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

Heat Stability Studies on Chelates from Schiff Bases and Polyazines of Salicylaldehyde Derivatives[1]

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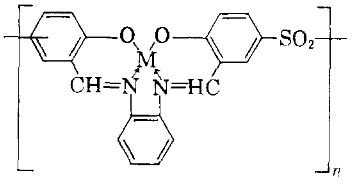
Poly-Schiff bases of higher molecular weight than previously obtained have been prepared from 5,5′-methylene-bis-salicylaldehyde and *o*-phenylenediamine by carrying out the condensation reaction in an emulsion system. Fairly good heat stability has been found for the metal chelates of the azine of salicylaldehyde and the polyazines of 5,5′-methylene-bis-salicylaldehyde and bis-salicylaldehyde-5,5′-sulfone. No polyazines with high molecular weight could be obtained.

Earlier work reported from this Laboratory[2,3] has demonstrated that the chelated nickel(II) and cadmium salts of the poly-Schiff base shown in formula I have good heat stability, but the molecular weights of the polymers thus far obtained are too low for these polymers to have practical usefulness. The polymers which had been prepared previously in tetrahydrofuran or acetic acid solution[2,3] were assumed to have a molecular weight of 10,000 based on an inherent viscosity of the polymer of 0.05 (1% in dimethylformamide). Numerous attempts had been made to increase the molecular weight of the polymer obtained, *i.e.*, variation in solvent systems, catalysts, use of dehydrating agents, azeotropic removal of water, temperature variations, but none had resulted in any significant improvement in molecular weight of the polymer.



I, M = Ni(II) or Cd

Haley and Maitland[4] have shown that Schiff bases can be formed in yields of 70–90% by mixing in equimolar portions saturated aqueous solutions of the two reactants. Use of solvent modified emulsion systems was therefore investigated in connection with the formation of the poly-Schiff bases from *o*-phenylenediamine and 5,5′-methylene-bis-salicylaldehyde since this dialdehyde is more readily available than is bis-salicylaldehyde-5,5′-sulfone. The emulsion type condensations with various added organic solvents with and without added catalyst are recorded in Table I.

It will be noted that the molecular weight of the polymer produced in the ethyl acetate modified emulsion system is improved over that obtained in solvent solutions,[2] but the product is still a powdery solid and not tough or plastic.

TABLE I

EMULSION CONDENSATION[a] OF 5,5′-METHYLENE-BIS-SALICYLALDEHYDE AND *o*-PHENYLENEDIAMINE

	Uncatalyzed		Acid catalyzed[b]	
Solvent	Yield, %[d]	Inherent viscosity[c]	Yield, %[d]	Inherent viscosity[c]
Xylene	22	0.111	102	0.108
Benzene	52	.090	99	.174
Chlorobenzene	10	.100	97	.141
Ethyl acetate	51	.146	92	.231
Chloroform	21	.093	83	.057
Cyclohexane	86	.067	95	.071
Carbon disulfide	93	.060	102	.055

[a] In 4-ounce screw-cap bottles, 25 ml. of organic solvent containing 1.2183 g. (0.005 mole) of 5,5′-methylene-bis-salicylaldehyde and 50 ml. of boiled deaerated water containing 0.5407 g. (0.005 mole) of *o*-phenylenediamine and 0.25 g. of polyvinyl alcohol (Elvanol 72-60, du Pont) shaken for 16 hours at room temperature. [b] One drop of concentrated sulfuric acid per emulsion bottle. [c] 1% in dimethylformamide. [d] Uncorrected for polyvinyl alcohol inclusion.

In Table II are recorded some experiments designed to test the effect of varying ratios of the two carefully purified reactants. It will be noted that although large deviations in the molecular weight of the poly-Schiff base formed do not occur, the highest molecular weight product in the range of concentrations of reactants studied occurred at an equimolar ratio of diamine to dialdehyde (Table II).

