

Water-Soluble Sulfonated Amino-Formaldehyde Resins. I. Melamine Resins, Synthesis

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Synopsis

The procedure for preparing sulfonated melamine formaldehyde resins and the factors affecting it were investigated. A four-step procedure was developed which results in reproducible water-soluble stable resins. The reactions that take place in the four steps are hydroxymethylation, sulfonation of the methylolmelamine intermediate, low pH condensation, and high pH rearrangement reaction. The reaction and the resins produced were found to be very sensitive to pH, temperature, sulfite/melamine, and formaldehyde/melamine molar ratios. The apparent molecular weight distribution of selected samples was also determined.

INTRODUCTION

New uses are continually being found for water-soluble sulfonated amino-formaldehyde resins in such industries as paper manufacturing and construction.¹⁻⁴ Melamine and urea resins have been known for a long time,⁵ and various preparation methods have been reported during the past 15 years.⁶⁻⁸ As with all other amino-formaldehyde resins, the preparation is affected by pH, reaction time, temperature, and preparation procedure.^{9,10} However, no systematic work to determine the exact effect of the factors on the preparation of the resins or to correlate the properties of the products with the preparation conditions has been reported.

Because of the industrial importance of these resins, we have initiated detailed studies on a number of amino-formaldehyde resins to build up a better understanding of this class of water-soluble resins and to assist in the systematic optimization of the preparation conditions. In this paper, we present results obtained on melamine-formaldehyde resin preparation and on the relationships between preparation conditions and selected properties of the resin. We found that sulfonated resins can be prepared reproducibly by a four-step procedure that leads to thermally stable products. We also found that pH, temperature, time, molar ratio of formaldehyde to melamine, and molar ratio of sulfite to melamine affect the properties of the resulting resin. We will discuss the molecular weight distribution of selected samples of the resins. The applications and the preparation of other sulfonated amino-formaldehyde resins will be reported in subsequent papers.

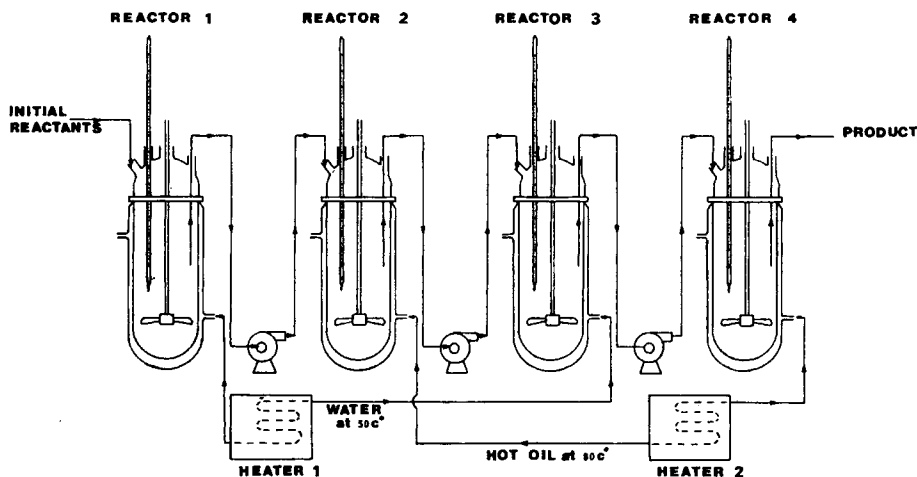


Fig. 1. Schematic diagram of the four-reactor system used in the development of the resin preparation procedure.

EXPERIMENTAL

Materials

Melamine was obtained from the Kuwait Melamine Industries Co. and used without further purification.

ANAL. Calcd for $C_3H_6N_6$: C = 28.6%; H = 4.8%; N = 66.7%. Found: C = 28.3%; H = 4.7%, N = 67%. Decomposition point: literature, 360°C; found, 370°C.

