

A Soluble Poly(arylene) with Large Degree of Depolarization.  
Poly(2,5-pyridinediyl) Prepared by Dehalogenation Polycondensation  
of 2,5-Dibromopyridine with Ni(0)-Complexes

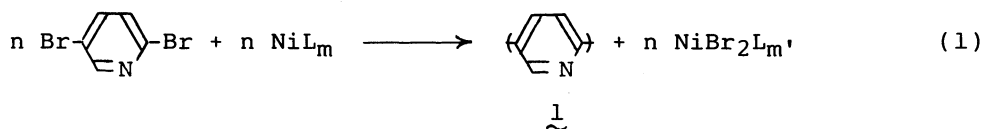
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Poly(2,5-pyridinediyl) was prepared by dehalogenation polycondensation of 2,5-dibromopyridine with Ni(0)-complexes. The polymer was soluble in formic acid, and the solution showed  $\lambda_{\max}$  at about 370 nm and large degree of depolarization.

Preparation and electrical properties of poly(arylene)s having  $\pi$ -conjugation system along the polymer chain is the subject of recent interest. Among the poly(arylene)s, poly(p-phenylene) has been most extensively studied, and preparation of the polymer by various methods<sup>1-4</sup>) has been reported. Compared with poly(p-phenylene), chemistry of its pyridine analogue, poly(2,5-pyridinediyl), has been much less explored. Our previous paper<sup>2</sup>) briefly reported Ni-catalyzed dehalogenation polycondensation of 2,5-dibromopyridine with magnesium. We now report a new preparation method to give poly(2,5-pyridinediyl) using zerovalent nickel complexes as the dehalogenation reagent of 2,5-dibromopyridine.



The polymerization method is based on dehalogenation coupling between aromatic halides with Ni(0) complexes.<sup>5</sup>)

Stirring a mixture of 2,5-dibromopyridine and Ni(0) complex (1.0-1.2 mol/mol of the monomer) in a solution gave yellow or yellowish orange precipitates of poly(2,5-pyridinediyl). The precipitates were washed repeatedly with hot toluene, warm aqueous solution (pH = 3) of EDTA, warm aqueous solution (pH = 9) of EDTA, warm aqueous solution (pH = 9) of NaOH, hot water and hot benzene, and dried under vacuum. Results of the polymerization are summarized in Table 1. As shown in Table 1, various Ni(0)-complexes were usable as the reactant. The reaction system containing 1 mol of PPh<sub>3</sub> per mol of Ni (Run 2) gave higher yield and higher molecular weight than the reaction system containing 4 mols of PPh<sub>3</sub> per mol of Ni (Runs 4 and 5). Analytical data<sup>6</sup>) approximately agreed with the structure of  $\underline{1}$ , although they showed presence of some bromine at terminal unit. The polymer showed no observable change when heated up to 330 °C, where color change to reddish brown started under air. TGA analysis showed high thermal stability of the polymer. The powder X-ray diffraction analysis showed peaks at

Table 1. Preparation of poly(2,5-pyridinediyl) according to Eq. 1

Run	Ni(0) complex	Temp °C	Time h	Solvent <sup>f)</sup>	Yield/% <sup>e)</sup>	$\lambda_{\max}$ /nm	Molecular weight ( $\times 10^3$ )
1	Ni(cod) <sub>2</sub> + cod + PPh <sub>3</sub> <sup>a)</sup>	rt <sup>d)</sup>	24	DMF	64	373	1.2
2	Ni(cod) <sub>2</sub> + cod + PPh <sub>3</sub> <sup>a)</sup>	60	16	DMF	95	372.4	1.9
3	Ni(cod) <sub>2</sub> + cod + PPh <sub>3</sub> <sup>a)</sup>	60	16	HMPA	95	373.5	1.3
4	Ni(PPh <sub>3</sub> ) <sub>4</sub> <sup>b)</sup>	60	16	DMF	59	369	1.6
5	Ni(PPh <sub>3</sub> ) <sub>4</sub> <sup>c)</sup>	60	16	DMF	66	372.4	1.4

a) A 1:1:1 mixture: cod = 1,5-cyclooctadiene. b) Prepared in situ from NiCl<sub>2</sub>, Zn, and PPh<sub>3</sub>. c) Isolated compound. d) room temperature. e) Based on carbon recovered. f) DMF = N,N-dimethylformamide. HMPA = hexamethylphosphorotriamide.

2 $\theta$  = 15.7 ° and 25.4 ° (Cu K $\alpha$ ). IR spectrum of the polymer was reasonable for the structure of 1.

The polymer was soluble in hydrochloric acid and formic acid, and UV-visible spectrum was measured by using the formic acid solution. No apparent color change was observed on dissolving. The spectrum showed relatively sharp single  $\pi$ - $\pi^*$  absorption peak at about 370 nm, and the  $\lambda_{\max}$  value was comparable to that ( $\lambda_{\max}$  = ca. 380 nm in the solid) of poly(p-phenylene) prepared by our method<sup>2)</sup> and remained constant within the experimental error in spite of change of the molecular weight (Table 1). The molecular weight of the polymer was measured by the light scattering method<sup>7)</sup> with the formic acid solution. The molecular weight corresponds to the degree of polymerization of 16-25. The light scattering method revealed also that the polymer solution gave large degree of depolarization,<sup>8)</sup>  $\rho_v = 0.33$ . The value of depolarization is, to our knowledge, the largest value reported for polymer compounds, and approximately agrees with a limiting value ( $\rho_v = 1/3$ ) calculated for a molecule in which the polarizability along a rod axis direction ( $\alpha_3$ ) is very large whereas the polarizability along the other two directions ( $\alpha_1$  and  $\alpha_2$ ) is negligible compared with  $\alpha_3$ . The result strongly suggests that the polymer has a rod-like rigid structure having  $\pi$ -conjugation system with mobile electrons along the polymer chain (presumably the direction of  $\alpha_3$ ).

#### References

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