[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Copolymerization Reactions of *trans*-1,2-Di(2-pyridyl)ethylene

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trans-1,2-Di(2-pyridyl)ethylene has been prepared and copolymerized with butadiene. Reactivity ratios of this monomer with styrene and acrylonitrile have been determined. The butadiene copolymer has no unusual qualities as an elastomer.

trans-Sibilene will copolymerize with butadiene but there is very little incorporation of this monomer from an 80/20 charge.[2] It was felt that 1,2-di(2-pyridyl)ethylene might lead to higher incorporations and, thus, allow assessment of the effect of this symmetrically disubstituted comonomer on the resulting butadiene elastomer.

1,2-Di(2-pyridyl)ethylene was first prepared by Harries and Lenart by the zinc chloride-catalyzed condensation of 2-picoline and pyridine-2-aldehyde.[3] It has also been reported as resulting from treatment of 1,2-di(2-pyridyl)ethane with selenium dioxide or N-bromosuccinimide.[4,5] The ethane derivative has been produced by the reaction of 2-picoline with sulfur,[4] and by the reaction of 2-picolyllithium with bromine.[5]

trans-1,2-Di(2-pyridyl)ethylene has now been prepared by two more satisfactory routes. The condensation of 2-picolyllithium and pyridine-2-aldehyde apparently gave the alcohol, which was dehydrated during the course of the reaction. Condensation of N-methyl-2-picolinium iodide with pyridine-2-aldehyde and subsequent thermal decomposition of the monomethiodide of the ethylene compound was the second method of synthesis. Peaks at 1330 and 975 cm.$^{-1}$ in the infrared absorption spectrum of this compound indicate a *trans* configuration at the ethylene linkage.

Under the same conditions of concentration it was found that *trans*-1,2-di(2-pyridyl)ethylene is more reactive in copolymerizations with butadiene than is *trans*-stilbene. The incorporation of dipyridylethylene with butadiene in an emulsion system using a 20/80 charge ratio was about 8% while the incorporation of stilbene was 1%.

The use of charge ratios greater than 85/15 butadiene/1,2-di(2-pyridyl)ethylene had little effect on the per cent incorporation of the pyridine derivative, and undissolved monomer was found in the latex before coagulation. Therefore, solubility effects in the emulsion system may be the cause of low incorporation of dipyridylethylene. Addition of a few milliliters of benzene to the charge increased the incorporation 2 or 3%. Determination of per cent incorporation of 1,2-di(2-pyridyl)-ethylene in butadiene copolymers is only accurate to about 2%, assuming 0.2% accuracy in nitrogen analyses. Table I shows the results of some typical copolymerizations.

Reactivity ratios of *trans*-1,2-di(2-pyridyl)ethylene with styrene and acrylonitrile were determined in bulk systems: r_1 (styrene) = 1.85 ± 0.1 and r_2 (dipyridylethylene) = 0.17 ± 0.1; r_1 (acrylonitrile) = 0.95 ± 0.05 and r_2 (dipyridylethylene) = 0.02 ± 0.05. As expected, r_2 is equal to or very nearly equal to zero. The error was estimated from the size of the triangles formed in the graphical solutions to the copolymer equation, Figures 1 and 2.[6]

An evaluation was made of vulcanizates of a 95/5 butadiene/*trans*-1,2-di(2-pyridyl)ethylene copolymer prepared in an emulsion system. In a tread type recipe the copolymer produced low tensile strength, low elongation, and was somewhat lifeless. It was quite flexible at low temperatures, but showed more tendency to crystallize than commercial GR-S. It was about the same in oil resistance properties as GR-S, but swelled less in solvents. In a carcass type compound the stress-strain properties were poor, but the temperature

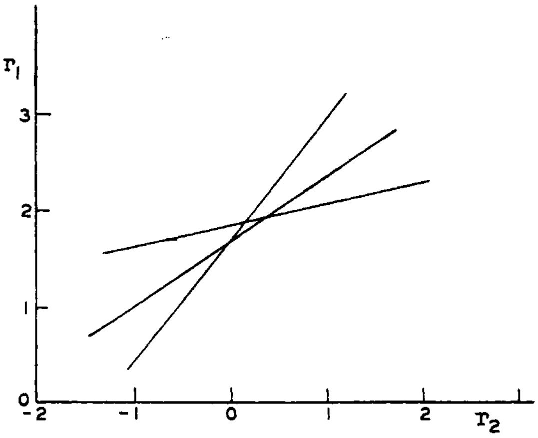

FIG. 1. REACTIVITY RATIOS FOR THE COPOLYMERIZATION OF 1,2-DI(2-PYRIDYL)ETHYLENE AND STYRENE

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[1] Taken from the thesis of A. T. Tweedie presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy at The University of Illinois, June, 1956.

[2] Marvel and Anderson, *J. Am. Chem. Soc.*, **76**, 5354 (1954).

[3] Harries and Lenart, *Ann.*, **410**, 95 (1915).

[4] Bergmann, Crane, and Fuoss, *J. Am. Chem. Soc.*, **74**, 5979 (1952).