TABLE II

EFFECT OF RATIO OF *o*-PHENYLENEDIAMINE TO 5,5′-METHYLENE-BIS-SALICYLALDEHYDE IN EMULSION CONDENSATIONS[a]

o-Phenylenediamine g.	moles × 10^3	Ratio	Yield, g.	Inherent viscosity[b]
0.260	2.4	0.60	0.550	0.047
.303	2.8	.70	.783	.078
.346	3.2	.80	.845	.078
.389	3.6	.90	.853	.080
.433	4.0	1.00	1.058	.086
.476	4.4	1.10	1.089	.084
.519	4.8	1.20	1.109	.084
.606	5.6	1.40	1.137	.071

[a] The dialdehyde (1.025 g., 0.004 mole) was dissolved in 20 ml. of ethyl acetate, the diamine in 70 ml. of boiled deaerated water. Each 4-ounce emulsion bottle contained one drop of concentrated sulfuric acid as catalyst and five drops of Triton X-301 as emulsifier (Rohm and Haas) and was shaken for 16 hours at room temperature. [b] 1% in dimethylformamide.

In the search for heat-stable polymeric metal chelates, we next turned to the use of hydrazine to replace *o*-phenylenediamine in the reaction with the dialdehyde since hydrazine is a more reactive reagent with aldehydes, and also some earlier work had indicated that a low molecular weight polyazine of terephthalaldehyde[5] did not decompose rapidly at 425°. To check the stability of azines and their chelates, salicylaldehyde azine was pre-

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(2) C. S. Marvel and N. Tarköy, THIS JOURNAL, **79**, 6000 (1957).

(3) C. S. Marvel and N. Tarköy, *ibid.*, **80**, 832 (1958).

(4) C. A. Haley and P. Maitland, *J. Chem. Soc.*, 3155 (1951).

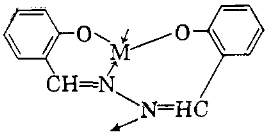
(5) C. S. Marvel and H. W. Hill, Jr., THIS JOURNAL, **72**, 4819 (1950).

TABLE III

HEAT STABILITY OF CHELATES OF SALICYLALDEHYDE AZINE IN AIR AT 250°

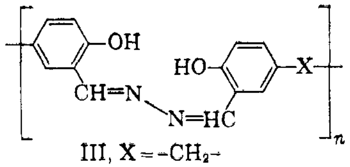
		Analyses, %						Loss % (hours)			
		C		H		N					
Chelate	Formula	Calcd.	Found	Calcd.	Found	Calcd.	Found	2	4	12	24
Nickel	$C_{14}H_{10}O_2N_2Ni$	56.53	56.55	3.39	3.42	9.44	9.41	1.06	1.24	1.73	2.40
Cobalt	$C_{14}H_{10}O_2N_2Co$	56.58	56.55	3.39	3.65	9.43	9.28	0.73	1.43	2.13	3.70
Cadmium	$C_{14}H_{10}O_2N_2Cd$	47.95	49.32	2.87	3.22	7.99	8.64	1.10	1.65	3.30	4.40

pared by the method of Cajar[6] and the chelates, II, of nickel(II), copper(II), cadmium, cobalt(II) and zinc were prepared from tetrahydrofuran and water solutions. The chelates were very insoluble and those of cadmium and zinc could not be obtained in a satisfactorily pure condition. Heat stabilities of these chelates are shown in Table III.



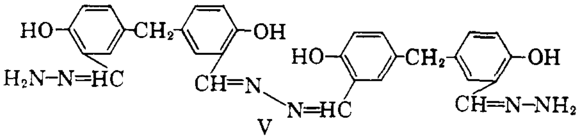
II, M = Ni, Co, Cu

The preparation of two polyazines (III and IV) in the hydroxyaldehyde series was then investigated. Reaction of 5,5′-methylene-bis-salicylaldehyde with hydrazine sulfate in acetic acid solution resulted in the precipitation of a yellow amorphous polymer. Analysis and infrared spectrum indicated that this polymer was low in molecular weight, had aldehyde end groups (strong aromatic aldehyde absorption at 1655 cm.$^{-1}$ and low nitrogen value) and probably was hydrated.



