From Government Chemical Industrial Research Institute, Honmachi,
Shibuya-Ku, Tokyo, Japan

Preparation and Polymerization of Vinylpyridine-N-oxide[1]

By T. TAMIKADO, T. SAKAI*, and K. SAGISAKA*

(Eingegangen am 23. September 1961)

SUMMARY:

Two kinds of vinylpyridine-N-oxide, 2-vinylpyridine-N-oxide (VPN) and 5-ethyl-2-vinylpyridine-N-oxide (EVPN) were prepared from the corresponding hydroxyethyl pyridines, and characterized. These N-oxides were polymerized with 2,2′-azo-bis-isobutyronitrile. The monomer reactivity ratios of the following systems were determined: St/VPN ($r_1 = 0.11 \pm 0.01$; $r_2 = 2.1 \pm 0.6$), MMA/VPN ($r_1 = 0.13 \pm 0.03$; $r_2 = 3.9 \pm 0.8$), St/EVPN ($r_1 = 0.10 \pm 0.01$; $r_2 = 2.6 \pm 0.3$), and MMA/EVPN ($r_1 = 0.12 \pm 0.02$; $r_2 = 4.7 \pm 0.6$). Moreover the reactivity difference between vinylpyridine and vinylpyridine-N-oxide in copolymerization was discussed.

ZUSAMMENFASSUNG:

Es werden die Darstellungen von 2-Vinylpyridin-N-oxyd (VPN) und 5-Äthyl-2-vinylpyridin-N-oxyd (EVPN) aus den entsprechenden Hydroxyäthylpyridinen beschrieben. Die N-Oxyde werden charakterisiert und bei 60°C mit Azo-bis-isobutyronitril polymerisiert. In der Copolymerisation mit Styrol (St) und Methacrylsäuremethylester (MMA) wurden die Copolymerisationsparameter für folgende Systeme bestimmt: St/VPN ($r_1 = 0{,}11 \pm 0{,}01$; $r_2 = 2{,}1 \pm 0{,}6$), MMA/VPN ($r_1 = 0{,}13 \pm 0{,}03$; $r_2 = 3{,}9 \pm 0{,}8$), St/EVPN ($r_1 = 0{,}10 \pm 0{,}01$; $r_2 = 2{,}6 \pm 0{,}3$) und MMA/EVPN ($r_1 = 0{,}12 \pm 0{,}02$; $r_2 = 4{,}7 \pm 0{,}6$). Der Unterschied der Reaktivität von Vinylpyridin und Vinylpyridin-N-oxyd bei der Copolymerisation wird diskutiert.

Introduction

In the previous papers of this series concerning with the copolymerization of vinylpyridines[1)], it was concluded that the pyridyl group acts as an electron donor for the double bond in α-, β-, and γ-positions, as does the phenyl group in the styrene molecule.

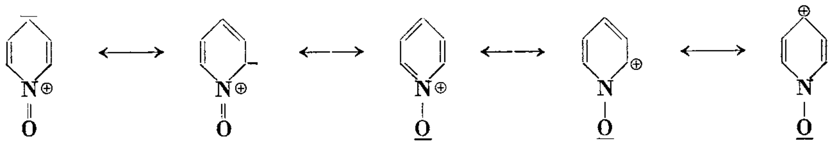
---

*) This paper is based on portions of the theses submitted by T. S. (1960) and K. S. (1961) in partial fulfilment of the requirements for the B. S. degree in Tokyo College of Science.

[1)] This is the 4th in a series of papers concerned with the copolymerization of vinylpyridines. For the latest paper of this series, see T. TAMIKADO, Makromolekulare Chem. **38** (1960) 85.

In relation to this conclusion, the authors were interested in the copolymerization behavior of vinylpyridine-N-oxide. The synthesis and substitution reactions of pyridine-N-oxide were extensively investigated by Ochiai and his collaborators[2].

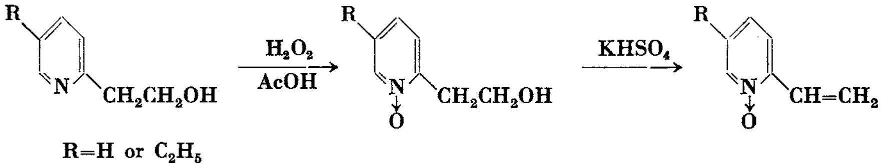
He concluded that the isolated molecule of pyridine-N-oxide has the remarkable property of being strongly polarizable in the directions I and III by the approaching reagent, and then the pyridine-N-oxide is susceptible to both electrophilic and nucleophilic substitutions in α- and γ-positions.