Paraformaldehyde technical grade from Kuwait Insulating Material Manufacturing Co. was used without further purification. The concentration of formaldehyde in paraformaldehyde was determined by the iodometric method; the average concentration was 94.6%. Sodium metabisulfite, $Na_2S_2O_5$ (BDH, laboratory reagent) was used without further purification.

Preparation Procedure for Resins

The properties of sulfonated melamine-formaldehyde resins vary considerably with the reaction conditions and the sequence of steps involved in the preparation. Thus, it is possible, by varying these conditions, to obtain resins with a wide range in properties from highly crosslinked water-insoluble to low viscosity water-soluble resins. Following is an example of the procedure used to prepare water-soluble resins. A special four-reaction flask set-up (Fig. 1) was used to ensure reproducibility. The procedure is divided in four steps as follows:

Step 1. A formalin solution of 18% concentration is prepared by dissolving 50.34 g of 94.6% paraformaldehyde in 230 mL of water. The reaction mixture is heated at 50°C for 30 min after its pH is raised to 11.0 by adding 0.5 mL of 10N NaOH solution. After the solution becomes clear, 88 mL of water is added and it is heated at 50°C for an additional 15 min. Then, the pH of the solution is raised to 11.35 and 50 g of melamine are added to it. Upon addition of melamine, it was noted that the temperature of the reaction mixture increases 4–5°C and then falls back to 50°C within 15 min, during which time

the melamine dissolves completely by reacting with the formaldehyde. Sodium metabisulfite (37.7 g) and water (20 mL) are then added to the solution, causing an increase in temperature of 4–5°C while the sulfite salt is dissolving.

Step 2. The solution is kept at around 50°C for 5 min and then the temperature is raised to 80°C in 15 min and kept at the new temperature for 45 min; the same pH is maintained.

Step 3. The solution is then cooled rapidly (approximately 5 min) to 50°C and 12 mL of 14.5*N* H₂SO₄ is added, causing a drop in pH to 3.50 and an increase in temperature of 4–5°C. The temperature drops back to 50°C within 15 min, and the solution is kept under these conditions with continuous stirring for 95 min, during which time it becomes very viscous. The solution is then neutralized by careful addition of a slurry of calcium oxide (CaO) in water. The amount of CaO needed is approximately 8 g.

Step 4. After neutralization, the solution is heated to 80°C in about 20 min and kept at that temperature for 60 min with continuous stirring. The solution is finally filtered to remove calcium sulfate and other solid particulates, cooled to room temperature, and treated with sodium hydroxide to adjust its pH to 9.5.

The solution prepared according to this procedure has a solid content of approximately 23% (determined by total water evaporation at 60°C). The solid content is adjusted to 20% by adding water, and the final viscosity of the solution at 20°C is 4.20 cP.

Concentration Effect Studies

Since concentration strongly affects the kinetics of polymerization reactions, a number of preparations were made in which the concentrations of reactants were increased to values higher than those in the standard procedure. In these concentration studies, the procedure was the same and the same masses of melamine, paraformaldehyde, and sodium metabisulfite were used, but the amount of water added initially during the preparation of paraformaldehyde was decreased and the additional water used in subsequent steps was eliminated. Table I provides a summary of the materials used and the final solid content of the resin solutions prepared at different concentrations.

TABLE I
Amount of Material and Solid Content at Various Concentrations

| Resin no. | H ₂ O (mg) | Paraformaldehyde (94.6%) | | Melamine | | Sodium metabisulfite | | Final solution resin content (%) |
|-----------|-----------------------|--------------------------|----------------------|------------|------|----------------------|------|----------------------------------|
| | | Weight (g) | Mole (for maldehyde) | Weight (g) | Mole | Weight (g) | Mole | |
| 1 | 338 | 50.34 | 1.59 | 50.0 | 0.40 | 37.7 | 0.20 | 23.5 |
| 2 | 410 | 50.34 | 1.59 | 66.67 | 0.53 | 50.26 | 0.26 | 23.2 |
| 3 | 235 | 50.34 | 1.59 | 50.0 | 0.40 | 37.7 | 0.20 | 28.4 |
| 4 | 186 | 50.34 | 1.59 | 50.0 | 0.40 | 37.7 | 0.20 | 33.0 |
| 5 | 300 | 100.68 | 3.17 | 100.0 | 0.80 | 75.4 | 0.20 | 38.4 |
| 6 | 245 | 100.68 | 3.17 | 100.0 | 0.80 | 75.4 | 0.20 | 42.7 |