[5] Campbell and Teague, *J. Am. Chem. Soc.*, **76**, 1371 (1954).

[6] Mayo and Lewis, *J. Am. Chem. Soc.*, **66**, 1594 (1944).

TABLE I

COPOLYMERS OF BUTADIENE AND *trans*-1,2-DI(2-PYRIDYL)ETHYLENE

Sample Number	OSR Soap, ml.	Hooker's Lauryl Mercaptan, g.	Butadiene, g.	Dipyridylethylene, g.	Benzene, ml.	Time, hours	Solubility in Benzene, %	Inherent Viscosity	Conversion, %	Incorporation, %
14A[a]	17.5	0.021	9.0	1.0	—	40	99	2.95	41	2.46
16A	17.5	0.042	9.0	1.0	—	12	—	2.79	75.6	6.15
16B	17.5	0.042	9.0	1.0	—	12	—	2.94	77.5	5.46
20A	17.5	0.100	8.0	2.0	—	12	100	1.12	82	7.0
20B	17.5	0.100	8.0	2.0	—	12	100	1.31	77	6.9
26B	17.5	0.050	8.5	1.5	—	12	100	1.71	72.8	7.2
30	17.5	0.050	8.5	1.5	—	9	100	1.94	59	6.1
32	17.5	0.050	8.5	1.5	2	9	100	0.94	41	6.1
36A	25	0.025	8.0	2.0	5	13	100	1.87	62.3	8.3
36B	24	0.025	8.0	2.0	5[b]	13	100	2.21	50.8	6.1
58A	25	0.025	8.5	1.5	10	13	98	1.8	48	7.5
58B	25	0.025	8.5	1.5	10[c]	13	96	2.4	55	8.5
58C	25	0.025	8.5	1.5[d]	10	13	88	1.8	38	—
60A	25	0.025	8.5	1.5	10	10	92	2.32	53	8.3
62[e]	25	0.025	8.5	1.5	10	13	95	1.1	29.5	7.9
66A	50	0.050	18.0	2.0	20	15	96	2.3	60.5	5.0
66B	50	0.050	18.0	2.0	20	15	95	1.7	66.0	5.8
76[f]	50	0.050	18.0	2.0	20	15	95	1.5	64	5.3

[a] All polymerizations were done at 50°, except 14A which was done at 35°. [b] Pyridine instead of benzene. [c] Cyclohexane instead of benzene. [d] *trans*-Stilbene, incorporation not determined. [e] Monomers were dissolved in benzene, then added to other ingredients. [f] Evaluation sample Illinois number 339.

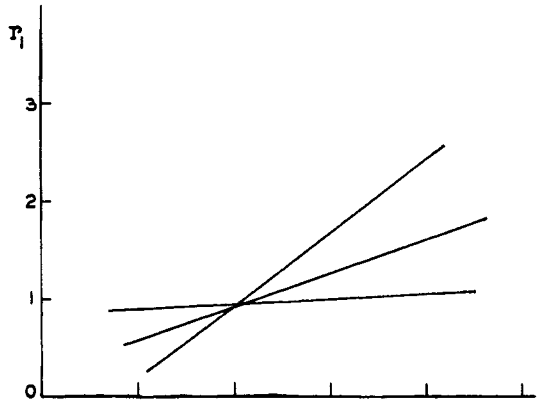

FIG. 2. REACTIVITY RATIOS FOR THE COPOLYMERIZATION OF 1,2-DI(2-PYRIDYL)ETHYLENE AND ACRYLONITRILE.

rise results were about the same as GR-S. In general, the material did not have any outstanding characteristics.

EXPERIMENTAL

trans-1,2-DI(2-PYRIDYL)ETHYLENE

A. Condensation of 2-picolyllithium and pyridine-2-aldehyde. A solution of 392 g. (2.5 moles) of dry bromobenzene in 200 ml. of anhydrous ether was dropped slowly into a stirred mixture of 2500 ml. of anhydrous ether and 31 g. (4.5 g.-atoms) of lithium in small pieces. After addition of the bromobenzene was complete the mixture was stirred until all of the lithium disappeared. 2-Picoline, 230 g. (2.5 moles), then was added slowly and the mixture was stirred for two hours. During this time the solution turned dark red in color. After chilling the mixture in an ice-salt bath, 214 g. (2 moles) of pyridine-2-aldehyde in 200 ml. of ether was introduced. In one hour the red color disappeared, and 400 ml. of water and then 400 ml. of concentrated hydrochloric acid were added. The aqueous layer was removed and poured into a solution of 455 g. of anhydrous sodium carbonate in 600 ml. of water. After extraction of the aqueous layer and the precipitate with chloroform, the extracts were combined and the solvent was removed by distillation. The residue was distilled under reduced pressure. After removal of unchanged starting materials the product distilled at 145–154° (1 mm.). This material, a brown waxy solid, was recrystallized from ether and then low-boiling petroleum ether to give a white crystalline material in 60 per cent yield, m.p. 119–120°.