III, X = $-CH_2-$
IV, X = $-SO_2-$

Because of the insolubility of hydrazine sulfate in all but strongly polar solvents, attention was turned to hydrazine hydrate for the formation of azines. By the use of pyridine solvent for the aldehyde and the addition of hydrazine hydrate, a polymeric azine was obtained which precipitated from solution. This polyazine had an infrared spectrum almost identical with that of salicylaldehyde azine, but the polymer was strongly hydrated as indicated by its low nitrogen and carbon values; the O–H region is smeared appreciably because of the hydrogen-bonding of the hydroxyl hydrogen with the azine nitrogen linkage.[7] It is interesting that with a 10:1 excess of hydrazine hydrate over dialdehyde in pyridine solution a product was isolated which analyzed accurately for a dimer with hydrazone end groups (V).



V

The polyazine of bis-salicylaldehyde-5,5′-sulfone (IV) was prepared by reaction with hydrazine hydrate in pyridine solution. It precipitated from solution as it was formed and when isolated was a high melting, > 300°, refractory orange powder. No water of hydration was observed.

The free polyazines showed fairly good heat stability at 250° in air (Table IV). The polyazine of 5,5′-methylene-bis-salicylaldehyde gained weight at first, perhaps by oxidation of the methylene bridge to a ketone bridge (appearance of a band at 1650 cm.$^{-1}$ in the infrared), then followed by a sudden loss in weight. The polyazine of bis-salicyaldehyde-5,5′-sulfone, on the other hand, showed a steady but slow loss in weight.

TABLE IV

THERMAL STABILITIES OF POLYAZINES AT 250° IN AIR

	Change in weight, %					
	Hours					
Material	2	4	12	24	48	10 days
Polyazine III	+0.25	+0.77	+1.06	−0.51	−7.70	
Polyazine IV	−1.37	−1.67	−2.08	−2.20	−3.42	−5.05

Because of the non-linearity of the azine linkage (*cf.* formula V), both nitrogen atoms are not sterically disposed to donate their electrons to form coördinate bonds with divalent metal cations in quadridentate cyclic chelates in the case of polyazines. Attempts to form the metal chelates of these polymeric hydroxy azines gave unsatisfactory results. Three different techniques were used in the hope of obtaining complete coördination of a metal ion with the polymeric hydroxy azine. (a) First, the polyazine was formed initially in dimethylformamide solution from which it separated in a finely dispersed colloidal state. This suspension then was stirred with an aqueous solution of the acetate salt of the metal to be chelated. (b) Second, the polyazine was formed *in situ* in a dimethylformamide solution containing the divalent metal acetate to be chelated. (c) Finally, an emulsion condensation to form the polyazine was run in benzene and water, the water containing the dissolved metal acetate. Reasonable and consistent analytical values could not be obtained for any of the metal derivatives investigated.

Experimental

Emulsion Condensations.—The emulsion condensations used to prepare the poly-Schiff bases were run in four-ounce screw-cap bottles fitted with Neoprene gaskets. The bottles were shaken for 16 hours at room temperature and the polymer precipitated by pouring the emulsion into about 500 ml. of methanol. The polymers were isolated by filtration, washed with water and dried at 120°. The results are recorded in Tables I and II.

Chelates of Salicylaldehyde Azine.—Salicylaldehyde azine was prepared according to the method of Cajar.[6] To a solution of 2.40 g. (0.01 mole) of salicylaldehyde azine dissolved in 150 ml. of dimethylformamide was added a solution of 0.02 mole of the divalent acetate dissolved in 30–50 ml. of water. After stirring for two hours the precipitated chelate was collected and extracted in a Soxhlet thimble for one hour with dimethylformamide and for one hour with

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[6] H. Cajar, *Ber.*, **31**, 2807 (1898).

[7] L. N. Ferguson and I. Kelly, THIS JOURNAL, **73**, 3707 (1951).

water. The chelate then was dried over phosphorus pentoxide at 0.1 mm. for 16 hours.

