

Self-Condensation of Aqueous Hexa(methoxymethyl)melamine: Effects of Concentration, pH, and Alcohol Content

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SYNOPSIS

Dilute aqueous solutions of hexa(methoxymethyl)melamine have been found to form colloidal suspensions of cross-linked polymer under acidic conditions in a manner similar to nonalkylated methylmelamines. Experiments have shown that the time to onset of turbidity is quite sensitive to solution pH, with a sharp maximum in the rate observed at pH 1.22 under the specific conditions used in this study. Solutions were unexpectedly stable at pH values below the maximum. Suppression of the condensation process was also observed in the presence of added alcohols, with the magnitude of the rate-retarding effect influenced by the alcohol structure. © 1992 John Wiley & Sons, Inc.

INTRODUCTION

Hexa(methoxymethyl)melamine (Compound **I**) and related compounds find extensive use as cross-linking agents in industrial thermoset coatings because of their ability to react with hydroxyl- and amine-functionalized polymers through acid-catalyzed condensation involving the $\text{—N—CH}_2\text{OR}$ groups.¹ Alkylated melamines are preferred in such applications because of their greater compatibility with the primary film-forming resins and lower reactivity (i.e., longer shelf life) relative to the precursor methylolmelamines.

The water solubility of **I** is quite limited; hence, it is used primarily in solvent-based or aqueous dispersion coating systems. However, during the examination of very dilute solutions in which Compound **I** was completely dissolved in acidified water, it was noted that the initially clear solutions would begin to turn cloudy after standing for varying periods of time. The solutions would eventually form an opaque white suspension resembling homogenized milk and would set to a loose gel. Initial ex-

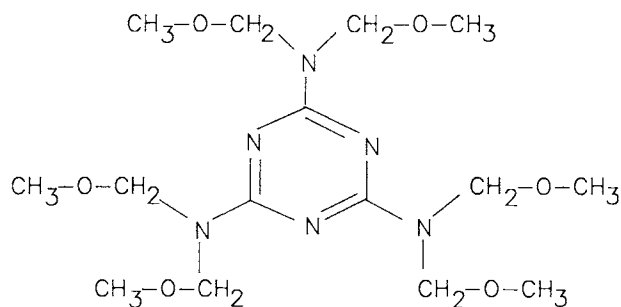
periments indicated that the time of onset of turbidity was quite sensitive to solution pH, with other factors also influencing the rate of the reaction.

A survey of the extensive literature on melamine-formaldehyde (MF) resins indicated that these results were consistent with earlier work in related areas. In the pulp and paper industry and textile industry, the use of aqueous dispersions of MF resins dates back to the 1940s. Solutions of freshly prepared MF adducts or trimethylolmelamine, when acidified with either mineral or carboxylic acids under proper conditions, polymerize by self-condensation to a colloidal dispersion of low molecular weight polymer that adsorbs efficiently on to cellulose fibers.²⁻⁴ After formation and aging, the adsorbed resin cures further to impart greatly increased dry and wet strength to the treated paper. It seemed reasonable to assume that a similar process was responsible for the results observed with dilute aqueous solutions of **I**.

Although some of the kinetic aspects of the MF colloid formation have been studied,⁵ we were unable to locate similar data on completely alkylated systems such as **I** where the reaction pathway must also include methylol-ether hydrolysis steps. Our study was aimed at determining the influence of solution acid concentration and other factors on the overall rate of the colloid formation from aqueous solutions of **I**.

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Compound I Hexa(methoxymethyl)melamine (IUPAC nomenclature: *N,N,N',N',N'',N''*-hexakis(methoxymethyl)-2,4,6-triamino-1,3,5-triazine; CAS Reg. No. 3089-11-0).

EXPERIMENTAL

The hexa(methoxymethyl)melamine (**I**) used in this study was a commercial grade of material (Resimene-745) from the Monsanto Company, which was utilized as received. Although it has been reported in the literature⁶ that **I** is soluble in water to the extent of 15% at 40°C, we were unable to achieve this concentration while working at normal room temperature. The highest concentration of **I** that would totally dissolve in neutral water under our conditions, 30 min vigorous agitation at 23°C, was 8.0×10^{-2} molar or approximately 3% by weight.

