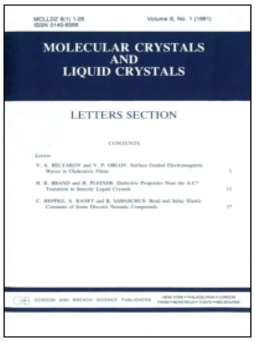

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An ionic polyacetylene from the non-catalyst polymerization of 2-ethynylpyridine using 1,6-dibromohexane: Synthesis and characterization

Yeong-Soon Gal[a], Sung-Ho Jin[b], Jong Wook Park[c], Tae-Kwan Son[d], and Kwon Taek Lim[e]

[a]Department of Fire Safety, Kyungil University, Gyeongsan, Gyeongsangbuk-do, Korea; [b]Department of Chemistry Education, Pusan National University, Busan, Korea; [c]Department of Chemistry, The Catholic University of Korea, Bucheon, Korea; [d]School of Mechanical & Automotive Engineering, Keimyung Universty, Dalseo, Daegu, Korea; [e]Department of Display Engineering, Pukyong National University, Busan, Korea

ABSTRACT
An ionic polyacetylene was prepared via the non-catalyst polymerization of 2-ethynylpyridine using 1,6-dibromohexane. The polymerization proceeded in homogeneous manner to give a high yield of polymer (88%). The polymer structure was characterized by such instrumental methods as IR, NMR, and UV-visible spectroscopies to have the conjugated polymer backbone with the designed bromohexylpyridinium substituents. The absorption spectrum exhibits several absorption peaks such as 289, 330, 387, and 489 nm and band gap was 2.44 eV. The photoluminescence spectrum of polymer showed the maximum peak at 550 nm. Overall redox current shape and values were very stable in the range of −1.5 V to 1.5 V under up to 50 cylcles. Oxidation and reduction were started at 0.35 and −0.6 V.

KEYWORDS
polyacetylene;
2-ethynylpyridine;
1,6-dibromohexane;
non-catalyst polymerization;
cyclic voltammogram

Introduction

Conjugated polymers attract a particular attention as promising materials for photovoltaics, displays, lasers, nonlinear optical materials, chemical sensors, and realted applications as well as for gas separation and permeation membranes [1–9]. Numerous experimental and theoretical studies on the conjugated polymers have been performed over past decades [1–5,10]. In most cases, the organic conjugated polymers were obtained via the coordination polymerization of corresponding alkynes induced with homogeneous transition metal catalysts. The increased requirements for a high purity of conjugated polymers essentially need a low level of catalyst residues in polymers [1,3].

Polyelectrolytes are charged macromolecules containing a large number of ionizable or ionic groups [11]. The methods for conjugated polymer-based polyelectrolytes include the modification of polyacetylene derivatives such as poly(6-bromo-1-hexyne) [12] and poly(N-hexyldipropargylamine) [13], and the direct polymerization of the corresponding substituted acetylenes using transition metal catalysts [14–16]. In 1978, the anion-radical TCNQ salt-like complexes of ethynylpyridine polymers was firstly prepared by mixing the quaternized poly(ethynylpyridine)-MeI(or EtI) homopolymers with Li-TCNQ or TCNQ in acetonitrile

CONTACT Yeong-Soon Gal ✉ ysgal@kiu.ac.kr 🖃 Department of Fire Safety, Kyungil University, Gyeongsan 38428, Gyeongsangbuk-do, Korea
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[17]. In the early 1990s, Blumstein et al reported a new family of mono- and di-substituted polyacetylenes that retain extensive conjugation through the catalyst-free polymerization of ethynylpyridines using alkyl halides [18–20]. These polymer systems were achieved by introducing one or two ionic charges into each repeating unit, thus endowing such polyacetylene polymers with some of the highest charge densities known. The electrostatic repulsion in polymer structures favors backbones with extended conformations and hence conjugation lengths are substantially higher than those of some noncharged polyacetylenes [21].

