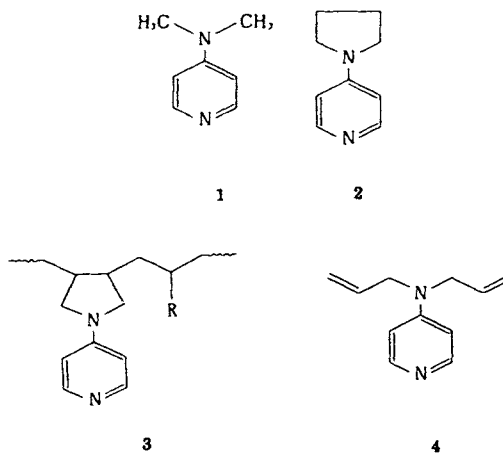


## NOTES

### Poly(*N-p*-pyridyl-2,3-dimethylenepyrrolidine) as a Supernucleophilic Reagent

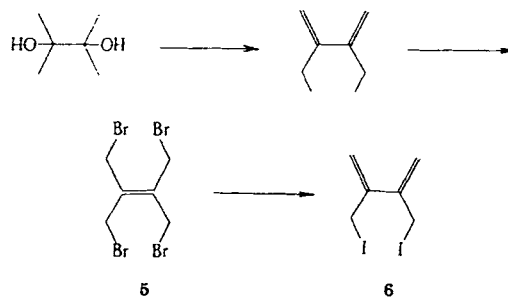
In 1967, Litvinenko and Kirichenko discovered that 4-(*N,N*-dimethylamino)pyridine (**1**, DMAP), when used as a supernucleophilic catalytic agent, could exercise a higher activity than that of pyridine over an acylation reaction.<sup>1</sup> Afterward, Steglich and Hofle proved in 1969 that the catalytic capacity of 4-pyrrolidinopyridine (**2**, PPY) was higher than that of DMAP.<sup>2</sup> From then on, many researchers have sought to have compounds of the type of 4-(*N,N*-dialkylamino)pyridine polymerized or polymerically fixed. They have also tried to introduce structures similar to DMAP or PPY groups into the structural units of macromolecular chains.

In 1985, Narang and Ramharack made a reaction involving 4-aminopyridine and maleic anhydride copolymers (**3**). After a reduction, the yield from such an action became poly-(4-*N*-pyrrolidinopyridine) copolymers. Besides, satisfactory results were obtained by them in catalyzing aquaternalization with benzyl chloride.<sup>3</sup> In the same year, Mathias et al. involved 4-chloropyridine in a reaction with diallylamine and obtained 4-(*N,N*-dialkylamino)pyridine (**4**, DAAP). Then, they obtained homopolymers and copolymers that contain the PPY structure by involving the DAAP monomer in a cyclopolymerization reaction with 2,2'-azobis(2-amidinopropane)hydrochloride (V-50) as an initiator.<sup>4</sup> In an experiment involving hexanoic acid and *p*-nitrophenyl esters in a hydrolysis reaction, DAAP polymers demonstrated a catalytic activity that was even higher than that of a PPY.<sup>5</sup>

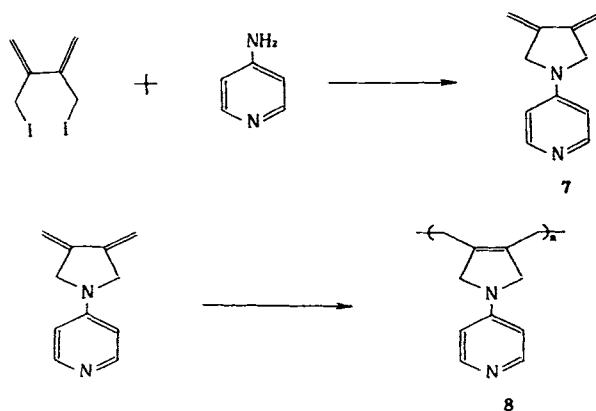


But the two separated double bonds in the DAAP monomer cannot enter into a cyclopolymerization reaction unless under the Butler's conditions of reaction.<sup>6</sup> In that case, the time the reaction takes is rather long and many byreactions may take place. The two separated double bonds tend to enter into copolymerization respectively with each of the other monomers to form cross-linked polymers, the structures of which are hard to control.