Acid solutions were prepared by dilution of a single stock solution of hydrochloric acid that had been standardized by titration to a phenolphthalein endpoint with reagent NaOH solution of known concentration. Alcohol solutions were likewise prepared by dilution of higher concentration stock mixtures prepared from reagent-grade materials.

Reaction times to the onset of turbidity were determined spectrophotometrically. Specific volumes of test solutions were pipetted into test tubes for mixing and then immediately transferred to cuvettes for insertion into a Milton-Roy Spectronic 20. With the wavelength set at 500 nm, the sample transmittance was monitored and the time required for it to fall to 95% was recorded. The 95% transmittance value corresponded to a solution in which a faint turbidity was just noticeable on visual inspection.

RESULTS AND DISCUSSION

The most striking feature of the colloid formation from Compound **I** is the maximum in the rate vs. pH curve. A solution concentration of $4.0 \times 10^{-2}M$ **I** was chosen to compare the reaction rates at various pH values and, for graphical purposes, the times to

onset of turbidity (in seconds) were compared with the fastest run in the series, i.e., the shortest reaction time was assigned a relative rate of 1.00. As was initially expected, increasing the acid concentration from basic through neutral toward lower pH increased the rate at which turbidity appeared in the solution. However, as Figure 1 shows, the rate reached a maximum at pH 1.22 and then declined sharply back to zero over a narrow range. Long-term storage of test solutions indicated that at pH values greater than 6.0 and less than 1.0 the solutions were stable and did not form colloids for periods in excess of 2 weeks at room temperature. At a given pH, as shown in Figure 2 for which the acid concentration corresponding to the maximum rate was used, decreasing the initial concentration of **I** gave a steady decrease in the observed reaction rate.

The reason for this behavior lies in the complex network of equilibria involved in the self-condensation. Using only one of the six methoxymethyl ether groups in Compound **I** for illustration, Scheme 1 outlines the relevant reactions and how they are interconnected. In the dilute aqueous solution, the predominance of water would be expected to strongly shift the equilibria involving water toward the hydrated species. The final two reactions in the sequence that give rise to the self-condensation product are also reversible under acidic conditions; however, the formation of polymer as an insoluble colloid should shift the overall equilibrium in the forward direction. Although thermally cured MF resins are believed to be cross-linked predominately through methylene bridges, model systems suggest that ether-linked species would also be significant under these mild conditions.⁷ Other studies have indicated that acid-catalyzed conversion of the methoxymethyl ether to the methylol group is considerably faster than the subsequent decomposition of the methylol group to the free amine and formaldehyde.⁸ Thus, the equilibria involving methylol groups would be expected to dominate the system. This conclusion is substantiated by the observation that dilute aqueous solutions of **I** do not give colloid formation under basic conditions. Other studies have shown that **I** does not undergo hydrolysis in basic solution,⁹ nor does the methylol group condense with the free amine above neutral pH.¹⁰ Of particular significance to our study are the results of Sato and Naito,¹¹ who observed a maximum in the rate of condensation vs. pH for the reaction of various methylolmelamine species in aqueous DMSO solution. Although the Sato and Naito results showed a curve of more symmetrical shape with the peak maximum at considerably higher pH (approximately 4.0), the overall

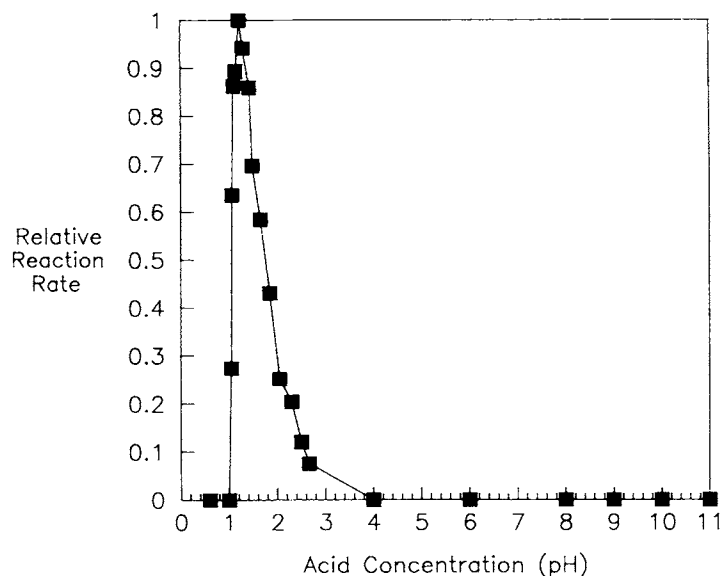


Figure 1 Relative reaction rates for onset of turbidity of 4.0×10^{-2} M aqueous I vs. solution pH.

similarity with our observations strongly suggests that dissolved Compound I is quickly hydrolyzed in the acid solution and the resulting methylol equilibria are responsible for the turbidity rate vs. pH effects.

