

# Communications

## A Pyridine-Containing Conjugated Polyelectrolyte: Poly(2-ethynyl-*N*-propargylpyridinium bromide) by the Cyclopolymerization of 2-Ethynyl-*N*-propargylpyridinium Bromide by Transition Metal Catalysts

Yeong-Soon Gal<sup>\*</sup>, Won-Chul Lee<sup>†</sup>, Ji-Hoon Lee<sup>‡</sup>, and Sam-Kwon Choi<sup>‡</sup>

Polymer Chemistry Laboratory, College of General Education

<sup>\*</sup>Department of Textile Engineering, Kyungil University, Hayang 712-701, Korea

<sup>‡</sup>Department of Chemistry, Korea Advanced Institute of Science and Technology, Taejon 305-701, Korea

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The polymerization of acetylene and its derivatives is one of the fundamental methods for the synthesis of linear conjugated polymers, which can be used as organic semiconductors, as membranes for gas separation and for liquid-mixture separation, as a side-chain liquid crystal, and for nonlinear optical materials.<sup>1-9</sup> Examples of polyelectrolytes having a conjugated backbone are scarce and restricted to the following cases: the solid-state polymerization of propiolic salts by  $\gamma$ -irradiation,<sup>10</sup> water-soluble polyene polymers by quaterization of poly(6-bromo-1-hexyne),<sup>11</sup> and the synthesis of mono- and di-substituted ionic polyacetylene by the activation of the acetylene bond in ethynylpyridine by the introduction of a strong electron withdrawing substituents in conjugation to it.<sup>12-15</sup>

Due to their extensive conjugation and ionic nature, these polymers have potential for use as materials for mixed ionic and electronic conductivity, energy storage devices such as batteries and permselective membranes<sup>12</sup>.

We reported the synthesis of water-soluble poly(2-ethynylpyridine) by the polymerization of 2-ethynylpyridine with W- and Mo-based catalysts<sup>16</sup>, and the synthesis of poly(*N*-propargylpyridinium bromide) by the polymerization of *N*-propargylpyridinium bromide by palladium- and platinum chlorides.<sup>17</sup>

Now we report the synthesis of a novel conjugated ionic polymer via an interesting cyclopolymerization reaction of 2-ethynyl-*N*-propargylpyridinium bromide (EPPB) having two acetylenic functional groups (acetylenic and propargyl) in the same monomer.

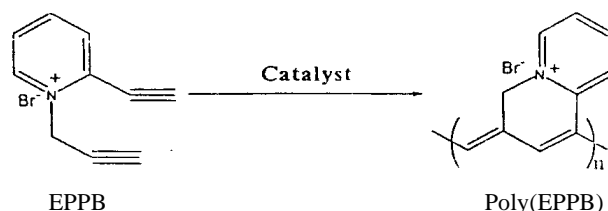
The monomer, EPPB, was prepared by the nucleophilic substitution reaction of 2-ethynylpyridine with propargyl bromide in ethyl ether. The polymerization of EPPB was carried out by PdCl<sub>2</sub>, PtCl<sub>2</sub>, and RuCl<sub>3</sub> catalysts. All procedures for the preparation of EPPB and catalyst system, and the polymerization were carried out under nitrogen atmosphere, because EPPB is hygroscopic and the active species of catalysts are sensitive to moisture and oxygen.

The ring-forming cyclopolymerization of EPPB having two acetylenic functional groups was carried out by transition metal catalysts (Scheme 1).

Table 1 shows the results for the polymerization of EPPB by the Pd, Pt, and Ru-based catalysts. In general, the poly-

mer yields were high. The polymerization of EPPB proceeded in a heterogeneous manner in solvents such as DMF, HCO<sub>2</sub>H, and pyridine. Some products were precipitated on the bottom of the reaction ampule during the polymerization. The soluble portion in the polymer was in the range of 15-39%. However, when DMSO and m-cresol were used for solvents, the solution was homogeneous throughout the polymerization and the polymer yield was quantitative. Other catalysts such as (Ph<sub>3</sub>P)<sub>2</sub>PdCl<sub>2</sub>, PtCl<sub>2</sub>, and RuCl<sub>3</sub> also polymerized EPPB effectively to give a high yield of polymer.

