Preparation of Polyamines by the Michael Reaction

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It is well known concerning the Michael reaction that amines containing an active hydrogen add to activated double bonds.[1-3] A few attempts have been made to prepare polyamines by the Michael reaction.[4,5]

In this paper the Michael reaction was used in the preparation of polyamines from piperazine and several divinyl compounds.

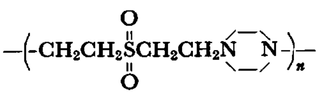
Polyamine from Piperazine and Divinyl Sulfone. A typical run of the preparative method of the polyamine is shown below.

To a solution of 9.370 g (0.108 mol) of anhydrous piperazine in 60 m*l* of absolute methanol was added dropwise a mixture of 12.84 g (0.108 mol) of divinyl sulfone and 20 m*l* of absolute methanol with vigorous stirring at room temperature. The exothermic reaction took place quite rapidly. The reaction mixture was stirred for 30 min. Then the separated white solid was filtered off and washed with methanol. The yield of dried material, melting at 232—234°C, amounted to 21 g (99.0% of the theoretical amount).

Found: C, 46.45; H, 8.10; N, 13.75; S, 15.56%. Calcd for $(C_8H_{16}N_2O_2S)_n$: C, 47.03; H, 7.48; N, 13.72; S, 15.67%.

The product was soluble in sulfuric acid, glacial acetic acid, and formic acid. However, it was insoluble in *n*-hexane, benzene, methanol, ethanol, ether, chloroform, tetrahydrofuran, dioxane, dimethylformamide, dimethyl sulfoxide, dimethyl sulfate, and methyl formate. It should be noted that the product is swollen with water. The product had an intrinsic viscosity of 0.36 in sulfuric acid and one of 0.30 in glacial acetic acid at 30°C.

As the electron density of the double bonds in divinyl sulfone is decreased by the electron-withdrawing character of the oxygen atom, divinyl sulfone acts as a strong electron-acceptor in the Michael reaction. The addition reaction of piperazine to divinyl sulfone proceeded rapidly at a low temperature and formed a polymeric substance in a high yield. The results of elementary analysis and the infrared spectrum (Fig. 1) showed the polymer to have the following polyamine structure:



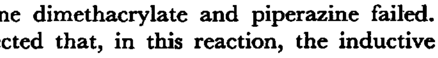
The influences of the solvents and the feed ratio of piperazine to divinyl sulfone on the yield and the molecular weight of polyamine were examined; the results are listed in Table 1. The polymer with the highest molecular weight was attained when the two reactants used were equimolar in amount. The polymerization method in which divinyl sulfone was slowly added to a solution of piperazine seemed to give a higher molecular weight and higher yield than when the two reactants were added at the same time.

No polymeric addition product was obtained by the reaction of *trans*-2,5-dimethylpiperazine with divinyl sulfone. The failure of this reaction may be due to the steric effect of the methyl group which would prevent, more or less, the attack of the nitrogen atom on the β-carbon of divinyl sulfone.

Polyamine from *p*-Phenylene Diacrylate and Piperazine. To a mixture of 10 m*l* of methanol, 40 m*l* of chloroform and 1.291 g (0.015 mol) of piperazine was added a solution of 3.273 g (0.015 mol) of *p*-phenylene diacrylate in 40 m*l* of chloroform with vigorous stirring over a period of 30 min. The temperature was maintained at 10°C during the addition of *p*-phenylene diacrylate. After the addition, the reaction mixture was refluxed for 60 min under a nitrogen atmosphere. Then the solvents were distilled off under reduced pressure. After the residual liquid has been poured into a large amount of ether, a white solid was filtered. After drying, 1.5 g of white powder was obtained, mp 180—182°C.

Found: C, 61.76; H, 6.91; N, 8.06%. Calcd for $(C_{16}H_{20}N_2O_4)_n$: C, 63.14; H, 6.22; N, 7.88%.

