

Synthesis and Properties of Water-Soluble Ionic Conjugated Polymer from the Polymerization of 2-Ethynylpyridine by Using 1,4-Butanesultone

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1. INTRODUCTION

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[1-3]. These properties regarding conjugated polymers have enabled conjugated molecules to be suitable candidates for displays, lasers, photovoltaics, and nonlinear optical materials. To date, the self-dopable π -conjugated polymers were also prepared to improve the rates of doping/undoping. Heeger and coworkers have prepared the self-dopable polymers poly[n-(3⁺-thienyl) alkanesulfonic acid]s and their sodium salts with alkanes of carbon numbers 2 and 4, in which the dopants are covalently bonded to the side chains. Upon electrochemical doping of these polymers in electrolyte solutions, a charge transfer accompanied by a generation of polaron/bipolaron occurs by ejection of protons or metal ions from the bonded dopant and simultaneous ejection of π -electrons from the conjugated main chains, as reflected by an increase of the proton or metal ion concentration in the electrolyte solution and the presence of free spins during the doping. Other examples of the heterocycle-based self-dopable polymers were reported.

In this presentation, we report the synthesis of a water-soluble ionic conjugated polymer, poly[2-ethynyl-N-(4-sulfobutyl)pyridinium betaine] (PESPB) by the activated polymerization of 2-ethynylpyridine with the ring-opening of 1,4-butanesultone, and the electro-optical and electrochemical properties of the resulting PESPB.

2. EXPERIMENTAL

2-Ethynylpyridine was prepared by the bromination of 2-vinylpyridine and the consecutive dehydrobro-

mination reaction. 1,4-Butane sultone (Aldrich Chemicals, 99+%) was used as received. The analytical grade solvents were dried with an appropriate drying agent and distilled.

PESPB was prepared by the activated polymerization of 2-ethynylpyridine with the ring-opening of 1,4-butanesultone without any additional initiator or catalyst in DMF solvent as follows. The 1:1 mixture of 2-ethynylpyridine (1.0 g, 9.7 mmol) and 1,4-butane sultone (1.32 g, 9.7 mmol) in DMF solvent was stirred for 24 hrs at 130 °C under nitrogen atmosphere. As the reaction proceeded, the color of reaction mixture changed from the light brown of the initial mixture into dark black. After the polymerization time, the resulting polymer solution was precipitation into a large excess amount of ethyl ether. The precipitated polymer was filtered and dried under vacuum at 40 °C for 24 hrs. The polymer yield was 82%.

The photoluminescence spectra were obtained by a 488 nm Ar laser as an excitation or Perkin Elmer luminescence spectrometer LS50 (Xenon flash tube). The emission signal was collected by using the conventional photoluminescence arrangement of a laser, samples, a cryostat (Air Products 1R02-A displax), a monochromator (Spex 750M), and a photomultiplier (Hamamatsu R943-02). The signal from the photomultiplier was amplified by an EG&G 5101 lock-in amplifier with the chopping frequency of 170Hz, and converted to the digital signal in the autoscan system. The measurements of AC electrical properties were performed for pellet samples of polyacetylene derivative. In order to measure AC electrical properties, aluminum electrodes were coated on top and bottom sides of the samples through vacuum evaporation based on ASTM D150-81 technique. The guard ring was used to minimize the effect of edge capacitance. The samples were located in the sample holder of metal

shielding case to eliminate the effect of external electromagnetic interference. The frequency range for AC electrical properties was from 10 Hz to 2 MHz by using QuadTech 7600 Precision RLC Meter. The temperature was controlled from 78 K to 300 K by using Delta-Design 9059 temperature chamber.

3. RESULTS AND DISCUSSION

The polymerization of ethynylpyridines by using simple alkyl halides such as methyl iodide, 1-octyl bromide, lauryl bromide, etc had been known to proceed well to give high yield of polymer. The present polymerizations of 2-ethynylpyridine by using 1,4-butanediol were carried out at the elevated temperature (130 °C). As the reaction proceeded, the color of reaction mixture changed from the light brown of the initial mixture into dark black. The polymer yield according to the polymerization time revealed that this polymerization proceeded gradually up to 24 hrs and the polymer yield after 24 hrs reaches 82 % and then plateaus.

We characterized the chemical structure of PESPB by NMR, infrared, and UV-visible spectroscopies. From these spectral data, we concluded that PESPB has an ionic conjugated polymer system bearing the sulfobetaine moieties.

This zwitterionic polymer, PESPB, was soluble in such polar protic solvents as water, methanol, DMF, DMSO, N,N-dimethylacetamide, or organic acids capable of hydrogen bonding with the sulfonate anion. The polymer aggregated by the attractive intracharge-charge interaction could be considerably expanded by the strong hydrogen bonding between the pendant sulfonate anion and protic polar solvents. This poly(sulfobetaine) was found to be more soluble in salt solution than in salt-free solution. Such unusual solution behavior can be explained in terms of a shift from intra- to inter-interactions. This polymer is phenomenologically interesting by virtue of its “antipolyelectrolyte” solution behavior, e.g. enhanced viscosities in salt solutions. The viscosity of this poly(sulfobetaine) was actually increased with increasing NaBr concentration from the initial 0.13 dL/g to the final 0.26 dL/g. This observation indicates that this polymer acts like an “antipolyelectrolyte”. The morphology of PESPB was also investigated by X-ray diffraction analysis. Because the peaks in the diffraction pattern were broad and the ratio of the half-height width to diffraction angle ($\Delta 2\theta/2\theta$) is

greater than 0.35 [1], the polymers were mostly amorphous.

The photoluminescence peak of PESPB is located at 530 nm corresponding to the photon energy of 2.34 eV.

The temperature-dependent photoluminescence spectra of PESPB film were also measured.

The photoluminescence intensity was increased as the temperature is increased. This phenomenon is because the non-radiative decay channels are increased as the temperature is increased. However, there were no changes in the location of the peak and the line shape of the spectrum as the temperature was varied. This means that the temperature does not affect excitation states of PESPB.

At 1 kHz and room temperature, this poly(sulfobetaine) has $k' = 5.7$ and $\sigma = 3.5 \times 10^{-9}$ S/cm. These values were somewhat higher than those of similar pyridine-based conjugated polymers. The cyclic voltammogram of PESPB was measured in 0.1 M tetraethylammonium tetrafluoroborate in DMF solution with a scan rate of 100 mV/s in the range of 0 – 1.6 V. The onset potential of *p* doping (or oxidation) was observed at 0.54 V versus Ag.

4. ACKNOWLEDGEMENT

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5. REFERENCES

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