Modified Procedure for the Preparation of SMF Resins

Water-soluble resins were also prepared according to the procedure of British Pat. 1,433,447.¹¹ The procedure combines the first two stages of the reaction into a single step. Thus, melamine and sodium metabisulfite are added simultaneously to the formalin solution at the beginning of the synthesis after the temperature is adjusted to 70°C. The reaction mixture is stirred under these conditions for 30 min; then the pH is lowered to acidic conditions, and the preparation is continued according to the standard procedure.

Characterization of the Resin. The prepared resin was freeze-dried with intermittent heating at 50°C, ground to a fine powder, and kept in a desiccator for 72 h before analysis.

ANAL.: C = 22.21%, H = 3.93%, N = 23.20%, Na = 8.59%, S = 3.40%.

In an alternative analytical procedure a solution of BaCl₂ was added to the resin solution in excess to precipitate the sulfonated product in the form of its barium salt. The precipitate was then filtered, oven-dried at 65°C for 24 h, ground to a fine powder, and kept in a desiccator for 72 h before analysis.

ANAL.: C = 17.56%, H = 3.24%, N = 20.29%, Na = 1.16%, Ba = 5.34%, S = 1.77%.

Molecular Weight Distribution

The molecular weight distributions of a few selected resins were analysed out by Mikro-analytisch Labor Pascher, Bonn, West Germany. The analysis was done by GPC at 50°C using distilled water as eluant and silica gel (10 μm) with pore sizes 6–100 μm as separating materials.

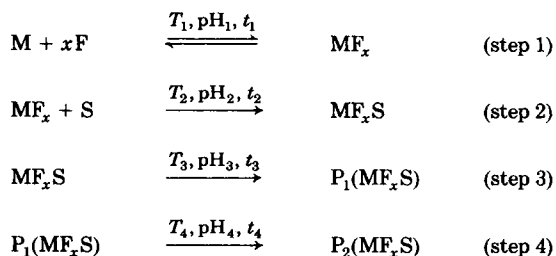
RESULTS AND DISCUSSION

Preparation Procedure for Superplasticizer

The preparation of sulfonated melamine–formaldehyde resins consists of four stages. The chemical changes during these four steps are hydroxymethylation, sulfonation, low-pH condensation, and high-pH stabilization (Scheme I). The complexity of the synthesis and the difficulties encountered stems from the multistep operation and the interdependence of the steps. Furthermore, each step is dependent on pH, temperature, and reaction time. During the very early stages of our work, we realized that the synthesis must involve initial preparation of a sulfonated monomer that condenses to the desired product during the subsequent stages of the reaction. But the exact conditions of pH, temperature, duration, and sequence of reactant addition were not known. Thus, many scouting experiments were done to determine the effects of several variables in broad terms and to arrive at a sequence of events that could lead to the desired soluble products. The results of the preliminary studies led to the development of the four-step synthesis route (Scheme I). Details of the steps of this route are presented below:

Hydroxymethylation. This reaction, the first step in the synthesis of the resins, is simply an addition reaction between the amino group of melamine and the carbonyl group of formaldehyde [reaction (1)] at pH 8 or above. It results in complete dissolution of the melamine and the establishment of an

equilibrium among the melamine, formaldehyde, and various methylol melamines:^{12, 13}



where M = melamine, F = formaldehyde, S = sulfite group, MF_xS = sulfonated melamine-formaldehyde monomer, $\text{P}_1(\text{MF}_x\text{S})$ = low-pH condensation intermediate resin, $\text{P}_2(\text{MF}_x\text{S})$ = sulfonated melamine-formaldehyde condensate, T_i = temperature of corresponding step, pH_i = pH of corresponding step, t_i = reaction time of corresponding step, and $x = 2-5$.