In our previous works, we have synthesized various ionic conjugated polymers having different functionalities by the non-catalyst polymerization of ethynylpyridines using functional alkyl halides [22–25]. And, we also modified the polymer properties of precursor poly(ethynylpyridine) derivatives via the ion-exchange reaction of corresponding polymers [26,27].

The conjugated polymers with ionic pyridine functionalities have been used as material candidates for the fabrication of ultrathin amphiphilic films [28], light-emitting materials [29], polyacetylene-silica nanohybrids [30], nanocrystalline CdS polymer sensitizer [31], SERS (surface-enhanced Raman spectroscopy) active π-conjugated polymer-Ag nanocomposites [32], sensing materials for ions and biological species [33], conjugated polymer-silver nanoparticles [34], fluorescence enhancer [35], and unipolar write-once-read-many-times (WORM) memory devices [36].

To date, the dihalo alkanes had not used as the activating reactant for the polymerization of ethynylpyridines. Here, we report the synthesis of a new ionic polyacetylene via the non-catalyst polymerization of 2-ethynylpyridine using 1,6-dibromohexane and the characterization of the resulting polymer.

Experimental

1,6-Dibromohexane (Aldrich Chemicals, 96%) was dried with calcium hydride and distilled. 2-Ethynylpyridine (Aldrich Chemicals, 98%) was vacuum distilled after drying with CaH_2 (85°C/12 mmHg) [37]. The solvents were analytical grade materials. They were dried with an appropriate drying agent and distilled.

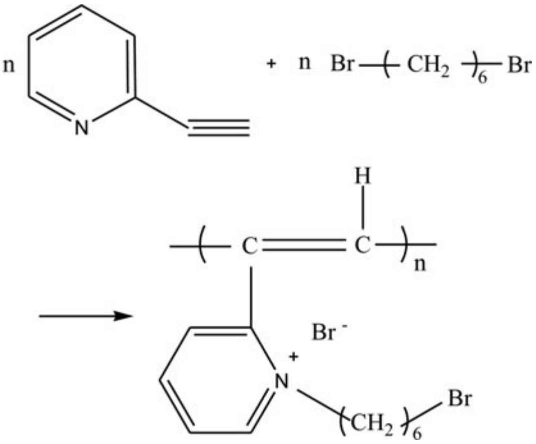
The polymer was synthesized by the non-catalyst polymerization of 2-ethynylpyridine by using 1,6-dibromohexane in DMF. A round-bottom flask (100 mL) was equipped with magnetic stirrer. The reaction procedure was as follows. After the reactor was charged with 30.0 mL of DMF ($[M]_0 = 0.30$ M), 2-ethynylpyridine (1.0 g, 9.70 mmol), and 1,6-dibromohexane (2.37 g, 9.70 mmol). After degassing with purified nitrogen, the polymerization reaction was carried out at 80°C for 24 hrs. The reaction solution was gradually turned into more viscous dark brown solution as time goes on, which indicates the formation of conjugated polymer. After the reaction time, the solution diluted with additional 15 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 88% yield.

Fourier transform infrared (FT-IR) spectra were obtained by using 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 recorded on a Varian 500 MHz FT-NMR spectrometer (Model: Unity INOVA) in DMSO-d_6. The chemical shifts are referenced to tetramethylsilane as an internal standard. The absorption and PL spectra were measured by using a HP 8453 UV-visible Spectrophotometer and a Perkin Elmer luminescence spectrometer LS50 (Xenon flash tube), respectively. The inherent viscosities of polymers were determined at a concentration of 0.5 g/dL in DMF at 30°C. Cyclic voltammetry (CV) was carried out with a Potentionstat/Galvanostat Model 273 A (Princeton Applied Research) at a scan rate of 30∼150 mV/sec. The polymer solution was prepared in DMF and the electrochemical measurements were performed under 0.1 M tetra-n-butylammonium tetrafluoroborate (TBA-TFB) in anhydrous DMF. 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

The non-catalyst polymerizations of ethynylpyridine involve the first quaternization of ethynylpyridine by alkyl halides or carbonyl chlorides. The monomeric ethynylpyridinium species are spontaneously polymerized to form highly conjugated, charged polyacetylenes without any additional initator or catalyst. Thus, this non-catalyst polymerization method can essentially eliminate the impurities that may be originated from the catalyst or initiator used during the polymerization.

