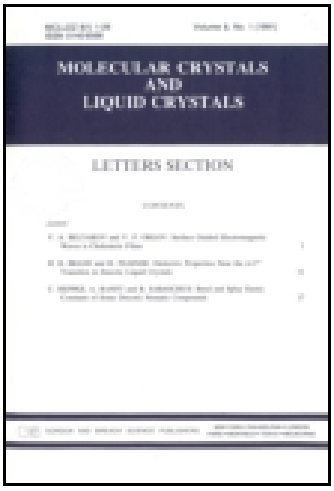

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A Polyacetylene via the Uncatalyzed Polymerization of 2-Ethynylpyridine Using 3-(Trimethylsilyl)propargyl Bromide: Synthesis and Characterization

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A Polyacetylene via the Uncatalyzed Polymerization of 2-Ethynylpyridine Using 3-(Trimethylsilyl)propargyl Bromide: Synthesis and Characterization

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A new ionic polyacetylene (PA) was synthesized in high yield via the uncatalyzed polymerization of 2-ethynylpyridine using 3-(trimethylsilyl)propargyl bromide. The activated acetylenic triple bond of N-substituted-2-ethynylpyridinium bromide, formed by the reaction of 2-ethynylpyridine and 3-(trimethylsilyl)propargyl bromide, was susceptible to linear polymerization, followed by an identical propagation step that contains the produced macroanion and quaternized monomeric species. The chemical structure of polymer was characterized by NMR (^{1}H-, ^{13}C-), IR, and UV-visible spectroscopies. This polymer showed characteristic wide UV-visible absorption band and green PL maximum value at 518 nm, which is corresponding photon energy of 2.39 eV. The cyclic voltammogram of polymer revealed that it shows stable electrochemical window in the range of of −1.85 V to 1.55 V.

Keywords Polyacetylene; 2-ethynylpyridine; 3-(trimethylsilyl)propargyl bromide; photoluminescence; cyclic voltammetry.

Introduction

The conjugated polymers featuring a delocalized electronic structure exhibited such unique properties as electrical conductivity, photoconductivity, paramagnetism, migration and transfer of energy, chemical reactivity and complex formation ability, high gas permeability, and high nonlinear optical susceptibility [1–10].

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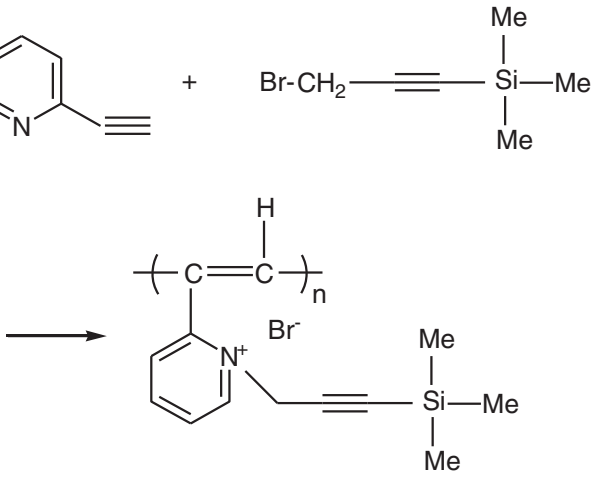
The incorporation of various substituents to acetylene and their subsequent polymerization may lead to the conjugated organic materials with the designed peculiar properties [1, 2]. Among substituted polyacetylenes (PAs), the ionic PAs have the conjugated backbone system with an ionic side group in each repeating unit. A new class of mono and disubstituted ionic PAs have been prepared through the activated polymerization of ethynylpyridines by using halogens or alkyl halides [11–13]. These conjugated polymers contain pyridinium ring substituents associated with halide, sulfonate or sulfate counter anions. We have also synthesized various ionic PAs by the activated polymerization of ethynylpyridines by using functional alkyl, carbonyl halides or cyclic compounds [14–20].