Anal. Calcd. for $C_{14}H_{10}O_2N_2Co$: C, 56.58; H, 3.39; N, 9.43. Found: C, 56.55; H, 3.65; N, 9.28. Calcd. for $C_{14}H_{10}O_2N_2Ni$: C, 56.63; H, 3.39; N, 9.44. Found: C, 56.55; H, 3.42; N, 9.41, 9.56. Calcd. for $C_{14}H_{10}O_2N_2Cd$: C, 47.95; H, 2.87; N, 7.99. Found: C, 49.32; H, 3.22; N, 8.64, 8.75.

When the chelates were prepared from tetrahydrofuran solutions of the azine, similar analytical values were obtained and in addition a copper chelate was formed which apparently contained one mole of water of hydration.

Anal. Calcd. for $C_{14}H_{10}O_2N_2Cu \cdot H_2O$: C, 52.57; H, 3.80; N, 8.76. Found: C, 51.98; H, 3.60; N, 8.50.

Polyazine of 5,5′-Methylene-bis-salicylaldehyde. a. Acetic Acid Solution.—5,5′-Methylene-bis-salicylaldehyde (6.4063 g., 0.025 mole) was dissolved in 300 ml. of acetic acid. The solution was heated on a steam-bath to 90–95° and a solution of hydrazine sulfate (3.2533 g., 0.025 mole) in 100 ml. of water was added in one portion. The reaction was stirred at 90–95° for six hours, cooled and filtered to give 7.0 g. of product (76%). It was redissolved in dimethylacetamide and precipitated in 5% aqueous sodium chloride solution. The polymer was collected, washed thoroughly and dried. The infrared spectrum is compatible with the proposed polyazine structure: broad band ~3500 cm.$^{-1}$, chelated hydroxyl; intense band 1630 cm.$^{-1}$, >C=N— stretching; 1325 cm.$^{-1}$, phenolic -OH. The infrared spectrum resembles that of salicylaldehyde azine quite closely with the exception of a strong band at 1655 cm.$^{-1}$ indicating aromatic aldehyde end groups.

Anal. Calcd. for $(C_{15}H_{12}O_2N_2)_x$: C, 71.41; H, 4.79; N, 11.11. Found: C, 69.31; H, 4.85; N, 8.61.

b. Pyridine Solution.—To a solution of 4.1000 g. (0.016 mole) of 5,5′-methylene-bis-salicylaldehyde dissolved in 600 ml. of pyridine (temperature 80°, nitrogen atmosphere) was added 20 ml. of glacial acetic acid and 1 ml. (0.016 mole) of hydrazine hydrate (85% solution). The solution was brought to reflux and within 30 minutes a gelatinous yellow precipitate separated. After four hours reflux, pyridine was distilled off to a final volume of 100 ml. The resultant suspension was poured into a dilute solution of acetic acid and the polymer which precipitated was collected, washed and dried; yield 4.1 g., quantitative, inherent viscosity 0.118 (0.2% in sulfuric acid).

Anal. Calcd. for $(C_{15}H_{12}O_2N_2)_n$: C, 71.41; H, 4.79; N, 11.11. Found: C, 69.23; H, 5.31; N, 8.51.

The analysis corresponds to a low molecular weight polymer with a D.P. of 4 to 6 and with aldehyde end groups.

Dimeric Azine of 5,5′-Methylene-bis-salicylaldehyde.—In a 500-ml. flask was placed a solution of 8.1616 g. (0.03185 mole) of 5,5′-methylene-bis-salicylaldehyde in 400 ml. of pyridine; 10 ml. of acetic acid was added, followed by 20 ml. of 85% hydrazine hydrate (0.3185 mole) (10× excess). The solution was refluxed for five hours and the product isolated by pouring the reaction mixture into two liters of dilute acetic acid. It was washed with dilute acetic acid, water, and dried to give 9.2 g. (90%) of a yellow powder which analyzed for the dimeric azine with hydrazone end groups.

Anal. Calcd. for $C_{30}H_{28}O_4N_6$: C, 68.51; H, 5.11; N, 14.24. Found: C, 68.52; H, 5.22; N, 14.65.