Here, we synthesized a new ionic polyacetylene with (N-6-bromohexyl)pyridinium substituents (Scheme 1) via the non-catalyst polymerization of 2-ethynylpyridine using 1,6-dibromohexane.



Scheme 1. Synthesis of polymer.

The reaction mixture of 2-ethynylpyridine and 1,6-dibromohexane 1,6-dibromohexane in DMF solvent was kept in heated oil bath with stirring (80°C) for 24 hrs. As the reaction reaction time passed, the color of reaction solution 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-(6-bromohexyl)-2-ethynylpyridinium bromide formed at the first step, has a highly bulky substituent, the polymerization proceeded easily in a homogeneous manner to give relatively a high yield of polymer (polymer yield: 88%). The mechanism of non-catalyst polymerization of ethynylpyridines involves the first quaternarization of 2-ethynylpyridine by 1,6-dibromohexane. The initiation step contains the nucleophilic attack on the activated acetylene functional group of the quaternarized monomeric salt by the nitrogen atom of unreacted 2-ethynylpyridine and/or the bromide anion. More detailed mechanism was described in our previous papers[23,24]. This polymerization behaviors were similar with those of the polymerizations of 2-ethynylpyridine using such alkyl bromides as

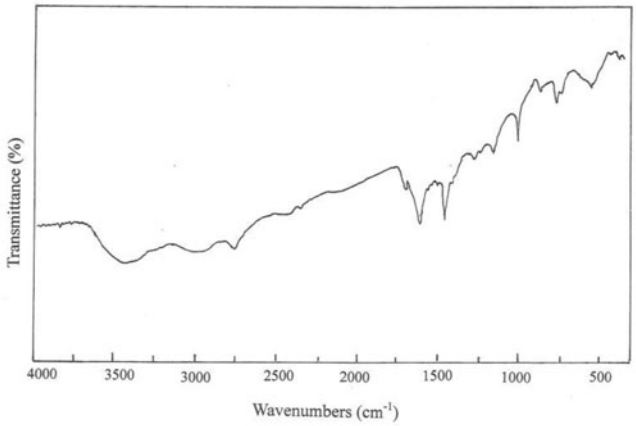


Figure 1. FT-IR spectrum of polymer in KBr pellet.

6-(N-carbazolyl)hexyl bromide, 3-(6-bromohexyloxy)methylthiophene, and bromocholine bromide [38–40].

The chemical structure of polymer was characterized by various instrumental methods such as IR, NMR, and UV-visible spectroscopies. Figure 1 shows the FT-IR spectrum of polymer measured in KBr pellet. 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 characteristic absorptions of the C≡C bond stretchings (2110 cm^{-1}) and ≡C-H bond stretchings (3293 cm^{-1}) seen in the IR spectrum of 2-ethynylpyridine have completely disappeared in the polymer spectrum. Instead, the C=C stretching frequency of conjugated polymer backbone around 1622 cm^{-1} became relatively more intense than those of the ring stretching frequencies of pyridyl substituents. The characteristic peaks at 568 cm^{-1} and 1020 cm^{-1} are due to the C-Br stretching of bromohexyl substituents and the ring breathing of pyridyl moieties, respectively.

The ^{1}H-NMR spectrum of polymer showed the pyridyl protons and the vinylic protons of conjugated backbone in the range of 6.2–9.6 ppm. The methylene protons adjacent to the N-atom of pyridine and the bromo atom of bromohexyl substituents were observed at 3.0–5.4 ppm, whereas the inner 4 methylene proton peaks were also observed at 0.5–2.0 ppm. The ^{13}C-NMR spectrum (Figure 2) showed the pyridyl carbon peaks and the vinyl carbons of conjugated polymer backbone in the range of 110–154 ppm. The 6 methylene carbon peaks were observed in the range of 16.0–60.5 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.