Ia Ib II IIIa IIIb

One of the main purposes of the present investigation was to evaluate the reactivity difference in copolymerization between vinylpyridine and its N-oxide in comparison with the above conclusions. Another purpose of this investigation was to find a convenient laboratory preparation method of this interesting vinyl monomer.

To our knowledge vinylpyridine-N-oxide has not yet been described in the literature. Only a patent[3] claims, without experimental details and characterization of the substance, that this monomer may be prepared by dehydration of hydroxyethyl pyridine-N-oxide in the presence of alkali metal hydroxide.

The scheme used by us for the preparation of the desired substances is:



IV V VI

---

[2] E. Ochiai, J. org. Chemistry 18 (1953) 534.

[3] U.S.P. 2,749,349 (1956) F. E. Cislak.

The 2-hydroxyethyl pyridine-N-oxide (V) was already described by BOEKELHEIDE and FEELY[4]. It has been found that the 2-vinylpyridine-N-oxide (VI) is obtained in over-all yields of 40–50 % (after redistillation) by distilling the 2-hydroxyethyl pyridine-N-oxide (IV) under reduced pressure in the presence of potassium acid sulfate as dehydrating reagent and methylene blue as polymerization inhibitor. The 5-ethyl-2-vinylpyridine-N-oxide has been also prepared by the same method although in somewhat lower yield (25–30 % after redistillation).

The monomers, 2-vinylpyridine-N-oxide and 5-ethyl-2-vinylpyridine-N-oxide thus obtained have been polymerized in alcohol with 2,2′-azo-bis-isobutyronitrile, and they have given white polymers having the intrinsic viscosities of 1.07 and 0.438 respectively in water at 25 °C.

The infrared spectra for several pyridines, pyrimidines, and their N-oxides were analyzed by WILEY and SLAYMAKER[5]. They assigned the strong band at 7.69–7.97 μ to the NO stretching vibration. For the present cases, it is characteristic that both the infrared spectra of the monomers and their polymers show an extremely strong absorption band at about 8 μ attributable to the NO stretching vibration.

The copolymerization reactions of these N-oxide monomers with styrene and methyl methacrylate at 60 °C. have been carried out in alcohol with 2,2′-azo-bis-isobutyronitrile. The monomer reactivity ratios for the systems have been determined. On the basis of these data, the predominance of the resonance structure III for the vinylpyridine-N-oxides is assumed.

Experimental

1. *Preparation of Monomers*

Starting materials

The 2-(β-hydroxyethyl) pyridine (b.p. 95 °C. at 3 mm.) and 2-(β-hydroxyethyl)-5-ethyl pyridine (b.p. 125 °C. at 5 mm., m.p. 42 °C.) were generously furnished by YŪKI-GŌSEI KŌGYO Co. and redistilled before use.

2-(β-Hydroxyethyl) pyridine-N-oxide

The procedure is essentially the same as those described in BOEKELHEIDE and FEELY's paper[4] except some of the modifications in the experimental detail.

---

[4] V. BOEKELHEIDE and W. FEELY, J. Amer. chem. Soc. **80** (1958) 2217.

[5] R. H. WILEY and S. C. SLAYMAKER, J. Amer. chem. Soc. **79** (1957) 2233.

A solution of 61.5 g. (0.5 mole) of 2-(β-hydroxyethyl) pyridine in 300 ml. of glacial acetic acid was heated at 55 °C. in a water bath. To the solution, 75 ml. of 30% hydrogen peroxide was added in small portions during 4 hrs. After a final addition of the hydrogen peroxide, heating was continued for further 16 hrs. The resulting solution was concentrated under reduced pressure, the residue was diluted with 500 ml. of water, and the residual acid was removed by means of an anion-exchange column (packed with 500 ml. of *Amberlite IRA-410*). After concentration of the aqueous eluate under reduced pressure, the residual oil was dissolved in 550 ml. of boiling ethyl acetate, the hot solution was filtered, and crystallized by seeding.

When the solution had been allowed to stand overnight in a refrigerator, the crystals were collected. The crystalline 2-(β-hydroxyethyl) pyridine-N-oxide so obtained weighed 55 g. (79%). After recrystallization from ethyl acetate, the melting point was 91 °C.

2-(β-Hydroxyethyl)-5-ethyl pyridine-N-oxide

The procedure described under the 2-(β-hydroxyethyl) pyridine-N-oxide was repeated except that 76 g. (0.5 mol.) of 2-(β-hydroxyethyl)-5-*ethyl pyridine* were used.

