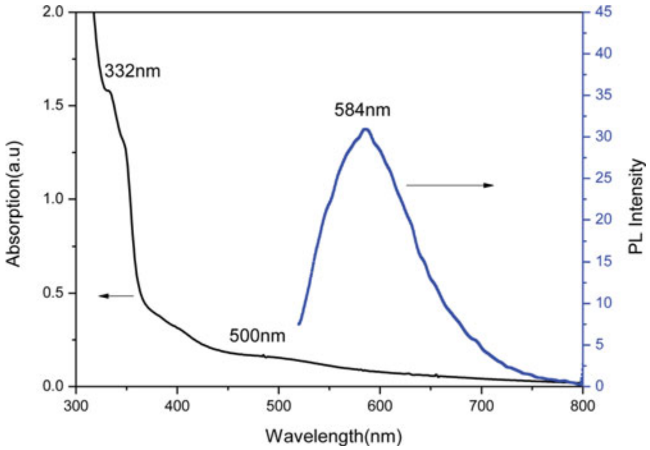


Figure 2. Optical absorption and photoluminescence spectra of PNESEPC (excitation wavelength: 500 nm, solvent: DMF).

transition of this conjugated polymer. Based on absorption spectrum, band gap was 2.16 eV. The photoluminescence spectrum of this ionic conjugated polymer showed the maximum peak of 584 nm corresponding to the photon energy of 2.12 eV when PL was checked with excitation of 500 nm wavelength. In order to exclude excitation light detection, PL was cut off at 515 nm. However, PL intensity was weak due to luminescence quenching of nitro group.

The electrochemical property was measured by cyclic voltammograms as shown in Figure 3. Oxidation and reduction were checked under consecutive scans up to 30 cycles. As the cycle numbers were increased, the oxidation was maintained and reduction current was slightly increased because of the repeated electrochemical reaction. The reason why it relatively happens at only reduction is not clear, but it may be explained by relatively

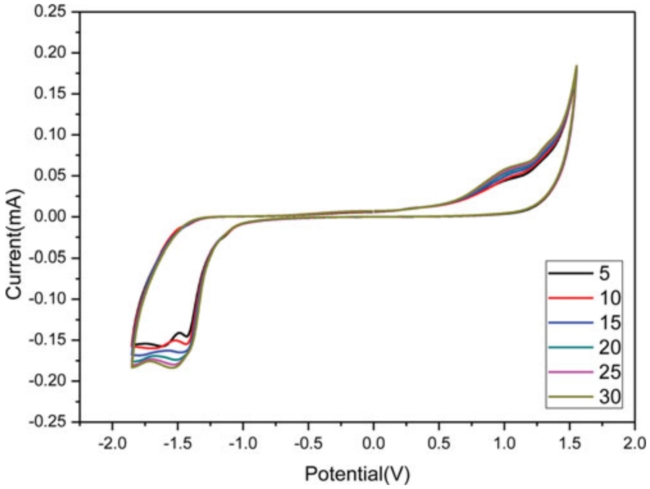


Figure 3. Cyclic voltammograms of PNESEPC in 4×10^{-4} M TBAT/DMF solution: consecutive scans up to 30 cycles.

stable anion of nitro group and sulfone group [36]. Oxidation and reduction were started at 0.43 and −0.9 V and had stable electrochemical property up to 30 cycles. Also, reduction current amount was larger than oxidation. Further studies on electrochemical reaction are underway.

Conclusions

The non-catalyst polymerization of 2-ethynylpyridine using 4-nitrobenzenesulfonyl chloride yielded a new ionic polyacetylene with N-(4-nitrobenzenesulfonyl)pyridinium substituents in 65 % yield. The activated ethynyl bond of N-(4-nitrobenzenesulfonyl)-2-ethynylpyridinium chloride formed at the initial reaction stage was susceptible to the polymerization, followed by an identical propagation process that contains the produced macroanion and the quaternarized monomeric species. Various instrumental analysis data indicated that the present polymer have a conjugated polymer backbone system with the designed substituents. This polymer was completely soluble in such organic solvents as DMF, NMP, and DMSO. The X-ray diffraction analysis data on PNESEPC powder indicated that this polymer is mostly amorphous. The cyclic voltammograms of PNESEPC exhibited irreversible electrochemical behavior between the oxidation and reduction peaks, but it showed stable electrochemical window in the range of −1.9 V to 1.5 V.

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