Scheme 1.

As soon as the methylol melamines form, condensation starts. Both reactions (condensation and hydroxymethylation) are dependent on pH, temperature, and concentration of reactants, but it is possible to control them and prevent premature condensation by the proper reaction conditions, namely, high pH (above 11.0) and low temperatures (around 50°C).

Sulfonation. The second step of the synthesis is initiated by the addition of sodium metabisulfite, which hydrolyzes in water to produce bisulfite ions to the methylolmelamines solution and raises the temperature up to 80°C.

Apparently, bisulfite reacts with methylolmelamines at relatively slow rates to form sulfonated products:



This reaction occurs concurrently with the condensation of the methylolmelamines. The rates of both reactions are dependent on pH and temperature. Maintaining pH at values above 10 and temperatures up to 80°C favors completion of sulfonation before extensive condensation takes place.

Low-pH Condensation. This step results in the formation of solid condensation products when the reaction is allowed to continue over a relatively long period. The exact type of condensation taking place is not known, but reaction conditions suggest that ether-linkage type products are formed:



This type of condensation is favored in the pH range of 2-5 at low temperatures. Thus, temperature and pH are chosen to control the extent of condensation to the desired level.

High-pH Rearrangement. This step apparently involves changes of bond cleavage in the polymer backbone, leading to lower molecular weight species

as manifested by the decrease in the viscosity of the solution during the progress of the reaction. The reaction probably involves cleavage of weak bonds such as ether linkages, but rearrangement of ether linkages to methylene type bonds may also occur simultaneously at a much slower rate. In any case, irrespective of the chemical change that occurs, the reaction results in stabilizing the resin toward further condensation and gelation.

This four-step process is necessary for the production of thermally stable water-soluble sulfonated melamine-formaldehyde resins. Modifications of the procedure were found to result in either gelation, precipitation, or the formation of unstable resin solutions that gel with time.

Factors Affecting the Properties of the Resin

Effect of pH. The pH is the most important factor affecting both the progress of the reaction at all four stages and the type of polymer formed. The dependence of reaction kinetics on pH is quite complex due to the large number of parallel reactions affected by pH that take place at every stage of the preparation procedure. For example, during the first step, several hydroxymethylation reactions, which result in the formation of methylol-melamine derivatives, and a Cannizzaro reaction, involving disproportionation of formaldehyde to methanol and formic acid, occur simultaneously. The effect of pH is specially important during this step. The value should be kept within the range 11.0–11.5. At lower pH values, condensation of melamine formaldehyde adducts is very fast and the resin usually precipitates at a fast rate (Table II, resins 1, 7, 8).

The pH of the solution was also found to affect strongly the low-pH condensation step (step 3). Thus, under the conditions of the preparation procedure, it was observed that lowering the pH from 3.5 to 2.5 caused an increase in condensation rate, reflected by the lower reaction time (t_3) needed to achieve the same viscosity for the final solution (Table II, resins 1, 9, 10).

The effect of pH on the viscosity of the final resin solution in the fourth step was insignificant (Table II, resins 1, 11, 12), but studies revealed a stabilizing effect. It was observed that, under the same conditions of tempera-

TABLE II
Effect of pH on the Viscosity of Synthesized Resins
at Various Steps

| Resin ^a no. | pH ₁ | pH ₂ | pH ₃ | pH ₄ | μ^b (cP) | Remarks |
|---------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|----------------|
| 1 | 11.35 | 11.35 | 3.5 | 7.0 | 4.30 | |
| 7 | 10.00 | — | — | — | — | Solid resin |
| 8 | 12.00 | 11.35 | 3.5 | 7.0 | 4.20 | Brown solution |
| 9 | 11.35 | 11.35 | 3.0 | 7.0 | 4.19 | |
| 10 | 11.35 | 11.35 | 2.5 | 7.0 | 4.30 | |
| 11 | 11.35 | 11.35 | 3.5 | 8.0 | 4.40 | |
| 12 | 11.35 | 11.35 | 3.5 | 9.5 | 4.24 | |

^a The reaction duration for experiments 1, 9, and 10 are 110, 92, and 80 min, respectively.