Ethynylpyridinium salts are spontaneously polymerized to form highly conjugated, charged polyacetylenes without any additional catalyst or initiator [11, 12, 21]. Thus, this method can essentially exclude the contamination that can be originated from the catalyst or initiator used during the process. Most of these ionic PAs are water-soluble, which allows them to be processed by environmental friendly method.

These ionic PAs have been used as material candidates for ultrathin amphiphilic films [22], intercalated nanocomposites [21], fluorescence quenchers for bioassays [23], cationic PA/silica hybrids [24], hybrid PA gels [25], PA-nanocrystalline CdS sensitizer [26, 27], PA-silver nanoparticles [28, 29], and unipolar write-once-read-many-times (WORM) memory devices [30].

In this article, we report the non-catalyst synthesis of an ionic PA via the activated polymerization of 2-ethynylpyridine using 3-(trimethylsilyl)propargyl bromide (Scheme 1) and the polymer properties.



Scheme 1. Synthesis of PETPPB

Experimental

2-Ethynylpyridine was prepared according to our previous paper [31]. 3-(Trimethylsilyl)propargyl bromide (98%) was purchased from Sigma-Aldrich and used as received. The analytical grade solvents were dried with an appropriate drying agent, distilled, and stored under nitrogen atmosphere. Poly(2-ethynyl-[N-(3-trimethylsilyl) propargyl]pyridinium bromide) [PETPPB] was prepared by the non-catalyst polymerization of 2-ethynylpyridine using 3-(trimethylsilyl)propargyl bromide.

PETPPB was synthesized via the following procedures: Equal mole ratio of 2-ethynylpyridine (1.0 g, 9.70 mmol) and 3-(trimethylsilyl)propargyl bromide (1.85 g, 9.70 mmol) was placed in two-necked, round-bottomed flask equipped with a magnetic stirrer in DMF (10 mL, $[M]_0 = 0.75$ M). The polymerization was carried out at 70°C oil bath and stirring was continued for 24 h under nitrogen atmosphere. The color of reaction mixture was changed from the light brown of the initial mixture into dark brown. The resulting polymer solution was diluted with additional 10 mL DMF and precipitated into a large excess of ethyl ether, followed by filtration. The collected product was dried in vacuo to give PETPPB as a dark brown powder (89%).

Infrared (IR) spectra were recorded on a Bruker EQUINOX 55 spectrometer in KBr pellets. Vibration transition frequencies were reported in wavenumber (cm^{-1}). ^1H- and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Varian 500 MHz FT-NMR spectrometer (Model: Unity INOVA) in dimethyl sulfoxide-d_6 (DMSO-d_6) solutions. The inherent viscosities of polymers were determined at a concentration of 0.5 g/dL in DMF at 30°C. Energy dispersive X-ray (EDX) analyses were performed by Hitachi JEOL system (S-4200). Cyclic voltammetric waves were measured by using a Hokuto Denko HA-301 potentiostat/galvanostat (AUTOLAB/PG-STAT12) equipped with a HA-301 functional generator and a X-Y reorder. The measurements were performed in 0.1 M tetraethylammonium tetrafluoroborate [$(t\text{-}Et)_4NBF_4$] containing DMF solution. Ag wire and platinum foil were used as a reference and a counter electrode, respectively. The optical absorption spectra were measured by a HP 8453 UV-visible Spectrophotometer. The photoluminescence spectra were obtained by Perkin Elmer luminescence Spectrometer LS55 utilizing a lock-in amplifier system with a chopping frequency of 150 Hz. Xenon lamp was used as the excitation source, and the incident beam took the maximum absorption peak of the polymers.

Results and Discussion

The non-catalyst polymerization method is a facile synthetic one for preparing ionic PAs containing long sequences of conjugated double bonds in the backbone with ionic charges adjacent to or in conjugation with them.

Herein, we synthesized a new ionic PA via the non-catalyst polymerization of 2-ethynylpyridine using 3-(trimethylsilyl)propargyl bromide. In our previous work, the propargyl bromide was used as functional alkyl halide for the synthesis of ionic PAs [16]. And also we prepared an ionic PA by the polymerization of N-propargylpyridinium bromide with transition metal catalysts [32]. In recent years, Chen et al also reported the synthesis of the same ionic PA via the reaction of pyridine and propargyl bromide under mild conditions [33].

