

The Polymerization of Formaldazine. II. The Polymerizability of Formaldazine and the Characterization of Its Polymer

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ABSTRACT: The optimum conditions for the storage of formaldazine, which had been considered difficult, were successfully investigated. Formaldazine can be stored for a long time above room temperature as a solution in completely dried tetrahydrofuran (THF) or triethylamine. The polymerizability of formaldazine was also studied by various catalysts. This monomer could not be polymerized by radical initiators; it could be polymerized anionically and cationically, which was consistent with the prediction of polymerizability from its spectrometric data (Part I). The polymer was found to be composed of 1,4 addition and 1,2 addition, like butadiene.

KEY WORDS Formaldazine / Monomer / Cationic Polymerization / Anionic Polymerization / 1,2 Addition / 1,4 Addition / Polymerizability / ESR Spectrum / Polyformaldazine /

Formaldazine was prepared for the first time by Neureiter in 1959.¹ He noticed that formaldazine was polymerized spontaneously at room temperature, but did not report what type of polymerization occurred in this case. As for chemical reactions, only the addition of hydrogen sulfide¹ and the photolysis²⁻⁴ have been reported. The scarcity of studies might be ascribed to the high polymerizability of formaldazine and the resulting difficulty of storage at room temperature. We investigated the optimum conditions for the storage of formaldazine and found that it could be stored above room temperature in a solution with some solvents like THF and triethylamine under rigorously dried conditions.

Then, studies concerning the polymerizability of the monomer and the characterization of the polymer were carried out. In addition, thermal polymerization was also carried out under the same conditions as Neureiter's¹ and the polymer was characterized.

EXPERIMENTAL

Monomer

Formaldazine was prepared and purified by the procedure described in Part I.⁵

Solvents

Benzene, toluene, *n*-heptane, diethyl ether, dioxane, and triethylamine were purified in the usual manner⁶ and were dried over metallic sodium. Tetrahydrofuran (THF) was refluxed over metallic sodium, distilled, dried over sodium, and finally distilled into a sodium-mirrored ampoule on a high-vacuum system. From this pale blue solution, the solvent was transferred to a reaction vessel on a vacuum system before use. Methanol and *n*-butyl alcohol were purified in the usual manner and were dried over magnesium ribbon. These solvents were distilled immediately before use.

Catalysts

According to the method of Ziegler,⁷ *n*-butyllithium (BuLi) was prepared in *n*-heptane, and the concentration (6.6 mol %) was determined by double titration.⁸ *n*-Butylmagnesium chloride was titrated by the method of Gilman.⁹ Sodium naphthalene was formed by distilling tetrahydrofuran from a graduated glass ampoule into an evacuated flask which contained a known amount of naphthalene and was coated with an excess of sodium film.¹⁰ The solution was filtered through a sintered glass filter under high vacuum and the concentration of sodium naphthalene in the filtrate was titrated by the method of Gilman.⁸

2,2'-Azobisisobutyronitrile was purified by recrystallization from 95-% ethanol. Benzoyl peroxide was purified by fractional precipitation from a chloroform solution, using ethyl alcohol as precipitant.

Preparation of Solutions of Formaldazine in Various Organic Solvents

A solution of the monomer in various organic solvents was prepared by distilling a given amount of formaldazine into an ampoule containing various volumes of solvents using a high-vacuum line. Formaldazine was polymerized in hydrocarbon, alcohol, and acetone even in dried and dilute solutions (below 1 volume percent) at room temperature. The occurrence of the polymerization was easily recognized by evaporating the monomer and solvent under high vacuum. Formaldazine was stable even at 80°C in a THF solution below 15 vol %. The stability of formaldazine in THF was investigated using the changes of the NMR spectra before and after heating.

Polymerization

Polymerization was carried out in a glass ampoule (which had been previously flamed out to remove the absorbed water, which is a good catalyst for formaldazine) on a high-vacuum line.

a) *Bulk Polymerization.* One ml of formaldazine was introduced into an ampoule from the graduated storing ampoule on the high-vacuum line. The reaction ampoule was placed in a thermostat at a given temperature. An explosive polymerization occurred above -10°C. Evaporation of the unreacted monomer yielded a pale yellow polymer in a quantitative yield. The polymer was washed with methanol and benzene and dried.

Anal. Calcd for $C_2H_4N_2$:

C, 42.84; H, 7.19; N, 49.97

Found: C, 42.18; H, 7.97; N, 50.38

b) *Thermal Polymerization in Various Solvents.*

A polymerization ampoule with a side arm connected to a breakable seal had been previously flamed out *in vacuo*. A given amount of solvent was put into it using a hypodermic syringe and degassed by the conventional freezing and melting cycles *in vacuo*. Then 1 ml of formaldazine was distilled into it. The polymerization ampoule

was sealed off *in vacuo* and placed in a thermostat for a fixed time. Unreacted formaldazine and solvent were removed through the breakable seal. The residual polymer was taken out, washed with methanol and benzene, and dried.