The relative importance of the equilibria that result in methylene vs. ether-linked products may be the key to understanding the unusual rate maximum in this system. As Scheme 1 shows, the formation

of the ether-linked product involves the reaction of one methylol group with the carbonium ion species derived from the loss of protonated water from another methylol group. In contrast, formation of the methylene-bridged product requires reaction of the carbonium ion species with the free —NH of de-formylated melamine. Increasing acid concentration at lower pH would tend to tie up a larger proportion of the free —NH as the protonated species

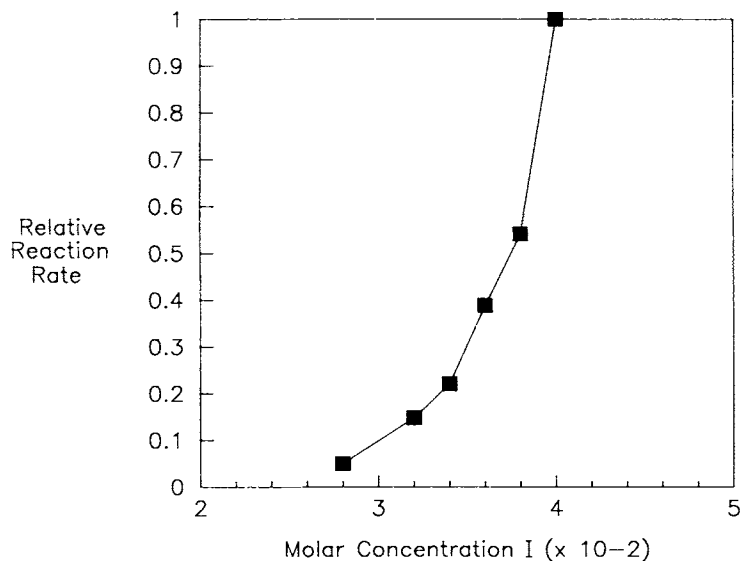
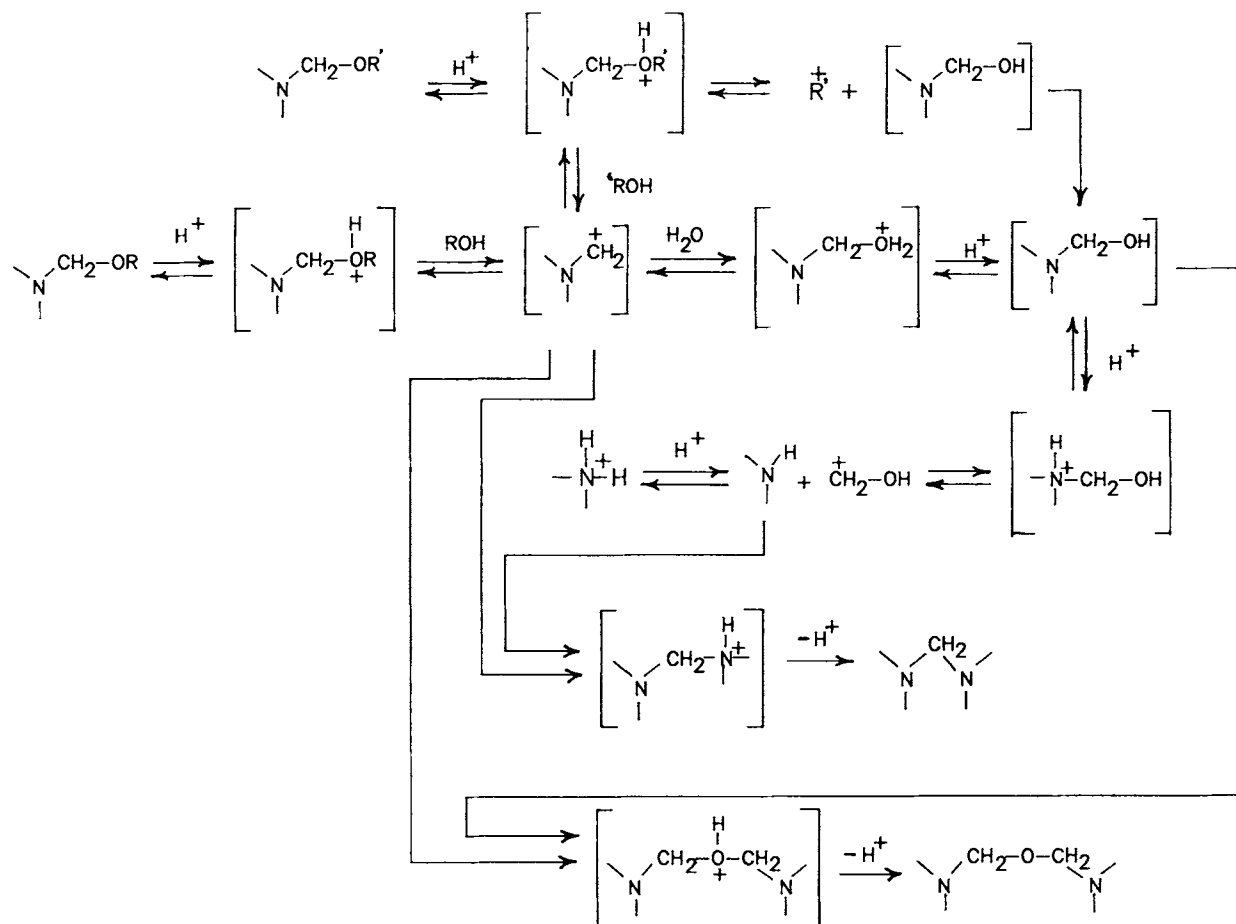