The reaction mixture of equal mole ratio of 2-ethynylpyridine and 3-(trimethylsilyl)propargyl bromide in DMF solvent was exposed in heated oil bath (70°C). As the reaction proceeded, the viscosity of reaction solution was gradually increased. And the color of reaction mixture was changed from the light brown of the initial mixture into dark reddish brown. The polymerization behaviors were found to be very similar with that of the same polymerization using simple propargyl bromide [16], regardlesss of the presence of bulky 3-trimethylsilyl groups. The dark-brown powder was obtained in 89% yield.

The molecular structure of PETPPB was characterized by such various instrumental methods as IR, NMR, and UV-visible spectroscopies. FT-IR spectra of 2-ethynylpyridine, 3-(trimethylsilyl)propargyl bromide, and PETPPB were measured and compared. FT-IR spectrum (Figure 1) of PETPPB did not show the ethynyl C≡C bond stretching (2110 cm^{-1})

and acetylenic ≡C−H bond stretching frequencies (3293 cm^{-1}) of 2-ethynylpyridine. Instead, the C=C stretching peak of conjugated polymer backbone around 1610 cm^{-1} became relatively more intense than those of the C=C and C=N stretching frequencies of 2-ethynylpyridine. The characteristic acetylenic C≡C bond stretching peak of 3-(trimethylsilyl)propargyl substituents is observed at 2165 cm^{-1}. The Si-C stretching peaks of trimethylsilyl groups are observed at 845 and 1250 cm^{-1}. The vinylic = C−H stretching peaks of polymer backbone and pyridyl moieties are observed around 3025 cm^{-1}, whereas the aliphatic C−H stretching peaks of 3-(trimethylsilyl)propargyl groups are observed around 2950 cm^{-1}.

The ^{1}H-NMR spectrum of PETPPB showed the aromatic protons of pyridyl moieties and the vinyl protons of the conjugated polymer backbone broadly at 5.0∼10.1 ppm. The methyl proton peaks of trimethylsilyl substituents are observed at −0.4∼0.5 ppm, whereas the methylene proton peaks of propargyl moieties were seen at 3.4∼4.5 ppm. The ^{13}C-NMR spectrum (Figure 2) of PETPPB showed the aromatic carbon peaks of pyridyl moieties and the vinyl carbons of conjugated polymer backbone at the range of 92∼155 ppm. The methyl carbon peak of trimethylsilyl groups is seen around −0.6 ppm, whereas the methylene carbon peak is observed at 46∼52 ppm, respectively. The UV-visible spectrum of polymer showed a characteristic absorption band in the visible region (up to 750 nm). These evidences confirmed that the conjugated polyene backbone system with the designed substituents was formed via the non-catalyst polymerization. The results from EDX analysis confirmed the presence of C, Si, and Br atoms. The multiple peaks of bromine atom means that the bromide ion has different form and/or different environments although we can't now interpret the exact form of bromide atom. PETPPB was completely soluble in water and such organic solvents as DMF, DMSO, and NMP and the inherent viscosity of PETPPB was 0.16 dL/g.

We studied the electro-optical and electrochemical properties of PETPPB by using UV-visible absorption and photoluminescence (PL) spectroscopies and cyclic voltammograms (CV). Figure 3 shows the UV-visible absorption and photoluminescence spectra of PETPPB solution.