The solvents used were benzene, toluene, *n*-heptane, methanol, *n*-butyl alcohol, ethyl ether, dioxane, tetrahydrofuran, and triethylamine.

c) *Catalyst Polymerization.* Formaldazine of 10 vol % in THF was prepared in another ampoule under high vacuum. The solution was distilled into a polymerization ampoule connected to a breakable seal, into which a catalyst solution had been previously added using a hypodermic syringe under nitrogen atmosphere; the ampoule was connected to a high-vacuum line and degassed by the conventional freezing—melting cycles. The polymerization ampoule was sealed off *in vacuo* and placed in a thermostat. After a given time, the unreacted monomer and solvent was removed through a breakable seal *in vacuo*. The residual polymer was dissolved in water, reprecipitated by methanol, filtered, and dried. In the typical case of anionic polymerization, the polymer precipitated during the polymerization. So the polymer was isolated by filtration and washed with methanol and THF in order to remove the unreacted monomer, solvent, and catalysts.

RESULTS AND DISCUSSION

(1) *Optimum Conditions for the Storage of Formaldazine*

Formaldazine could not be stored in neat or in many common organic solvents at room temperature because of its spontaneous polymerization. However, this monomer could be stored without polymerization in tetrahydrofuran or triethylamine solution, if optimum conditions for the concentration were selected. These results are shown in Table I.

If the concentration of formaldazine in THF is lower than 15 vol %, formaldazine is stable even at 80°C for several hours. The polymer was not obtained at room temperature for 3 days at 15 vol %; the solution became a little turbid after 1 week. In the case of triethylamine, the limiting concentration was 20 vol %. The concentration is quite important for the storage

Table I. Solvents for storage of formaldazine at room temperature

Et ₃ N	(below 20 vol %)	+
THF	(above 15 vol %)	-
THF	(below 15 vol %)	+
Dioxane	(10 vol %)	-
Ether	(3 vol %)	-
Toluene	(3 vol %)	-
Heptane	(3 vol %)	-
Methanol	(3 vol %)	-
Acetone	(3 vol %)	-

+, no polymerization; -, polymerization.

of formaldazine without polymerization. Two reasons can be speculated. One would be that some impurity is contained in the formaldazine. Another reason might be a self-induced polymerization which is characteristic of formaldazine, because formaldazine is liable to accept and donate an electron by itself.⁵

The former speculation was investigated by preparing various concentrations of THF solutions with a constant volume of formaldazine and the solutions with a constant volume of THF. In both cases, formaldazine was spontaneously polymerized above 15 vol %, but was stable in the solutions below 15 vol % for 3 days. If the impurities in formaldazine were important, the polymerization would be independent of the concentration because the volume of formaldazine used was constant in all solutions and the amount of impurities contained must be constant. Thus, the former speculation can be rejected.

There is some indirect information about the latter speculation from the UV spectra of formaldazine.⁵ The UV spectra of formaldazine were measured in a THF solution and in a pure gas state. The spectra are different at the $n-\pi^*$ transitions.⁵ In the gas state, there are two absorption bands assigned to the $n-\pi^*$ transition at 228 and 283 nm. The two absorption bands in the gas state coalesce into a broader absorption band about 240 nm in the THF solution. Two absorption bands in the gas state come from the nonbonding splitting of the energy level of the lone pair of nitrogen on account of the nonbonding interaction between lone pairs of neighboring nitrogens in formaldazine, as shown in diazo compound.¹¹ In the THF

solution, however, the interaction may decrease because of the interaction of the lone pair with the THF. The interaction with solvents will be supported in the next section. Thus, the nonbonding splitting of the energy levels is less in the tetrahydrofuran than in the gas. Formaldazine seems to be more stable in basic solvents like THF and triethylamine.

(2) Polymerizability of Formaldazine

The results of the polymerization by various initiators are shown in Table II. Formaldazine was not polymerized by radical initiators. This is reasonable from the fact that radical polymerization has not been found to occur in many compounds having a carbon-heteroatom double bond.