After concentration of the aqueous eluate, the residual oil was distilled under reduced pressure using a short path still. The yield of the material, b.p. 164 °C. at 0.3 mm., was 70 g. (84%). The N-oxide was a pale yellow, viscous oil which solidified by seeding; it was a very hygroscopic solid which liquefied on exposure to the atmosphere.

Its structure was confirmed with formation of phenyl urethan with phenyl isocyanate: a benzene solution of the N-oxide was refluxed with an equivalent of freshly distilled phenyl isocyanate for a few minutes on a water bath; after cooling, the phenyl urethan of the N-oxide separated as white crystals. They were recrystallized twice from carbon tetrachloride and melted at 117—117.5 °C.

Anal., Calcd. for $C_{16}H_{18}N_2O_3$ C 67.13 H 6.32 N 9.78
Found C 67.20 H 6.41 N 9.85

2-Vinylpyridine-N-oxide

An intimate mixture of 2.1 g. of finely powdered, freshly fused potassium acid sulfate, 30 g. of powdered 2-(β-hydroxyethyl) pyridine-N-oxide, and 0.7 g. of methylene blue, prepared by grinding them together in a mortar, was placed in a 50 ml. vacuum distilling flask. The mixture was heated in a vacuum at 2 mm. *in an oil bath maintained* at 160 to 165 °C. until liquid no longer distilled over. After a vacuum redistillation in the presence of 0.5 g. of methylene blue, the yield of 2-vinylpyridine-N-oxide, distilling at 100.5—102 °C. at 0.42 mm., was 11.8 g. (45.2%). On cooling, the distillate solidified and gave a very hygroscopic yellow solid, which gradually liquefied on exposure to the atmosphere and polymerized slowly at room temperature. This monomer melting at about 45 °C. was soluble in water, alcohol, acetone, and chloroform and insoluble in ether, petroleum ether, benzene, and carbon tetrachloride. It decolorized bromine water and potassium permanganate solution.

Anal., Calcd. for C_7H_7NO N 11.57 Found N 11.65

The freshly distilled N-oxide was treated with picric acid in alcohol. The picrate of the 2-vinylpyridine-N-oxide was separated as yellow crystals. They were recrystallized twice from alcohol and melted at 112.5—113.5 °C. The picrate gave a good test for unsaturation, decolorizing bromine water and potassium permanganate solution.

Anal., Calcd. for $C_{13}H_{10}N_4O_8$ C 44.58 H 2.88 N 16.00
Found C 44.50 H 2.91 N 16.11

5-Ethyl-2-vinylpyridine-N-oxide

A mixture of 2.3 g. of potassium acid sulfate, 30 g. of 2-(β-hydroxyethyl)-5-ethyl pyridine-N-oxide, and 0.7 g. of methylene blue was prepared, as described under the 2-vinylpyridine-N-oxide. The dehydration distillation in a vacuum at 2 mm. was carried out in an oil bath kept at 160—170 °C. After redistillation in the presence of 0.5 g. of methylene blue, the yield of 5-ethyl-2-vinylpyridine-N-oxide, boiling at 118—119 °C. at 0.3 mm., n_D^{26} 1.5801, was 7.2 g. (27.5 %). The N-oxide was a yellow liquid, easily soluble in water, alcohol, and chloroform and slightly soluble in ether and benzene. It decolorized bromine water and potassium permanganate solution, and polymerized slowly at room temperature.

Anal., Calcd. for $C_9H_{11}NO$ N 9.39 Found N 9.74

The picrate of the 5-ethyl-2-vinylpyridine-N-oxide was separated as yellow crystals from alcoholic solution, it melted at 130.5—131.5 °C. after two times of recrystallization, and decolorized bromine water and potassium permanganate solution.

Anal., Calcd. for $C_{15}H_{14}N_4O_8$ C 47.63 H 3.73 N 14.81
Found C 47.66 H 3.81 N 14.70

2. *Polymerization*

Polymerization of 2-vinylpyridine-N-oxide

The 2-vinylpyridine-N-oxide (4.6 g.) was dissolved in 10 ml. of alcohol, followed by addition of 0.01 g. of 2,2′-azo-bis-isobutyronitrile. The solution was then transferred to a polymerization tube, it was sealed under nitrogen atmosphere, and placed in a constant temperature bath at 60 °C. for 7 hrs. The resulting viscous reaction mixture was poured into 500 ml. of acetone with stirring.The precipitated polymer was collected by filtration, washed with acetone, and further, subjected to an acetone-extraction with a Soxhlet's extractor. After the polymer was dried in a vacuum oven, a hygroscopic, white powder, 3.4 g. (74 % conversion), was obtained. It was soluble in water and alcohol, and insoluble in chloroform and nonpolar solvents. The intrinsic viscosity in water at 25 ± 0.02 °C. was 1.07.