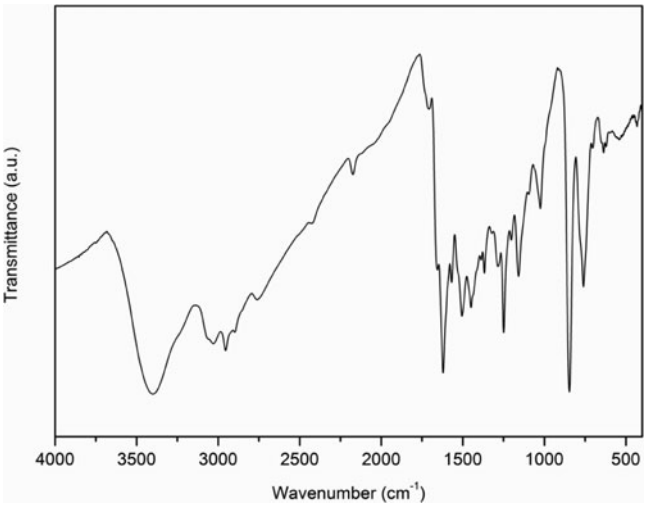


Figure 1. IR spectrum of PETPPB in KBr pellet.

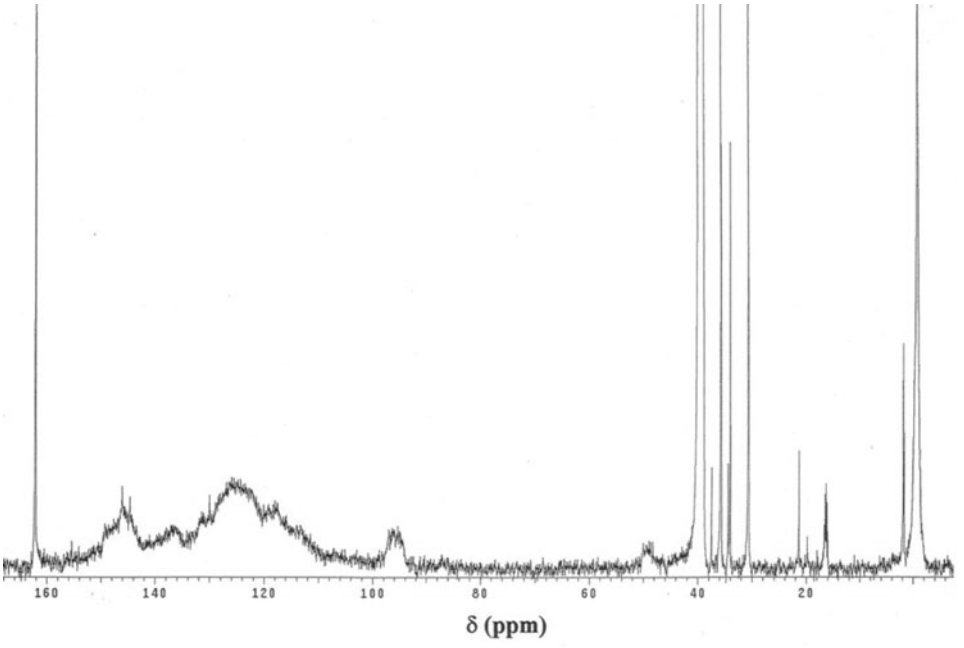


Figure 2. ^{13}C-NMR spectrum of PETPPB in DMSO-d_6.

The absorption spectrum starts from 750 nm to shorter wavelength region and exhibits absorption maximum value of 451 nm, which is due to the $\pi \rightarrow \pi^*$ interband transition of this conjugated polymers. The photoluminescence spectra of this ionic conjugated polymer showed broad emission band in the range of 460 nm and 700 nm under the 451 nm excitation and the maximum peak of 518 nm corresponding to the photon energy of 2.39 eV. In our previous study [16], the optical properties of poly(2-ethynylpyridinum bromide) having

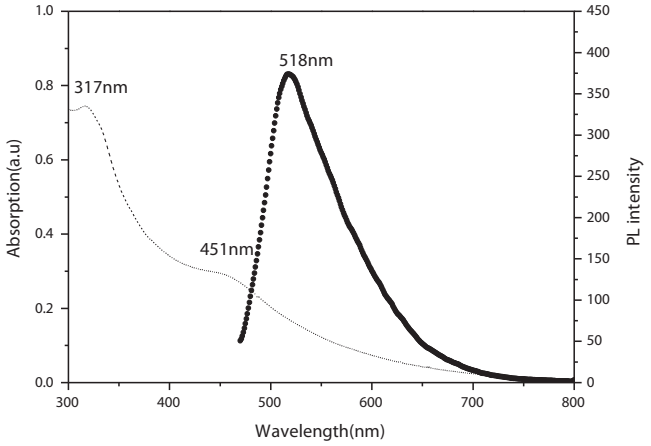


Figure 3. Optical absorption (1.0×10^{-4} M, DMF solution) and PL spectrum (1.0×10^{-4} M, DMF solution, excitation wavelength: 451 nm) of PETPPB.

