

Synthesis and Properties of Ionic Conjugated Polymers with Aromatic Heterocycles

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1. INTRODUCTION

Polyacetylene (PA) is the best-known conjugated polymer, in which its doped form shows high conductivity that stands in comparison with that of copper. Unfortunately, applications of this promising material have remained limited because the polymer is insoluble, infusible, and thermally unstable. In order to overcome these problems, a number of mono- and di- substituted PAs has been prepared by the simple linear polymerization of the corresponding acetylene monomers by various catalyst systems.¹⁻³ The polymers, having a conjugated backbone, are expected to exhibit unique properties such as electrical conductivity, paramagnetism, migration, energy transfer, color, chemical reactivity and complex formation ability.¹ These properties regarding conjugated polymers have enabled conjugated molecules to be suitable candidates for displays, lasers, photovoltaics, and nonlinear optical materials.³

We have recently prepared various ionic conjugated polymers having different functionalities by using the activation polymerization of ethynylpyridines,^{4,5} and modified the polymer properties by the ion-exchange reaction of the resulting ionic conjugated polymers. Since these conjugated polymers contain extensive conjugation and ionic natures, these ionic PAs show potential as materials for mixed ionic and electronic conductivity, energy storage devices such as batteries, permselective membranes, and light-emitting devices.

In this work, we report the synthesis of a new ionic conjugated polymer with aromatic functional groups via the activated polymerization of 2-ethynylpyridine by using 4-(methylthio)benzyl bromide and the characterization of the resulting polymer.

2. EXPERIMENTAL

Poly[2-ethynyl-N-(4-(methylthio)benzylpyridinium bromide)] (PEMBPB) was synthesized by the activated polymerization of 2-ethynylpyridine by using 4-(methylthio)benzyl bromide in various polar solvents without any additional initiator or catalyst.

FT-IR spectra were obtained with a Bruker EQUINOX 55 spectrometer using a KBr pellet. The inherent viscosities of polymers were determined at a concentration of 0.5 g/dL in DMF at 30 °C. 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.

The optical absorption spectra were measured by using a HP 8453 UV-VIS-NIR spectrometer. A Perkin Elmer luminescence spectrometer LS50 (Xenon flash tube), utilizing a lock-in amplifier system with a chopping frequency of 150Hz, was used for photo- and electro-luminescence spectroscopies. 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 to 150 mV/s. PEMBPB was dissolved in acetonitrile (AN) with 0.1 M tetrabutylammonium perchlorate as an electrolyte. A platinum working electrode and saturated Ag/AgNO₃ reference electrode were used. Ferrocene was used for potential calibration (all reported potentials are reference against ferrocene/ferrocenium, FOC) and reversibility criteria.

3. RESULTS AND DISCUSSION

PEMBPB, a polyacetylene derivative with

aromatic functional groups, was prepared through the activated polymerization of 2-ethynylpyridine by using 4-(methylthio)benzyl bromide in various organic solvents without any additional catalyst or initiator. The present polymerization of 2-ethynylpyridine by using 4-(methylthio)benzyl bromide proceeded easily in a homogeneous manner to provide the corresponding polymer in high yield. The color of the reaction mixture changed from light brown into dark brown as the polymerization process proceeded. The present polymerization seems to proceed in anionic mechanism. It contains the first quaternization of 2-ethynylpyridine by 4-(methylthio)benzyl pyridinium bromide. The initial step involves a nucleophilic attack by the nitrogen atom of unreacted 2-ethynylpyridine and/or the bromide anion on the electrophilic N-ethynyl triple bond of the quaternized acetylenic monomer. The activated acetylenic triple bond of 2-ethynyl-N-4-(methylthio)benzylpyridinium moieties formed at the initial reaction times is susceptible to the linear polymerization, followed by an identical propagation step that contains the produced macroanion and the quaternized monomeric species. Finally, this reaction is terminated by a reaction of macroanionic species with 4-(methylthio)benzyl pyridinium bromide and/or other components.

The chemical structure of PEMBPB was characterized by means of such instrumental methods as NMR, IR, UV-visible spectroscopies. The present PEMBPB also showed a characteristic UV-visible absorption band at 446 nm, and this polymer exhibited a PL maximum peak at 508 nm corresponding to the photon energy of 2.44 eV. Considering PL maximum results regarding PEMBPB and poly[2-ethynyl-N-(3-thienylmethyleneoxy)-hexyl pyridinium bromide], the functional groups of PEMBPB has a role similar to a thiophene group of poly[2-ethynyl-N-(3-thienylmethyleneoxy)-hexylpyridinium bromide] due to similar aromatic substituent size. As a result, it is believed that the side chains within this molecule shifts PL maximum values because it makes different molecular arrangements.

In order to characterize electrochemical kinetic behavior in an electrochemically stable window, the cyclic voltammograms (CVs) of PEMBPB, including a consecutive scan and various scan rates (30mV/s ~ 150mV/s), were recorded.

It has been observed that the shape of CVs is almost unchanged, with the conclusion that PEMBPB is fairly stable without any severe degradation up to 30 cycles of the consecutive

scan.

The oxidation current of PEMBPB versus the scan rate is approximately a linear relationship in the range of 30 mV/sec ~ 150 mV/sec where the exponent of scan rate, x value is found to be 0.4771. This is explained by the fact that the kinetics regarding the redox process are very close to the diffusion-control process.

Although PEMBPB is one of self-doping type polymers, it shows very low electrical conductivity (3.55×10^{-10} S/cm) in comparison to poly(2-ethynylpyridinium-N-benzoylsulfonate) (5.7×10^{-9} S/cm) and poly[2-ethynyl-N-(4-sulfobutyl)pyridinium betaine] (3.5×10^{-9} S/cm). The electrical conductivity of polymer increased significantly through chemical doping by using an acceptor-type dopant such as iodine. Polymer pellet subjected to vapor-phase iodine doping showed large, irreversible iodine uptakes with no significant decrease in iodine content even after prolonged vacuum pumping (6 hrs). The polymer pellet was changed eventually into a lustrous, soft, pasty material. The electrical conductivity of the iodine-doped PEMBPB pellet [sample composition: (PEMBPB)₁(I₂)_{0.39}] was 1.20×10^{-3} S/cm. The FT-IR spectra of iodine-doped PEMBPB showed a broad absorption in the range of 3700-1600 cm⁻¹, arising due to electronic transitions from the valence to the conduction bands in conjugated polymer systems

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