Anal., Calcd. for $(C_7H_7NO)_n$ N 11.57 Found N 11.35

Polymerization of 5-ethyl-2-vinylpyridine-N-oxide

The polymerization of 5-ethyl-2-vinylpyridine-N-oxide (6.9 g.) was carried out, as described for 2-vinylpyridine-N-oxide. The resulting viscous reaction mixture was poured into 500 ml. of ether with stirring. The precipitated polymer was collected, purified with an ether-extraction, and dried. A hygroscopic, white powder, 4.5 g. (65 % conversion), was obtained. The polymer was soluble in water, alcohol, and chloroform, and insoluble in nonpolar solvents.

The intrinsic viscosity in water at 25 ± 0.02 °C. was 0.438.

Anal., Calcd. for $(C_9H_{11}NO)_n$ N 9.39 Found N 9.51

Copolymerization

The comonomers, styrene and methyl methacrylate, were commercial materials, fractionally distilled before use, and stored under refrigeration.

Bulk and alcoholic solution copolymerizations of the N-oxides with styrene and methyl methacrylate at 60 ± 0.1 °C. were carried out on various molar ratios of monomers in sealed tubes in absence of air. The reaction mixtures were composed of 10 g. of total monomers and 0.02 g. of 2,2′-azo-bis-isobutyronitrile. For the solution copolymerizations, 10 ml. of alcohol was added. The initial copolymers ($<$ 10% conversion) were isolated and purified with three times of reprecipitations. All copolymers were soluble in alcohol and were precipitated with acetone for 2-vinylpyridine-N-oxide systems and with ether for 5-ethyl-2-vinylpyridine-N-oxide systems.

In order to analyze the copolymers, the modified KJELDAHL method for nitrogen by COLE and PARKS⁶⁾ was used in macro scale. The accuracy was tested for the pure N-oxide polymers, and the results were satisfactory. The nitrogen contents shown in Tables 1, 2, and 3 are the mean values of duplicate analyses.

3. *Infrared spectra*

The infrared spectra of these N-oxides were determined by the usual Nujol mull or undiluted liquid technique. For the polymers, the film and KBr disk were used. The apparatus was a SHIMADZU Model IR double beam recording spectrophotometer with a sodium chloride optics. All measurements were calibrated against the absorption bands for polystyrene.

In these spectra, it is characteristic that a strong absorption occurs at about 8 μ: 2-(β-hydroxyethyl) pyridine-N-oxide 8.14; 2-(β-hydroxyethyl)-5-ethyl pyridine-N-oxide 7.93; 2-vinylpyridine-N-oxide 8.12; 5-ethyl-2-vinylpyridine-N-oxide 7.99; poly(2-vinylpyridine-N-oxide) 8.20; and poly-(5-ethyl-2-vinylpyridine-N-oxide) 7.98 μ respectively. These are attributable to the NO stretching vibration.

The characteristic double bond absorptions of the N-oxide monomers were observed: 2-vinylpyridine-N-oxide 6.99, 7.72, 10.04, 10.67, and (6.17) μ; and 5-ethyl-2-vinylpyridine-N-oxide 7.15, 7.53, 10.09, 10.75, and (6.19) μ. The values in the brackets are attributed to the double bond stretching vibration.

Results and Discussion of Copolymerization

The results of the experiments are summarized in Table 1, 2, and 3.

In these experiments, alcoholic solution copolymerizations were carried out instead of bulk one for the convenience of handling. From WILEY and SLAYMAKER's paper⁵⁾, it is clear that a hydrogen bond is formed between N-oxide and alcohol. The formation of the hydrogen bond may prevent the contribution of the resonance structure I and lead to a differ-

---

⁶⁾ J. O. COLE and C. R. PARKS, Analytic. Chem. **18** (1946) 61.

ent reactivity from bulk copolymerizations. For the methyl methacrylate and 5-ethyl-2-vinylpyridine-N-oxide system, bulk and solution copolymerizations were run in parallel.

