

Poly(3-vinylpyridazine): Synthesis and Properties

Nan-Loh Yang,^{*a} S. S. Wang,^a C. J. Hou,^a L. Rodriguez,^a J. Jolson,^b and J. Waggoner^b

^a City University of New York, Chemistry Dept., College of Staten Island, N.Y. 10301, U.S.A.

^b Catalyst Research Corporation, Baltimore, MD 21109-9987, U.S.A.

Poly(3-vinylpyridazine) has been synthesized for the first time and found to form semiconducting adducts with iodine.

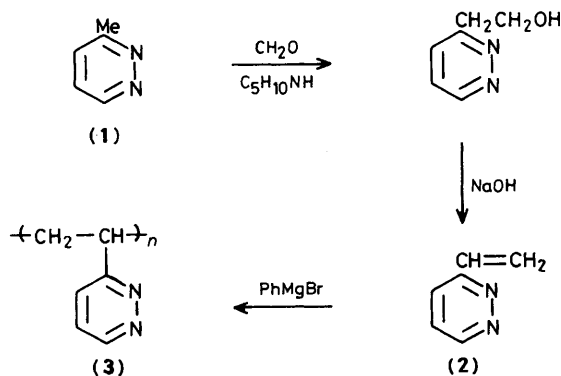
The pyridazine-iodine adduct has been a subject of considerable interest.¹⁻³ We report here the first synthesis of 3-vinylpyridazine (**2**) and poly(3-vinylpyridazine) (**3**).

The monomer, 3-vinylpyridazine (**2**), was synthesized using 3-methylpyridazine (**1**) as the starting heterocyclic material. Hydroxymethylation of (**1**) (20.5 g, 0.22 mol in 40 ml H₂O) with 37% aqueous formalin (30 g, 0.33 mol) was carried out in the presence of a catalytic amount of piperidine (0.7 g) under a nitrogen pressure (ca. 175 psi) at 150 °C for 6 h in an autoclave with mechanical stirring. The intermediate 3-(β-hydroxyethyl)pyridazine was obtained by the removal of unreacted

formalin, water, and remaining starting material. The product is a brown viscous liquid.

Treatment of a mixture of 3-(β-hydroxyethyl)pyridazine (19.7 g) and 4,4'-methylenebis(2,6-di-*t*-butyl)phenol as a radical inhibitor (0.1 g) with powdered sodium hydroxide (1.5 g) under reduced pressure (1.0 Torr) at 120 °C in a Kuegelrohr distillation apparatus yielded a clear, yellow liquid, 3-vinylpyridazine (**2**), (4.9 g).[†]

Phenylmagnesium bromide was used as initiator for anionic polymerization of (**2**). Toluene (40 ml, previously dried by CaH₂, then redistilled) was stirred and 3 M PhMgBr (1 ml) was added. All manipulations were performed under N₂. The monomer (**2**) (4.9 g in 10 ml toluene) was added dropwise. The molar ratio of the monomer to the catalyst is ca. 15:1. Polymerization was carried out for 2 h in a water bath at room temperature. The solution became dark brown, and the viscosity increased progressively. At the conclusion of polymerization, 50 ml of distilled water was added and stirring was continued to allow dissolution of polymer and some monomer in the water layer. After separation of the water layer from the



[†] ¹³C{¹H} N.m.r. data were obtained on an IBM WP-200SY n.m.r. spectrometer, pulse angle 30°, relaxation time 4 s, *T* 298 K. Under these conditions not all carbon atoms are equally relaxed.

¹³C N.m.r. (**2**) (CDCl₃) δ 120.5 (C_α), 123 and 126 (C-4, -5), 150 (C_β), and 157 (C-6); (**3**) δ (D₂O) 30 and 44 (C_α, C_β), 129.5 and 131 (C-4, -5), 151 (C-6), and 162 (C-3); for comparison (**1**) δ (D₂O) 23.5 (C_α), 130 and 131 (C-4, -5), 150 (C-6), and 162 (C-3).

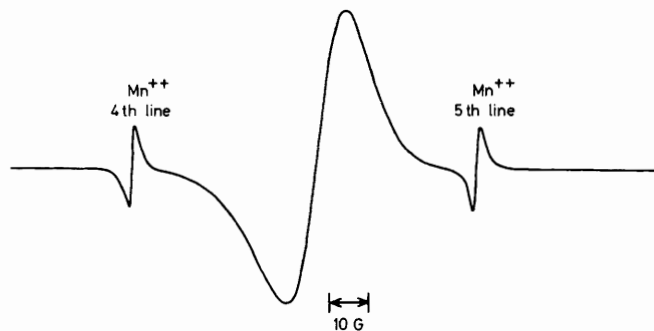


Figure 1. E.s.r. spectrum of poly(3-vinylpyridazine)-I₂ adducts.

toluene layer, the water was removed *in vacuo*. A brown crude polymer was obtained. The crude polymer was first washed with toluene and then dried under vacuum at 120 °C for 0.5 h. The polymer is obtained as a coloured solid material [(3) 1.5 g].†

The monomer can also be polymerized *via* radical polymerization using azobisisobutyronitrile as initiator.

When the polymer (3) was mixed with iodine in molar ratios of 1 : 2 and 1 : 4 pyridazine-ring to iodine and heated in sealed tubes for 24 h, the adducts exhibited low d.c. electronic resistivities in the range of 1000–500 ohm cm. The resistivity was measured at 27 °C using a two-probe method. As in the case for pyridazine-iodine adducts,¹ the variation in stoichiometry did not lead to a large change in resistivity. The composition of the adduct through iodine vapour up-take by the polymer was tentatively assigned to be one pyridazine ring to 1.5 iodine, I₂, molecules.

These poly(3-vinylpyridazine)-I₂ adducts displayed a strong e.s.r. signal (Figure 1).

We thank Professor Y. Okamoto of Polytechnic Institute of New York for the use of a pressure reaction vessel.

Received, 20th June 1985; Com. 868

References

- 1 R. J. Hoare and J. M. Pratt, *Chem. Commun.*, 1969, 1320.
- 2 R. Dratler and P. Laszlo, *Chem. Commun.*, 1970, 180.
- 3 J. I. Hoppe and B. R. T. Keene, *Chem. Commun.*, 1970, 188.