Formaldazine was explosively polymerized by typical anionic catalysts. The reaction system colored orange-red as soon as the polymerization started, as seen in the anionic polymerization of butadiene. The polymerization finished within a few minutes, even at -78°C , and the polymer precipitated. The fact that formaldazine is likely to polymerize anionically is

Table II. Polymerization of Formaldazine by various catalysts^a

Catalyst ^b	Temp, °C	Time, min	Yield, %	1,2-Content, %	η_{sp}/c^c 100 ml/g
(Naph) ⁻ Na ⁺	-78	15	100	90	Insol ^d
BuLi	-78	15	100	90	Insol
"	0	15	100	90	Insol
BuMgBr	-78	15	100	90	Insol
H ₂ O	0	15	99.6	38	0.28 ^d
<i>n</i> -BuOH	0	15	97.3	36	0.25
Bulk	-10	15	98.5	47	0.40
MeOH	-10	15	88.2	41	0.23
TCNE	0	15	97.9	34	0.15
Chloranil	0	15	99.4	34	0.18
BPO	60	1200	0		
AIBN	60	1200	0		

^a Formaldazine was used as 10-vol % THF solution except for bulk polymerization.

^b Catalyst concentration = 1/50, 1/100 mol % of formaldazine.

^c 0.5% H₂O solution, 30°C.

^d Insoluble in organic solvents.

^e Soluble in H₂O, partially soluble in DMSO and THF; insoluble in methyl alcohol, benzene, and acetone.

consistent with the result speculated from the half-wave potential of azine compounds.⁵ Formaldazine was polymerized by protic solvents such as water and methanol without coloration. Judging from the fact that formaldazine can be stored in basic solvents such as triethylamine and THF, the polymerization by water and methanol may be related to their active hydrogen.

Formaldazine was polymerized by strong electron acceptors such as tetracyanoethylene and chloronil at -30°C . The NMR spectra and IR spectra of the polymers obtained by electron acceptors were very similar to that of the polymer obtained by spontaneous polymerization, except for the intensity. The IR spectra of the polymers were different from that of the anionically obtained polymers. An anion radical was detected during the polymerization by electron acceptors by ESR spectroscopy, but a cation radical which should have been produced simultaneously was detected only in chloranil—formaldazine. So the cation radical seems to be more reactive than the anion radical.

From these facts the bulk polymerization also seems to be initiated by a cation radical prepared by the reaction of two formaldazine molecules. The addition of THF might inhibit the interaction of the formaldazines by solvation. The solvation is supported by the change of internal shifts between the CH_3 group and the CH group of acetaldazine, a higher homolog of formaldazine, with solvents as shown in Table III. The internal shift in the THF solution is larger than that in neat and in benzene. Shooley^{12,13} shows that the internal shift depends on the

electronegativity of the X group in $\text{CH}_3\text{CH}_2\text{X}$. The electronegativity of the nitrogen atom of formaldazine might be changed because of the interaction with THF. Thus, formaldazine might be stabilized by THF and thus the polymerization would be prevented.

Another support for the interaction of formaldazine with itself comes from the ESR spectrum of the polymer obtained from the spontaneous polymerization. The ESR spectrum was measured immediately after the spontaneous polymerization. The spectrum was weak and broad and no information was obtained about the structure of the radical. But the presence of a radical in the polymerization system makes us speculate that formaldazine interacts with itself to make an anion radical and a cation radical which might become good initiators. Further investigation of formaldazine polymerization will be necessary to draw a firm conclusion about its polymerization mechanism.

(3) *The Characterization of the Polymer Obtained Spontaneously*

The polymer obtained spontaneously was a pale-yellow solid and had a softening temperature of around 120°C and an inherent viscosity in water (0.5% concn, 30°C) of 0.25–0.4. The polymer was soluble in water, tetrahydrofuran, and dimethylformamide, and insoluble in methanol, ether, heptane, and benzene.

The result of the elementary analysis of the polymer shows that this polymerization is of the addition type. The IR and NMR spectra of the polymer are shown in Figures 1 and 2.

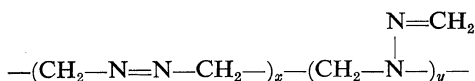
The IR spectra showed absorption bands at 3240 ($\nu_{\text{N-H}}$), 3060 ($\nu_{\text{C-H}}$), 2880 (ν_{CH_2}), and 1580 cm^{-1} ($\nu_{\text{C=N}}$, $\nu_{\text{N=N}}$). In addition, the strong absorption bands at 1200–1000 cm^{-1} were assigned to the stretching frequency of C–N.