This polymer was readily soluble in chloroform dimethylformamide, dimethyl sulfoxide, and acetic acid. The intrinsic viscosity of this polymer was 0.11 in glacial acetic acid at 30°C. The infrared spectrum of this polymer, as shown in Fig. 2, indicates the following polyester-amine structure:



An attempt to obtain a polymeric substance from *p*-phenylene dimethacrylate and piperazine failed. It is expected that, in this reaction, the inductive effect of the methyl group is not significant, while

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1) C. B. Pollard, J. P. Bain and D. E. Adelson, *J. Am. Chem. Soc.*, **57**, 199 (1953).

2) V. E. Stewart and C. B. Pollard, *ibid.*, **58**, 1980 (1936).

3) A. A. R. Sayigh, H. Ulrich and M. Green, *J. Org. Chem.*, **29**, 2042 (1964).

4) G. E. Hulse, U. S. Pat. 275993 (1956).

5) Farbwerke Hoechst A. G., Belgian Pat. 612398 (1962).

TABLE 1. POLYAMINE FROM PIPERAZINE AND DIVINYL SULFONE

Reactant		Solvent, *ml*		Reaction			Polymer				
PZ mol	DVS mol	PZ	DVS	Process	Time min	Temp. °C	Yield %	N%	S%	Mp, °C	η_{sp}/C*
0.0300	0.0300	MeOH 40 $CHCl_3$ 30	$CHCl_3$ 20	A	30 30	10 35	80.3	12.26	15.70	232—234	0.32
0.1080	0.1080	MeOH 60	MeOH 20	A	30 30	25 25	99.0	13.75	15.56	232—234	0.38
0.0300	0.0240	MeOH 50 $CHCl_3$ 10	$CHCl_3$ 10	A	30 30	10 35	85.7	13.55	14.49	229—232	0.19
0.0300	0.0294	MeOH 50 $CHCl_3$ 10	$CHCl_3$ 10	A	30 30	10 35	70.0	13.00	15.75	233—235	0.28
0.0300	0.0306	MeOH 50 $CHCl_3$ 10	$CHCl_3$ 10	A	30 30	10 35	68.5	12.89	15.36	232—234	0.35
0.0300	0.0360	MeOH 50 $CHCl_3$ 10	$CHCl_3$ 10	A	30 30	10 35	68.5	12.62	15.76	232—234	0.14
0.0300	0.0300	MeOH 100	MeOH 100	B	30 30	25 70	73.4	12.13	15.87	213—215	0.19
0.0300	0.0300	EtOH 100	EtOH 100	B	30 30	25 70	70.1	12.20	15.74	215—216	0.17
0.0200	0.0200	MeOH 20 DMF 30	DMF 50	A	30 30	20 150	—	—	—	—	—

PZ: Piperazine; DVS: Divinyl sulfone; DMF: Dimethylformamide.

Process A: The solution of DVS was added slowly to the solution of PZ for 30 min and the mixture was stirred for another 30 min at a given temperature.

Process B: The two reactants were mixed at the same time and the mixture was maintained at room temperature for 30 min.

* $C=0.5$ g/100 *ml* of acetic acid (30°C).

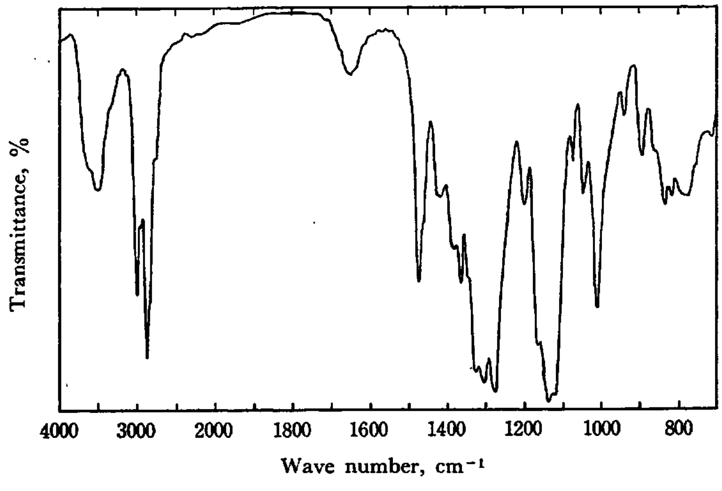

Fig. 1. Infrared spectrum of the polymer from piperazine and divinyl sulfone.

the steric hindrance of the methyl group cannot be disregarded. That is, in the Michael reaction the rate-determining step[6,7] is the attack of the nitrogen atom on the β-carbon of the vinyl group, and not only the stability of the ambient anion formed, but also the steric effects of reactants play an important role.