^b The viscosity is measured when the resin solution is at 20°C after dilution to 20% solid content.

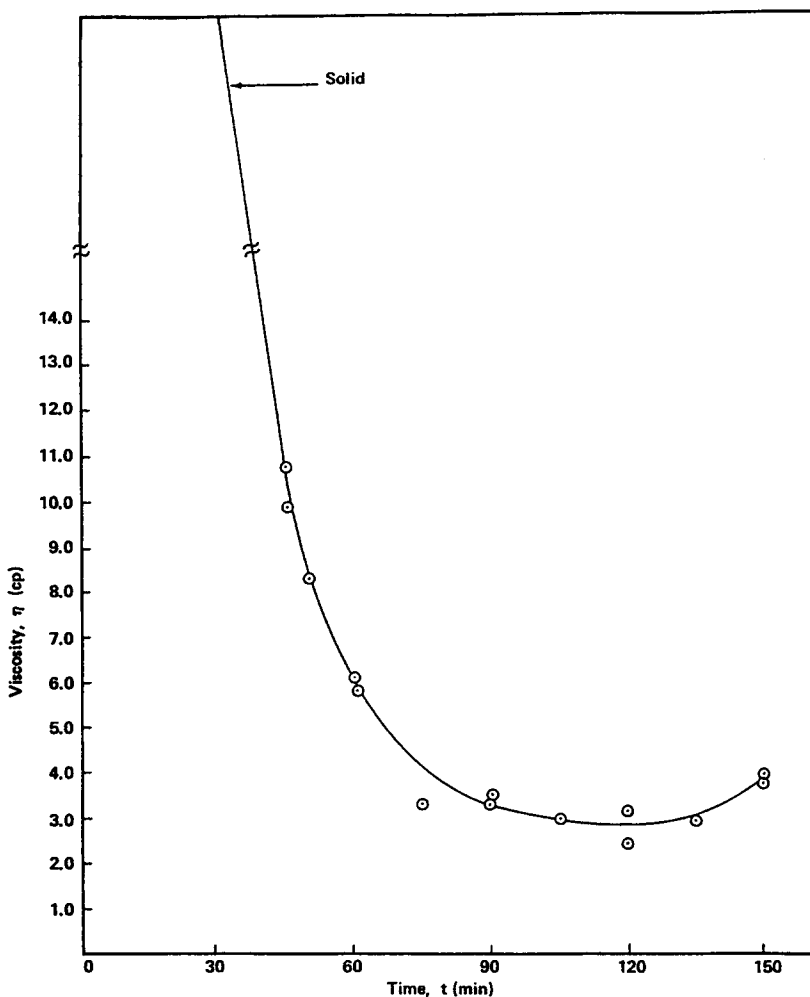


Fig. 2. Effect of solfonation time at 80°C on the viscosity of final resin solution.

ture and time, more stable resins are formed at lower pH values (7–9.5), as will be discussed in more detail in a subsequent paper in this series.

Effects of Temperature and Time. Temperature and time have similar effects on the progress of the reaction at different stages of the preparation. In the first step, increasing the temperature to values higher than 50°C or the reaction time to values longer than 15 min accelerate the condensation reaction and precipitation of the resin. At lower temperatures, reaction times longer than 15 min can be tolerated. In the second step, solfonation is probably complete within 30–60 min at 80°C. The reaction time was extended to the maximum value in our procedure to ensure that the sulfite had completely reacted. Figure 2 shows the effect of time (t_2) on the viscosity of the final solution. As t_2 is decreased, solfonation is incomplete, leading to extensive condensation and cross linking in steps 3 and 4. The reaction duration could be reduced in this step by increasing the temperature. In the low-pH condensation step, the effect of temperatures in the range 45–55°C