The NMR spectrum is divided into two groups, at around δ 6.7 and around δ 3.8. The peaks at around δ 3.8 were assigned to the $-\text{CH}_2$ group and the peaks at around δ 6.7 to $-\text{N}=\text{CH}_2$.¹³ No change of the NMR spectrum with the measurement temperature from room temperature to 80°C was observed. Therefore a peak due to the NH group was not found. This shows that the amount of the NH group is very small. These results suggest that the polymer

Table III. Chemical-shift difference between the methyl proton and the methine proton of acetaldazine in various solvents (10% solution)

Solvents	$\delta\text{CH}_3-\delta\text{CH}$, Hz
Triethylamine	346.2
Tetrahydrofuran	354.5
Neat	358.3
Dioxane	360.0
Ethyl ether	361.8
Heptane	363.0
Toluene	368.0
Benzene	368.2

consists of a mixture of 1,4 addition and 1,2 addition, as in polybutadiene. The small amount of the NH group in the IR spectra may be due to the end group and hydrazone rearrangement in the polymer. In addition, the volatile compound from the pyrolysis of this polymer was determined to be predominantly nitrogen molecules, using high-resolution mass spectrometry. The elementary analysis of the pyrolysis residue also shows a decrease of the nitrogen content. This suggests the presence of the $-\text{CH}_2-\text{N}=\text{N}-\text{CH}_2$ unit in the polymer. Thus the predominant structure of the polymer may be as follows.



The ratio of 1,4 to 1,2 addition was calculated from the area under the peaks in the NMR spectrum by using the following formula.

$$(1,4 \text{ addition } \%) = \frac{A-B}{A+B} \times 100$$

where A is the area under the peak due

to the $-\text{CH}_2$ group and B to the $-\text{N}=\text{CH}_2$ group.

The 1,2 content thus estimated for the polymer is shown in Table II, along with the results of the polymerization obtained by catalysts.

(4) *The Characterization of the Polymer Obtained by Catalysts*

The polymers obtained by protic solvents such as water and methanol and by electron acceptors such as tetracyanoethylene were similar to that obtained thermally in their solubilities, IR spectra, and NMR spectra. The microstructures of the polymers were obtained from their NMR spectra. But the polymers obtained by typical anionic catalysts were insoluble in most common organic solvents and even in water. Therefore, the NMR spectrum of the polymer could not be measured. The ratio of the 1,2 structure to 1,4 structure, which was estimated with the water-soluble polymers from the NMR spectra, was found to be almost linearly related to the ratio of optical densities at 3060 and 2880 cm^{-1} in the IR spectra. The correlations are shown in Figure 3.

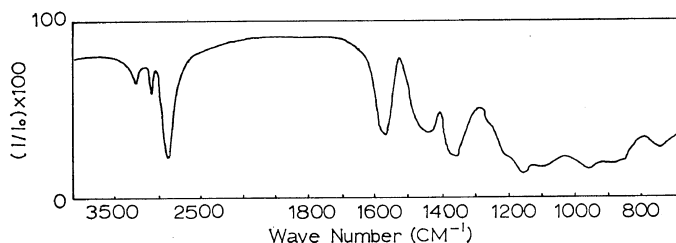


Figure 1. IR spectrum of polyformaldazine obtained spontaneously.

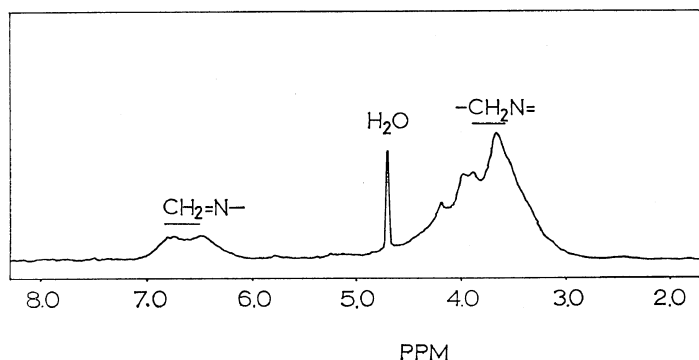


Figure 2. NMR spectrum of polyformaldazine obtained spontaneously: Solvent, D_2O ; 5-% solution.

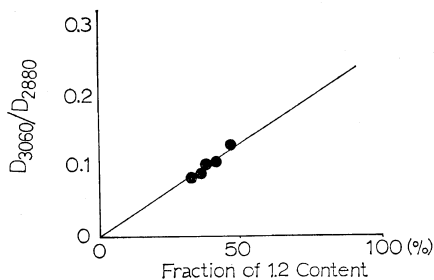


Figure 3. The relation between D_{3060}/D_{2880} and 1, 2 content.

The microstructure of the insoluble polymer was approximately estimated from the IR spectra, using the relationship in Figure 3. The polymers obtained with the typical anionic catalysts predominantly consist of the 1,2 structure (Table II). The insolubility of the polymer may be ascribed to cross-linkings due to the side reaction of the propagating anion with the pendant double bond. Judging from the possibility of an addition reaction of the organometal compounds to the carbon—nitrogen double bond,¹⁴⁻¹⁵ the cross-linking is quite possible.

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