Table 1. Alcoholic solution copolymerizations of 2-vinylpyridine-N-oxide with styrene and methyl methacrylate

N-oxide in monomer mixture (mole-%)	Analyses of combined N-oxide N %	Calcd. contents of N-oxide in copolymers (mole-%)
	Comonomer, Styrene	
9.95	4.84	38.2
30.03	7.48	61.1
50.03	7.15	76.5
70.02	10.12	85.7
90.02	10.79	92.2
	Comonomer, Methyl methacrylate	
10.35	5.20	40.3
29.80	8.61	70.6
49.96	9.86	82.7
69.96	10.33	87.4

Table 2. Alcoholic solution copolymerizations of 5-ethyl-2-vinylpyridine-N-oxide with styrene and methyl methacrylate

N-oxide in monomer mixture (mole-%)	Analyses of combined N-oxide N %	Calcd. contents of N-oxide in copolymers (mole-%)
	Comonomer, Styrene	
10.20	4.69	41.0
19.67	5.69	51.7
29.92	6.81	64.8
50.06	7.79	77.3
70.01	8.31	84.3
	Comonomer, Methyl methacrylate	
9.95	4.99	43.2
15.01	5.74	51.3
20.20	6.23	56.9
35.00	7.62	74.3
60.01	8.71	89.6

Table 3. Bulk copolymerization of 5-ethyl-2-vinylpyridine-N-oxide with methyl methacrylate

N-oxide in *monomer mixture* (mole-%)	Analyses of combined N-oxide N %	Calcd. contents of N-oxide in copolymers (mole-%)
9.50	4.99	43.2
16.85	6.09	55.3
20.00	6.44	59.4
29.75	7.62	74.2
49.23	8.46	85.9
70.53	8.88	92.1

Table 4. Monomer reactivity ratios in copolymerizations of vinylpyridine-N-oxides with styrene and methyl methacrylate*)

Comonomer	r_1 comonomer	r_2 N-oxide
2-Vinylpyridine-N-oxide		
Styrene	0.11 ± 0.01	2.1 ± 0.6
Methyl methacrylate	0.13 ± 0.03	3.9 ± 0.8
5-Ethyl-2-vinylpyridine-N-oxide		
Styrene	0.10 ± 0.01	2.6 ± 0.3
Methyl methacrylate (in bulk)	0.11 ± 0.01	5.5 ± 0.5
(in solution) ...	0.12 ± 0.02	4.7 ± 0.6

*) These were calculated according to BENNETT and FRANKLIN⁷⁾.

In determining the monomer reactivity ratios, the FINEMAN and ROSS method[8] was used. The values obtained are listed in Table 4. In Table 4, the difference in the reactivity ratios between bulk and solution copolymerizations seems to be within experimental errors, and therefore the difference is neglected in the following discussion.

To obtain a direct measure of the tendency of a monomer to alternate with other monomers, the products of the reactivity ratios have been convenient. In the previous papers of this series[1], the polarities of the vinyl groups attached to the α-, β-, and γ-positions of pyridyl group were compared with one another.

---

[7] C. A. BENNETT and N. L. FRANKLIN, Statistical Analysis in Chemistry and the Chemical Industry, WILEY, New York 1954, p. 227 and 230.

[8] M. FINEMAN and S. ROSS, J. Polymer Sci. 5 (1950) 259.

Table 5. Monomer reactivity ratio products for copolymerizations of vinylpyridines and their N-oxides with styrene and methyl methacrylate

Styrene							
0.95	5-Ethyl-2-vinylpyridine						
0.74		2-Methyl-5-vinylpyridine					
0.50			2-Vinylpyridine				
0.38				4-Vinylpyridine			
0.26					5-Ethyl-2-vinylpyridine-N-oxide		
0.23						2-Vinylpyridine-N-oxide	
0.24*)	0.27	0.28	0.34	0.45	0.56	0.51	Methyl methacrylate

*) Data of LEWIS *et al.*[9].

The comparison of their polarities was based on the table of the reactivity ratio products. The same table containing the data of the present work has been shown in an abbreviated form (Table 5). It is clear that the positions to be occupied by the vinylpyridine-N-oxides are lower than those for the corresponding vinylpyridines, although this treatment is a rather rough approximation.

On the basis of these data, it may be concluded that the electron density on the vinyl group attached to the pyridyl group is decreased by the introduction of the N–O coordinate bond, and this is attributed to the participation of the resonance structure III.

Acknowledgement is made to the staff of YŪKI-GŌSEI KŌGYO Co., Tokyo for the hydroxyethyl pyridines.

---

[9] F. M. LEWIS, C. WALLING, W. CUMMINGS, E. R. BRIGGS, and F. R. MAYO, J. Amer. chem. Soc. **70** (1948) 1519.