

# The Color and Spectroscopic Properties of Polyacetylene Derivatives (IX): Synthesis and Properties of a Water-Soluble Conducting Polymer by the Ring-Opening Method

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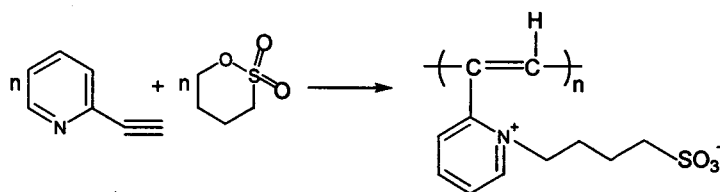
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## 1. Introduction

For more than 40 years, electric conduction in organic solids has been one of the most fascinating topics for synthetic chemists and solid-state physics [1-7]. This considerable interest was triggered by the discovery of high electric conductivity in molecular crystals of tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) in 1973 [4] and in the oxidized form of  $\pi$ -conjugated polyacetylene (PA), a few years later [5]. The polyacetylene is structurally the simplest one, and it can be made free-standing thin film by using Shirakawa catalysts [5-7]. However, the drawbacks are that PA is insoluble, infusible, and unstable to air oxidation. Thus it was difficult for practical applications to opto-electronic devices as an active material. To overcome these problems of polyacetylene itself, more stable heterocycle-based polymers such as polypyrrole and polythiophene were prepared, and these materials can be easily obtained in their oxidized conducting form by means of one-step electrochemical synthesis.

To date, the self-dopable  $\pi$ -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  $\pi$ -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.

Here we report a very facile synthetic method of a self-dopable conjugated polybetaine, poly[2-ethynyl-N-(4-sulfobutyl)pyridinium betaine] (PESPB) by the activated polymerization of 2-ethynylpyridine with 1,4-butanediol without any additional initiator or catalyst (Scheme 1).



Scheme 1. Synthesis of water-soluble conjugated polymer by the ring-opening method.

## 2. Experimental

2-Ethynylpyridine was prepared by the bromination of 2-vinylpyridine and the consecutive dehydrobromination 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-butanedithione 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-butanedithione (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 an 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 %.

## 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 even at the mild reaction condition of low temperature (<50 °C). The activated acetylenic triple bonds of N-alkyl-2-ethynylpyridinium halide was found to be susceptible to the polymerization under mild conditions. However, the present polymerization did not proceed at the somewhat low temperatures. Thus the polymerizations 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 plateau. This polymerization also proceeded well in such organic solvents as DMF, DMSO, and NMP. The polymerization behavior of 2-ethynylpyridine with 1,4-butanedithione was found to be similar with that of the polymerization reaction of 2-ethynylpyridine with 6-(N-carbazolyl)hexyl bromide.

The photoluminescence peak 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 dose not affect excitation states of PESPB. Similar results were also observed in the

other similar pyridine-containing conjugated polymer, poly(2-ethynylpyridinium bromide) having propargyl side chain.

In order to measure the electrical conductivity, we also measured dielectric constant value of PESPb. The frequency and temperature dependences of  $K'$  and  $\sigma$  of this poly(sulfobetaine) were measured. Dielectric behavior of this poly(sulfobetaine) is qualitatively analogous to that of polyaniline (PANI)-Emeraldine Base (EB). At 1 kHz and room temperature, this poly(sulfobetaine) has  $K' = 5.7$  and  $\sigma = 3.5 \times 10^{-9}$  S/cm. This zwitterionic polymer was found to be more hygroscopic, and 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 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, which means that this poly(sulfobetaine) acts like an "antipolyelectrolyte".

#### 4. Conclusions

In this article, we dealt with the synthesis and properties of a self-dopable conjugated ionic polymer (PESPb). PESPb was prepared by the direct polymerization of 2-ethynylpyridine and 1,4-butanediol without any additional initiator or catalyst. This polymerization proceeded well in such organic solvents as DMF, DMSO, and NMP. The dielectric constant ( $K' = 5.7$ ) and electrical conductivity ( $\sigma = 3.5 \times 10^{-9}$  S/cm) of PESPb were somewhat higher than those of similar pyridine-based conjugated polymers, which is due to the self-dopable properties of the present polymer.

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