Figure 2 Relative reaction rates for onset of turbidity of aqueous I at pH 1.22 vs. molar concentration of I.



Scheme 1 Network of equilibria involved in hydrolysis and subsequent reactions of a single *N*-methoxymethyl group on Compound I.

$-\text{NH}_2^+$, making it less available for the reaction and, hence, decreasing the overall rate of condensation.

During the study of this process, it was also noted that the rate of self-condensation could be significantly retarded by the presence of additional alcohol in the solution. Figure 3 shows how the relative rate of turbidity onset decreased with increasing concentration of added methanol at constant initial pH and concentration of I. These results are clearly consistent with the importance of the methylol-related species in the equilibrium network shown in Scheme 1. Increased concentration of CH_3OH would be expected to suppress the initial hydrolysis of I, lowering the equilibrium concentration of the key methylolated species and decreasing the overall rate of condensation. By similar reasoning, the equilibria resulting in transesterification would also be expected to suppress the onset of turbidity in the presence of other alcohols. This aspect of the mechanism

was examined briefly by comparing the rate-retarding effect of added alcohols of varying structure where the same molar concentration of each alcohol was used at the pH corresponding to the rate maximum.

Table I summarizes the results of the study utilizing water-soluble alcohols up to C_4 . It was initially thought that the least sterically hindered primary alcohols would favor formation of the corresponding methylol-ether species; hence, they would more significantly retard the colloid formation than the more sterically hindered secondary and tertiary alcohols. Steric influences would also be reinforced by electronic effects in the alternate hydrolysis pathway that proceeds from the protonated methylol-ether to generate the alkyl carbonium ion and the free methylol species. Factors that shift this equilibrium in the forward direction, such as stability of the resulting carbonium ion, would also increase the concentration of the key methylol species and further