The resulting poly(EPPB)s were dark-brown or black powders. The polymers prepared in the solvents of DMSO and m-cresol were soluble in polar solvents such as DMF, DMSO, m-cresol, acetone, formic acid, and they were partially soluble



Scheme 1. Ring-Forming Cyclopolymerization of EPPB

Table 1. Polymerization of EPPB by PdCl<sub>2</sub>, PtCl<sub>2</sub>, and RuCl<sub>3</sub> catalysts<sup>a</sup>

Exp. No	Catalyst	M/C <sup>b</sup>	Solvent	Polymer yield <sup>c</sup>	$\eta_{inh}^d$
1	PdCl <sub>2</sub>	25	DMF	95	0.13
2	PdCl <sub>2</sub>	50	DMF	90	0.14
3	PdCl <sub>2</sub>	25	DMSO	100	0.19
4	PdCl <sub>2</sub>	25	m-cresol	100	0.17
5	PdCl <sub>2</sub>	25	HCO <sub>2</sub> H	89	0.09
6	PdCl <sub>2</sub>	25	pyridine	93	0.10
7	(PPh <sub>3</sub> ) <sub>2</sub> PdCl <sub>2</sub>	25	DMF	85	0.08
8	PtCl <sub>2</sub>	25	DMF	87	0.08
9	RuCl <sub>3</sub>	25	DMF	99	0.12

<sup>a</sup>Polymerization was carried out at 90°C for 24 h. Initial monomer concentration ([M]<sub>0</sub>) was 0.5 M. <sup>b</sup>Monomer-to-catalyst mole ratio.

<sup>c</sup>ethyl ether-insoluble polymer. <sup>d</sup>Measured at a concentration of 0.5 g/dl in DMSO at 25°C.

in methanol and water, but insoluble in chlorobenzene, toluene, benzene, carbon tetrachloride, chloroform, *n*-hexane, etc.

The inherent viscosities were in the range 0.08-0.19. These values are superior to those of conjugated polymers from monopropargyl salt monomers such as propargyltriphenylphosphonium bromide<sup>18</sup> and propargylpyridinium bromide.<sup>17</sup> Also these values are similar with those of simple poly(2-ethynylpyridine).<sup>16</sup>

The <sup>1</sup>H-NMR spectrum of poly(EPPB) prepared by using PdCl<sub>2</sub> as the catalyst in DMSO showed broad peaks due to the conjugated double bonds and aromatic pyridyl protons at 6.0-9.2 ppm, and the methylene protons were observed in the range 2.5-3.2 ppm. The IR spectrum of poly(EPPB) did not show the acetylenic (C≡C) frequencies at 2129 and 2220 cm<sup>-1</sup> and the acetylenic ≡C-H stretching frequencies at about 3300 cm<sup>-1</sup>. Instead the carbon-carbon double bond stretching frequencies were observed at about 1620 cm<sup>-1</sup> with the characteristic peaks of pyridyl moiety. The UV-visible spectrum of poly(EPPB) exhibit the characteristic broad absorption peak of 400-700 nm which originated from the π → π\* transition of the conjugated polyene, which had not been observed at the UV-visible spectrum of monomer. The values of elemental analysis for poly(EPPB) agreed well with the calculated values. Anal. calcd. for (C<sub>10</sub>H<sub>8</sub>NBr)<sub>n</sub>: C, 54.08%, H, 3.64%, N, 6.31%, Br, 35.98%. Found: C, 53.21%, H, 3.55%, N, 6.30%, Br, 35.51%. These results suggest that poly(EPPB)s have a conjugated polyene backbone structure with cyclic recurring units fused with pyridinium ring.

In conclusion, an interesting conjugated polyelectrolyte was synthesized in a high yield via a cyclopolymerization of EPPB by the Pd, Pt, and Ru-based catalysts. A more detailed description of these and other studies on electrophysical properties of the poly(EPPB) will be discussed elsewhere.

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## Dehydrogenative Dimerization of Phenylacetylene by Electrochemical Activation of Vaska's Complex

Kyu Yeon Jun, Kang Min Ok, Chong Shik Chin\*, Woonsup Shin\*

Department of Chemistry, Sogang University, Seoul 121-742, Korea

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The homogeneous catalytic transformation of organic substrates by transition-metal complexes is a very active research area<sup>1</sup> and generally involves the two distinctive steps, oxidation (addition of an organic substrate to a metal) and reduction (elimination of the substrate from metal) of the central metal ion.<sup>2</sup> There is also interest in using electrochemical techniques in conjunction with metal complex catalysts.<sup>3</sup> Electrochemical oxidation or reduction of metal complexes may produce reactive species which could be used to cata-

lyze the organic reactions.

Reactions of terminal alkynes with transition metal complexes produce various kinds of oligomers.<sup>4</sup> There are few examples of the electrocatalytic oligomerization of alkynes in the presence of metal complexes. In this communication, we report the first example of the electrocatalytic dimerization of phenylacetylene using Vaska's complex, IrCl(CO)-(PPh<sub>3</sub>)<sub>2</sub> (Eq. 1). Vaska's complex does not show the catalytic activity for the dimerization unless it is activated by electro-