Experimental

Materials. Anhydrous piperazine, *trans*-2,5-dimethylpiperazine, and divinyl sulfone may be obtained from commercial sources. Anhydrous piperazine and *trans*-2,5-dimethyl piperazine were purified by the azeotropic distillation of water with benzene. Divinyl sulfone was purified by distillation under reduced pressure. Most of the solvents were dried and subjected to a simple distillation. Chloroform was freed of any alcohol stabilizer by washing it with a 5% sodium bicarbonate solution and water successively. It was

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[6] Y. Ogata, M. Okano, Y. Furuya and I. Tabushi, *J. Am. Chem. Soc.*, **78**, 5426 (1956).

[7] E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Company, Inc., New York (1959), p. 392.

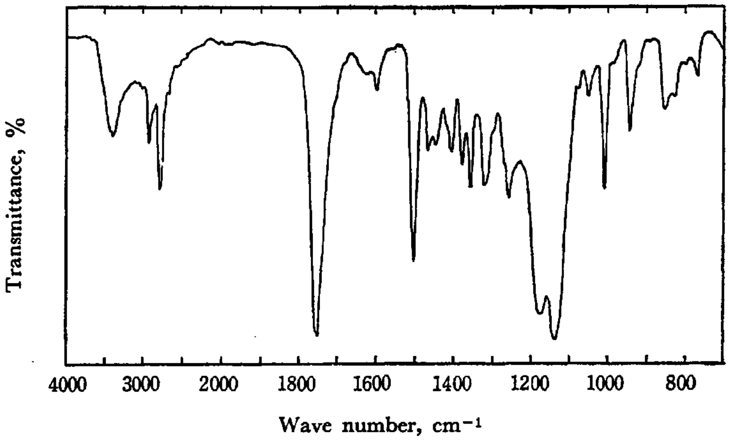

Fig. 2. Infrared spectrum of the polymer from piperazine and *p*-phenylene diacrylate.

dried over calcium chloride and then distilled. *p*-Phenylene dimethacrylate was prepared by the following method. To 23.12 g (0.12 mol) of hydroquinone in a 300 m*l*, four-necked flask, 16.8 g (0.42 mol) of sodium hydroxide in 200 m*l* of water was added with stirring under a nitrogen atmosphere. Then 43.85 g (0.42 mol) of methacrylyl chloride were added, drop by drop, over a 30-min period at 30°C. The reaction mixture was extracted with 400 m*l* of ether, and the extract was washed three times with 150 m*l* of a 5% sodium bicarbonate solution. The ether solution was then dried over 50 g of anhydrous sodium sulfate overnight, and the ether was removed. Eighteen grams of white needles were obtained by two recrystallizations from ether, mp 88°C.

Found: C, 68.17; H, 5.78%. Calcd for $C_{14}H_{14}O_4$: C, 68.28; H, 5.78%.

IR (KBr disk): 3420, 2940, 2910, 2830, 1734, 1635, 1504, 1445, 1395, 1373, 1320, 1295, 1185, 1145, 1123, 1013, 934, 885, 807 cm.$^{-1}$

p-Phenylene diacrylate was prepared from 23.12 g (0.21 mol) of hydroquinone and 37.01 g (0.42 mol) of acrylyl chloride in the presence of 16.8 g (0.42 mol) of sodium hydroxide according to a method similar to that used in the case of *p*-phenylene dimethacrylate. Seven grams of white needles were obtained after two recrystallizations from a mixture of ether and petroleum ether (1 : 1), mp 84—85°C.

Found: C, 65.64; H, 4.80%. Calcd for $C_{12}H_{10}O_4$: C, 66.04; H, 4.62%.

IR (KBr disk): 3419, 3090, 3040, 1740, 1723, 1630, 1500, 1400, 1290, 1250, 1150, 1008, 980, 908, 793, 770 cm.$^{-1}$