This polymer was soluble in such organic solvents as DMF, NMP, and DMSO although the 1,6-dibromohexane was used as an active reactant. The inherent viscosity of polymer was 0.18 dL/g.

The electro-optical and electrochemical properties of polymer were measured. Figure 3 shows UV-visible (UV-Vis.) and photoluminescence (PL) spectra of polymer solution (1.0×10^{-4} M, DMF). The absorption spectrum exhibits several absorption peaks in UV-Vis. wavelength region. Peak values of 289, 330, 387, and 489 nm were found and absorption range of 450∼550 nm was due to the $\pi \rightarrow \pi^*$ interband transition of this conjugated polymer.

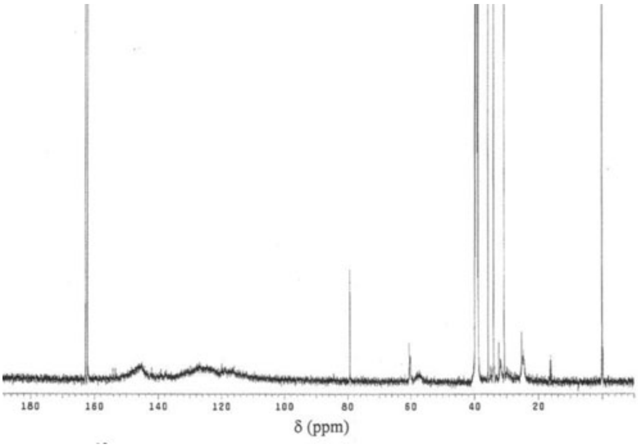


Figure 2. ^{13}C-NMR spectrum of polymer in DMSO-d_6.

Based on absorption spectrum, the band gap was 2.44 eV. The photoluminescence spectrum of polymer showed the maximum peak of 550 nm corresponding to the photon energy of 2.25 eV when PL was measured with excitation of 489 nm wavelength. In order to exclude excitation light detection, PL was cut off at 515 nm.

The electrochemical property of polymer was measured by cyclic voltammograms as shown in Figure 4. Oxidation and reduction stability of polymer was tested under consecutive scans up to 50 cycles (see Figure 4 (a)). As the cycle numbers were increased, the oxidation and reduction current was very slightly increased because of the repeated electrochemical reaction. However, the overall redox current shape and values were very stable under repeated cylcles. Oxidation and reduction were started at 0.35 and −0.6 V. Also, oxidation current amount was slightly larger than that of reduction, which means that oxidation is relatively easier than reduction in this polymer. Figure 4 (b) showed redox current shapes under the various scan rates. As the scan rates increased from 30 mV/sec to 150 mV/sec, oxidation and reduction current values were also increased. All redox current shapes were stable in the range of −1.5 V to 1.5 V under fast scan rates of 150mV/sec. Based on optical and CV data, HOMO and LUMO level values were 5.12 and 2.68 eV, respectively.

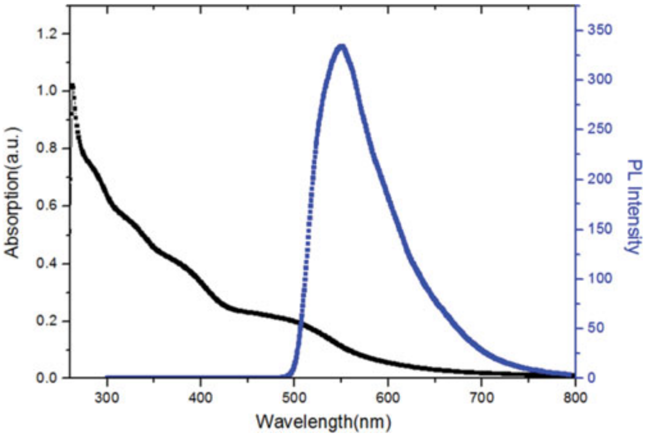


Figure 3. Optical absorption and photoluminescence spectra of polymer in solution state (excitation wavelength: 489 nm, solvent: DMF).