Polyazine of Bis-salicylaldehyde-5,5′-sulfone.—In a one-liter flask was placed a solution of 4.9006 g. (0.016 mole) of bis-salicylaldehyde-5,5′-sulfone and 20 ml. of acetic acid in 300 ml. of pyridine. At a temperature of 80°, 1 ml. (0.016 mole) of hydrazine hydrate was added and the solution brought to reflux. Within three minutes the solution had become cloudy yellow. After five hours reflux, pyridine was distilled off to a final volume of 100 ml. and then poured into dilute acetic acid. The polymer was isolated by filtration, washed and dried; yield 3.7 g. (76%).

Anal. Calcd. for $(C_{14}H_{10}O_4SN_2)_n$: C, 55.62; H, 3.33; N, 9.27; S, 10.61. Found: C, 55.62; H, 3.81; N, 8.79; S, 10.75.

Thermal Stabilities.—The thermal stabilities of the metal chelates of salicylaldehyde azine and the polyazines of 5,5′-methylene-bis-salicylaldehyde and of bis-salicylaldehyde-5,5′-sulfone were determined by a thermobalance similar to that described by Winslow and Matreyek.[8] The results are given in Tables III and IV.

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(8) F. H. Winslow and W. Matreyek, *J. Polymer Sci.*, **22**, 315 (1956).

URBANA, ILL.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENTS, UNIVERSITY OF NOTRE DAME AND UNIVERSITY OF PENNSYLVANIA]

Copolymerization Characteristics of Two Vinylsilanes

BY CHARLES E. SCOTT AND CHARLES C. PRICE

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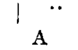
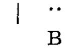
Copolymerization of vinyltriethoxysilane (I) with styrene and acrylonitrile indicates the polar and resonance reactivity factors to be $e = 0.1$ and $Q = 0.03$. For vinyltrimethylsilane (II), $e = -0.1$ and $Q = 0.03$. The very low resonance factors are supported by the ultraviolet spectra of I and II, which show considerably less conjugation than methyl vinyl sulfide. The unshared 3p-electrons on the latter thus would seem to be more important for resonance than vacant 3d orbitals on both sulfur and silicon.

In earlier studies of copolymerization and spectra of vinyl sulfides[1] and related compounds, it seemed evident from the relatively large resonance stabilization factor in copolymerization,[2] $Q = 0.3$–0.4, and the relatively intense ultraviolet absorption band, λ_{max} 225–240, E_{max} *ca.* 10,000, for vinyl sulfides, that a sulfide sulfur atom can provide appreciable resonance stabilization for an adjacent odd electron, either in the free-radical intermediate in copolymerization or in the excited state.



$-\dot{C}-\ddot{\underset{\cdot\cdot}{S}}-R$

A



$-C=\dot{\underset{\cdot\cdot}{S}}-R$

B

For the corresponding sulfones, the resonance factor in copolymerization is markedly reduced, $Q \simeq 0.07$, as is the ultraviolet absorption, λ_{max} *ca.* 210, E_{max} *ca.* 300.[1,3]

The purpose of the present investigation of vinylsilanes was to determine to what extent the difference between sulfide and sulfone was due to lack of unshared 3p electrons on the latter sulfur rather than its marked difference in electrical charge. The silicon atom of a vinylsilane would not have the strong electron-attracting inductive effect of the sulfone group but would have similar available 3d orbitals.

Experimental[4]

Styrene was redistilled under reduced pressure in a stream of nitrogen, b.p. 38° (13 mm.). **Acrylonitrile** was

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(1) C. C. Price and J. Zomlefer, THIS JOURNAL, **72**, 14 (1950); C. C. Price and R. D. Gilbert, *ibid.*, **74**, 2073 (1952); C. C. Price and H. Morita, *ibid.*, **75**, 4747 (1953).

(2) T. Alfrey and C. C. Price, *J. Polymer Sci.*, **2**, 101 (1947).

(3) E. A. Fehnel and M. Carmack, THIS JOURNAL, **71**, 231 (1949).

(4) Microanalyses by Micro-Tech Laboratories, Skokie, Ill.