Consequently, we adopted the method formulated by Cope and Kagan.<sup>7</sup> In this way, we obtained, first, 1,4-dibromo-2,3-bis(bromomethyl)-2-butene (**5**), which was then changed into 2,3-bis(iodomethyl)-1,3-butadiene (**6**) owing to our involving it in a reaction according to the method formulated by Hamon and Spurr.<sup>8</sup>



Then, the *N*-alkylation method was again used for preparing the *N-p*-pyridyl-3,4-dimethylenepyrrolidine (**7**, PDMP) monomer. Next, the conjugate bonds in the monomer were involved in a homopolymerization in the presence of a conventional initiator. This yielded poly-PDMP (**8**) with a unsaturated double bond and PPY structural units:



Still open to further exploration, however, are such issues as copolymerization involving the monomer and other monomers, further cross-linkage of double bonds in the structure units, and the method for testing the activity of this kind of polymeric catalyst.

## EXPERIMENTAL

4-Aminopyridine was a donation from Sigma Chemical Co. The means of representation were as follows: The FTIR instrument was the Nicolet 5DX Model, which was used for analyzing functional groups. The H-NMR identifying the structure of the monomer was the Bruker Model AP-P 200. For carrying out C, H, and N analyses, an element analysis instrument, Model PE-2400, was used.

### Synthesis of Monomer (7)

Into a 500 mL four-necked flask that contained a 200 mL solution of 9.40 g (0.1 mol) of 4-aminopyridine in methanol was added 33.40 g (0.1 mol) of newly produced 2,3-bis(iodomethyl)-1,3-butene. Then, the flask was energetically stirred at 60°C for 1 h under the protection of nitrogen. The suspension liquid was yellow in color. Next, into the reaction system was added 8.00 g (0.02 mol) of granulated KOH and the reaction continued for 10 h.

The yield from the reaction was filtered. The filtrate was condensed with a rotatory evaporator. The residual liquid underwent a precipitation with ether. The precipitated matter was placed in a Soxhlet extractor for an extraction with water for 10 h. After that, the extracted matter underwent a dissolving/precipitating with methanol and chloroform three times before it was vacuum-dried. The final product was 13.1 g (in a 75% yield) of brown solid matter. NMR (DMSO- $d_6$ ):  $\delta$ 2.51 (s, 4H), 5.05–5.56 (m, 4H), 6.82 (m, 2H), 8.15 (m, 2H); IR: 2923, 1602, 1536, 1507, 831.

ANAL: Calcd for  $C_{11}H_{12}N_2$ : C, 76.74%; H, 6.98%; N, 16.28%.

Found: C, 76.23%; H, 7.15%; N, 17.01%.

### Polymerization (8)

In a 100 mL four-necked flask, 10.0 g (0.058 mol) of *N-p*-pyridyl-3,4-dimethylenepyrrolidine was dissolved in a 14 mL 15% hydrochloric acid solution at 0°C. Then, 0.10 g of  $(NH_4)_2S_2O_8$  was added to the solution, which was left

to undergo a reaction for 24 h at 60°C under the coverage of nitrogen.

Next, to the reactants was added an aqueous 5% of NaCl to effect a dialysis of them. The organic layer underwent a dissolving/precipitating process with methanol and chloroform three times before it was vacuum-dried. The final product was 9.29 g (in a 92% yield) of brown solid. NMR (DMSO- $d_6$ ):  $\delta$ 2.51 (s, 4H), 2.09 (t, 4H), 6.79 (m, 2H), 8.03 (m, 2H); IR: 2920, 1664, 1695, 1512, 830.

ANAL: Calcd for  $C_{11}H_{12}N_3$ : C, 76.47%; H, 6.98%; N, 16.28%.

Found: C, 77.07%; H, 7.03%; N, 15.29%.

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