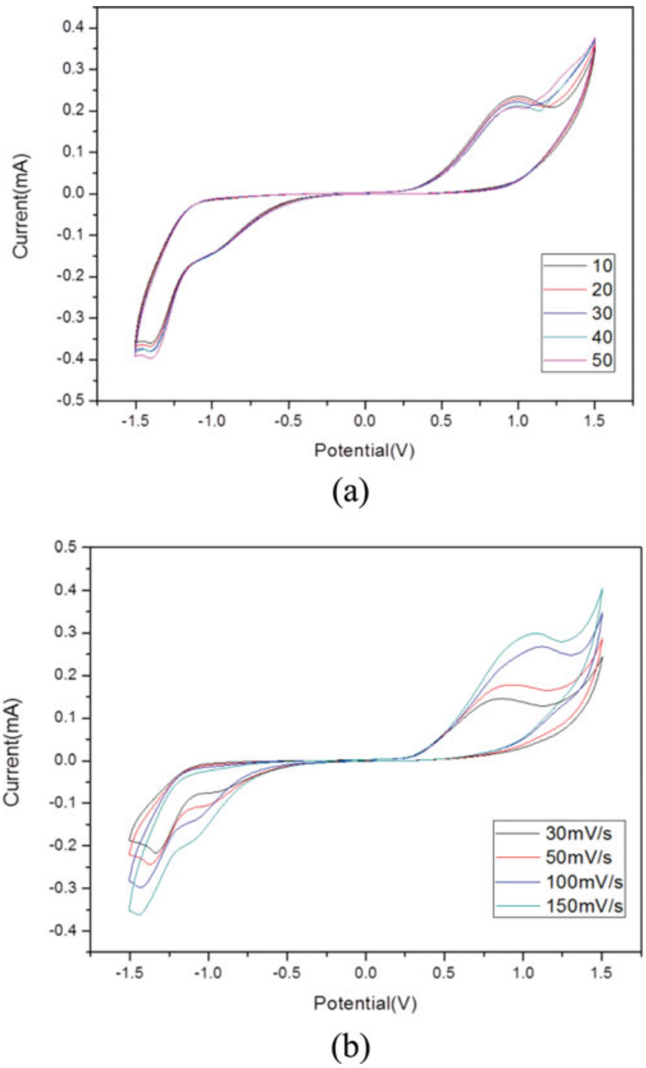


Figure 4. Cyclic voltammograms of polymer in 0.1 wt% TBA-TFB/DMF solution: consecutive scans up to 50 cycles (a) and various scan rates in the range of 30 mV/sec to 150 mV/sec (b).

Conclusions

The non-catalyst polymerization of 2-ethynylpyridine using 1,6-dibromohexane proceeded homogeneously to give a new ionic polyacetylene with N-(6-bromohexyl)pyridinium bromide as substituent in high yield. The monomeric compound, N-(6-bromohexyl)-2-ethynylpyridinium bromide, formed at the first quaternarization of 2-ethynylpyridine by 1,6-dibromohexane, was susceptible to the spontaneous polymerization without any additional initiator or catalyst. The chemical structure of resulting polymer was characterized by various instrumental analysis methods that the polymer have a conjugated polymer backbone with the N-(6-bromohexyl)pyridinium bromide as substituent. This polymer was completely soluble in such organic solvents as DMF, NMP, and DMSO. The photoluminescence spectrum of polymer showed the maximum peak of 550 nm corresponding to the photon energy of 2.25 eV. Oxidation and reduction of polymer were started at 0.35 and −0.6 V, and all redox current shapes were stable in the range of −1.5 V to 1.5 V under fast scan rates of 150 mV/sec. Due to its good solubility and electro-optical properties, this ionic conjugated material is expected to have potentials for organic semiconductor materials for OLEDs, OTFTs, DSSCs, and WORM memory devices.

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