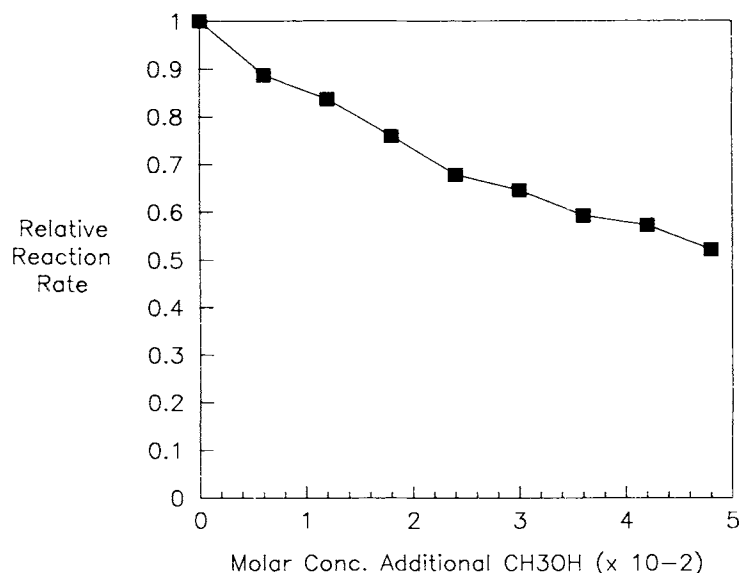


Figure 3 Relative reaction rates for onset of turbidity of $4.0 \times 10^{-2} M$ aqueous I at pH 1.22 vs. molar concentration of added methanol.

negate the rate-retarding effect of the primary transesterification equilibrium. As a result, alcohols with large steric requirements that also generate tertiary carbonium ions would be expected to show the smaller rate-retarding effects while primary alcohols of smaller steric bulk would be expected to show the

larger rate-retarding effects. Although this general trend was observed, there were obvious anomalies. The largest rate-retarding effect was seen for isobutanol, which, while a primary alcohol, should also have a larger steric bulk than the linear primary alcohols in the series tested. A larger rate-retarding

Table I Relative Reaction Rates for Onset of Turbidity of $4.0 \times 10^{-2} M$ Aqueous I at pH 1.22 in the Presence of $1.8 \times 10^{-2} M$ Added Alcohols of Varying Structure

Structure of Added Alcohol	Relative Reaction Rate
$\text{CH}_3\text{-OH}$.759
$\text{CH}_3\text{-CH}_2\text{-OH}$.726
$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-OH}$.774
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{-CH-CH}_2\text{-OH} \end{array}$.671
$\begin{array}{c} \text{OH} \\ \\ \text{CH}_3\text{-CH-CH}_3 \end{array}$.703
$\begin{array}{c} \text{OH} \\ \\ \text{CH}_3\text{-CH}_2\text{-CH-CH}_3 \end{array}$.854
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{-C-CH}_3 \\ \\ \text{OH} \end{array}$.822

effect was also seen for the moderately hindered secondary alcohol isopropanol. Investigation of the anomalous position of these alcohols in the sequence relative to the other primary and tertiary members is continuing.

REFERENCES

1. I. H. Updegraff, in *Encyclopedia of Polymer Science and Engineering*, Wiley, New York, 1985, Vol. 1, pp. 753-789.
2. W. F. Linke, T. F. Ziegler, E. C. Eberlin, and R. R. House, *TAPPI J.* **45**(10), 813 (1962).
3. Rhode Island Section—American Association of Textile Chemists and Colorists, *Am. Dyestuff Repr.*, **Nov. 28**, 843 (1949).
4. W. B. Berard, E. K. Leonard, and W. A. Reeves, *Am. Dyestuff Repr.*, **50**(17), 29 (1961).
5. M. Okano and Y. Ogata, *J. Am. Chem. Soc.*, **74**, 5728 (1952).
6. E. M. Smolin and L. Rapoport, in *The Chemistry of Heterocyclic Compounds*, Interscience, New York, 1959, Vol. 13, p. 341.
7. I. H. Anderson, M. Cawley, and W. Steedman, *Br. Polym. J.*, **1**, 24 (1969).
8. A. Berge, B. Kvaeven, and J. Ugelstad, *Eur. Polym. J.*, **6**, 981 (1970).
9. A. Berge, S. Gudmundsen, and J. Ugelstad, *Eur. Polym. J.*, **5**, 171 (1969).
10. I. H. Updegraff, in *Encyclopedia of Polymer Science and Engineering*, Wiley, New York, 1985, Vol. 1, p. 759.
11. K. Sato and T. Naito, *Polym. J.*, **5**(2), 144 (1973).

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