Anal. Calc'd for $C_{12}H_{10}N_2$: C, 79.09; H, 5.53; N, 15.38. Found: C, 79.26; H, 5.59; N, 15.35.

The infrared spectrum of this compound in 10% chloroform solution shows peaks at 3050 (w.), 2960 (m.), 1595 (s.), 1575 (m.), 1480 (s.), 1440 (s.), 1330 (m.), 1155 (m.), 1095 (w.), 1075 (w.), 995 (w.), and 975 (m.) cm.$^{-1}$. The ultraviolet spectrum of this compound shows peaks as follows: $\lambda_{max.}^{EtOH}$ 330 mμ (log ε 4.40) 315 (4.55) 303 shoulder (4.44) 267 (4.34) 225 (3.88) 218 (4.03).

B. Condensation of N-methyl-2-picolinium iodide and pyridine-2-aldehyde. To a solution of 186 g. (2 moles) of 2-picoline in 300 ml. of acetone chilled in an ice-bath, 355 g. (2.5 moles) of iodomethane in 150 ml. of acetone was introduced. After allowing the mixture to stand for five hours at room temperature, 214 g. (2 moles) of pyridine-2-aldehyde in 200 ml. of ethanol and a few drops of piperidine were added. The mixture was refluxed for eight hours after standing for two days. When the excess solvent was evaporated the product precipitated. After several recrystallizations from ethanol, the monomethiodide of 1,2-di(2-pyridyl)ethylene melted at 205–207° and the yield was 92%.

Anal. Calc'd for $C_{13}H_{13}IN_2$: C, 48.15; H, 4.01. Found: C, 48.39; H, 3.84.

C. Decomposition of the monomethiodide of 1,2-di(2-pyridyl)ethylene to the free base. Heating 20 g. (0.06 mole) of the monomethiodide of 1,2-di(2-pyridyl)ethylene at 200–220° (3 mm.) yielded 3 g. or 25.2% of 1,2-di(2-pyridyl)ethylene, which was characterized by mixture melting point determinations with an authentic sample.

Typical emulsion polymerization recipe. The following recipe is typical of all the emulsion polymerizations de-

TABLE II

REACTIVITY RATIOS OF 1,2-DI(2-PYRIDYL)ETHYLENE WITH STYRENE AND ACRYLONITRILE

Sample	Dipyridylethylene, g.	Comonomers, g.	N, %	r_1	r_2
106A	1.50	8.50 (Sty)*	1.34	1.85 ± 0.1	0.17 ± 0.1
111A	4.00	7.10 (Sty)*	3.29	(r_1, styrene)	
111B	5.00	5.00 (Sty)*	4.72		
113A	1.50	8.50 (AcN)*	24.78	0.95 ± 0.05	0.02 ± 0.05
123A	5.00	5.00 (AcN)*	21.44	(r_1, acrylonitrile)	
123B	3.00	7.00 (AcN)*	19.44		

* (Sty) = Styrene, (AcN) = Acrylonitrile.

scribed in this article. A four-ounce screw-capped bottle was charged as follows: 50 ml. of 2.9% Office of Synthetic Rubber soap solution, 0.050 g. of Hooker's lauryl mercaptan, 2.00 g. of 1,2-di(2-pyridyl)ethylene, 2 ml. of a 3% solution of potassium persulfate, 20 ml. of benzene, and 18.0 g. of butadiene. Excess butadiene was allowed to boil out in order to sweep air from the bottle. The bottle was tumbled for 15 hours in a 50° bath. After cooling, its contents were emptied with stirring onto 10 ml. of a saturated methanolic solution of N-phenyl-2-naphthylamine antioxidant. The latex was coagulated with 10 ml. of salt-acid coagulant, shredded, washed with water, and then dried in a vacuum desiccator. A sample for analysis was reprecipitated three times from benzene into methanol.

Reactivity ratios. For determination of reactivity ratios a total charge of 10 g. of monomers was reacted in 50 ml. of solvent at 60°. Styrene copolymers were allowed to react for two hours and acrylonitrile copolymers for two hours and 50 minutes. In each case, 0.040 g. of azo-*bis*-isobutyronitrile served as initiator. Benzene was used as the solvent in the styrene copolymerizations and N,N-dimethylformamide in the acrylonitrile reactions. After reaction, the styrene/1,2-di(2-pyridyl)ethylene copolymers were precipitated in low-boiling petroleum ether and the excess monomer was extracted with petroleum ether in Soxhlet extractors. The acrylonitrile copolymers were precipitated in water and then the excess monomer was extracted as before. Table II shows the values necessary for solution of the copolymer equation[6] and Figures 1 and 2 show graphical solutions for 1,2-di(2-pyridyl)ethylene with styrene and acrylonitrile. All conversions in the polymerizations used for reactivity ratio calculations were less than 10%.

No satisfactory copolymer of 1,2-di(2-pyridyl)ethylene with butadiene was obtained in benzene solution. Therefore, reactivity ratios are not reported for this pair of monomers.

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