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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

Takakazu YAMAMOTO,* Takayori ITO, and Kenji KUBOTA †
Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 227
†Colledge of Technology, Gumma University, Tenjincho, Kiryu 376

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 λ_{max} at about 370 nm and large degree of depolarization.

Preparation and electrical properties of poly(arylene)s having π-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$^{1-4)}$ 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$^{2)}$ 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.

1

(1)

The polymerization method is based on dehalogenation coupling between aromatic halides with Ni(0) complexes.$^{5)}$

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_3 per mol of Ni (Run 2) gave higher yield and higher molecular weight than the reaction system containing 4 mols of PPh_3 per mol of Ni (Runs 4 and 5). Analytical data$^{6)}$ approximately agreed with the structure of 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 peakes at

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

Run	Ni(0) complex	Temp/°C	Time/h	Solvent$^{f)}$	Yield/%$^{e)}$	λ_{max}/nm	Molecular weight (x 10^3)
1	$Ni(cod)_2$ + cod + $PPh_3$$^{a)}$	rt$^{d)}$	24	DMF	64	373	1.2
2	$Ni(cod)_2$ + cod + $PPh_3$$^{a)}$	60	16	DMF	95	372.4	1.9
3	$Ni(cod)_2$ + cod + $PPh_3$$^{a)}$	60	16	HMPA	95	373.5	1.3
4	$Ni(PPh_3)_4$$^{b)}$	60	16	DMF	59	369	1.6
5	$Ni(PPh_3)_4$$^{c)}$	60	16	DMF	66	372.4	1.4

a) A 1:1:1 mixture: cod = 1,5-cyclooctadiene. b) Prepared in situ from $NiCl_2$, Zn, and PPh_3. c) Isolated compound. d) room temperature. e) Based on carbon recovered. f) DMF = N,N-dimethylformamide. HMPA = hexamethylphosphorotriamide.

2θ = 15.7 ° and 25.4 ° (Cu K_α). 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 π-π^* absorption peak at about 370 nm, and the λ_{max} value was comparable to that (λ_{max} = ca. 380 nm in the solid) of poly(p-phenylene) prepared by our method$^{2)}$ 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$^{7)}$ 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,$^{8)}$ ρ_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 (ρ_V = 1/3) calculated for a molecule in which the polarizability along a rod axis direction (α_3) is very large whereas the polarizability along the other two directions (α_1 and α_2) is negligible compared with α_3. The result strongly suggests that the polymer has a rod-like rigid structure having π-conjugation system with mobile electrons along the polymer chain (presumably the direction of α_3).

References

1) P. Kovacic and C. Wu, J. Polym. Sci., 47, 45 (1960).

2) T. Yamamoto and A. Yamamoto, Chem. Lett., 1977, 353; T. Yamamoto, Y. Hayashi, and A. Yamamoto, Bull. Chem. Soc. Jpn., 51, 2091 (1978).

3) H. Hirai, N. Toshima, K. Kanaka, and A. Koshirai, Chem. Lett., 1987, 1461.

4) E. Tsuchida, K. Yamamoto, T. Asada, and H. Nishide, Chem. Lett., 1987, 1541.

5) M. Tiecco, L. Testaferri, M. Tingoli, D. Chianelli, and M. Montanucci, Synthesis, 1984, 736.

6) Found: C, 76.0; H, 3.9; N, 16.9; Br, 0.6%. Calcd for $\left(\!-C_5H_3N-\!\right)_n$: C, 77.9; H, 3.9; N. 18.2%.

7) K. Kubota and B. Chu, Biopolymers, 22, 1461 (1983).

8) N. Saito, "Kobunshi Butsurigaku," Shyokabo, Tokyo (1976), p. 181.

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