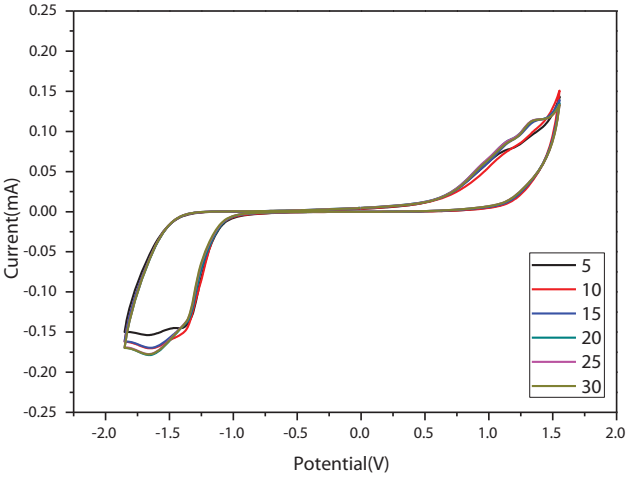


Figure 4. Cyclic voltammograms of PETPPB in 0.1 M $(n\text{-}Bu)_4NBF_4$/DMF solution: 30 consecutive scans at 100 mV/sec scan rate.

propargyl groups (PEPBP) was reported. PEPBP had same main chain and side group, but it does not include trimethylsilyl group unlike PETPPB. PEPBP had absorption maximum value of 540 nm, PL maximum value of 760 nm, and band gap of 2.01 eV. Comparing PETPPB with PEPBP, PETPPB has some steric hinderance effect between trimethylsilyl side group and main chain of conjugated polyene. It made blue shift effect in UV-visible absorption and PL spectra. The UV-visible maximum value changed 89 nm blue shift, and PL maximum value moved 142 nm blue shift. Bulky trimethylsilyl side group broke the conjugation length and planarity of polyene. Thus, band gap was changed from 2.01 eV to 2.33 eV. When stokes shift value is compared between two polymers, PEPBP showed 120 nm but PETPPB was 67 nm. It means that stokes shift value of conjugated polyene was decreased under steric hinderance.

The electrochemical kinetic behavior through the cyclic voltammograms (CVs) of PETPPB solution with 30 consecutive scans at 100 mV/s scan rate was also investigated as shown in Figure 4. During 30 scans, the stable cyclic voltammograms was verified in the range of −1.85 V to 1.55 V. Also, oxidation was started at 0.36 V and HOMO level can be calculated to 5.09 V. Based on band gap of absorption data, LUMO level was 2.76 V.

Conclusions

The non-catalyst synthesis of an ionic PA was successfully performed by the reaction of 2-ethynylpyridine and 3-(trimethylsilyl)propargyl bromide without any additional initiator or catalyst. The non-catalyst polymerization of 2-ethynyl-[N-(3-trimethylsilyl)propargyl]pyridinium bromide proceeded in homogeneous manner to give the resulting polymer in high yield yield (89%). The instrumental analysis data for polymer structure revealed that PETPPB have an ionic conjugated polymer system bearing the N-(3-trimethylsilyl)propargyl]pyridinium bromides. The photoluminescence spectrum of polymer showed that the photoluminescence peak is located at 518 nm, corresponding to a photon energy of 2.39 eV. Trimethylsilyl side group made breakage of conjugation and planarity for polyene and it made overall blue shift in optical data. The cyclic voltammogram of PETPPB exhibited irreversible electrochemical behavior between the oxidation

and reduction peaks, but it showed stable electrochemical window in the range of −1.85 V to 1.55 V.

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