TABLE III
Effects of Temperature and Time in the Fourth Step
of the Reaction

| Resin no. | T_4 | t_4 | μ |
|-----------|-------|-------|-------|
| 13 | 80 | 60 | 4.33 |
| 14 | 80 | 120 | 4.08 |
| 15 | 80 | 180 | 3.87 |
| 16 | 90 | 60 | 3.92 |
| 17 | 90 | 120 | 3.62 |
| 18 | 90 | 180 | 3.54 |
| 19 | 100 | 60 | 3.41 |
| 20 | 100 | 120 | 3.33 |
| 21 | 100 | 180 | 3.31 |

^aThe viscosity is measured for the resin solution at 20°C after dilution to 20% solid content.

was studied at various stages of the project. As expected, the condensation reaction is faster at higher temperatures, but is much harder to control because of the accelerated buildup of the solution's viscosity as the reaction proceeds. Finally, in the fourth step, the rearrangement reaction that takes place was studied carefully at 80, 90, and 100°C for 1, 2, and 3 h (Table III, resins 13–21). Viscosity decreased to an equilibrium value at a faster rate at higher temperatures. Furthermore, the resin solutions, prepared at higher temperatures and longer durations, were more thermally stable in terms of viscosity changes.

The Effect of Sulfite / Melamine Molar Ratio. Since the sulfonate group plays a major role in solubilizing melamine–formaldehyde resins, and in blocking one of the active chain propagation centers, the sulfite/melamine molar ratio is expected to affect strongly the properties of the admixture and the reaction conditions during the condensation step. The molar ratio of sodium metabisulfite to melamine was varied between 0.4 and 0.6, i.e., sulfite/melamine ratios of 0.8–1.2 (Table IV, resins 1, 22–25). At values lower than 1.0, the resin tends to form during the third step at a rapid rate or to gel

TABLE IV
Effects of Sulfite/Melamine Molar Ratio (S/M), Reaction Solution Concentration,
and Formaldehyde/Melamine Molar Ratio (F/M)

| Resin no. | F/M | S/M | t_3 (min) | Reaction solid content (%) | μ^a (cP) |
|-----------|-----|-----|-------------|----------------------------|--------------|
| 21 | 4 | 0.8 | 20 | 23.8 | 9.9 |
| 23 | 4 | 0.9 | 65 | 24.3 | 5.4 |
| 1 | 4 | 1.0 | 110 | 23.5 | 4.3 |
| 24 | 4 | 1.1 | 225 | 23.5 | 3.9 |
| 25 | 4 | 1.2 | 255 | 23.6 | 3.0 |
| 26 | 4 | 1.0 | 37 | 33.0 | 4.8 |
| 27 | 4 | 1.0 | 13 | 41.0 | 3.4 |
| 28 | 3 | 1.0 | 70 | 23.0 | 3.9 |

^aThe viscosity is measured when the resin solution is at 20°C after dilution to 20% solid content.

and precipitate out of the solution. At higher ratios, limited polymerization takes place, and the viscosity of the resin solution does not exceed 2.5 cP.

Effect of Concentration. The concentration of resin in the final solution before it is diluted to 20% solid content was increased from 23–24 to 41% (Table IV, resins 1, 26, 27) by lowering the amount of water used during preparation of the resin. Concentration variation apparently affects the reaction time in the third step only. Thus, the time required for the viscosity of the solution to build up in the third step drops significantly, from 110 to 13 min when the concentration is raised from 23 to 41%.

Effect of Formaldehyde / Melamine Molar Ratio. The F/M molar ratio was varied from 2.0 to 5.0. Soluble products formed at ratios up to 4.5. At higher ratios, extensive crosslinking takes place, and the resin precipitates. A more careful comparative study was conducted at F/M = 4.0 and 3.0. In general, we observe that the F/M ratio does not affect the viscosity of the final resin solution. However, under exactly the same conditions, a longer reaction time is required during the low-pH condensation step for F/M = 4 than for F/M = 3 to attain the same viscosity (Table IV, resins 1, 28). Furthermore, the two resins have different average molecular weights and molecular weight distributions.

Molecular Weight Distribution

The molecular distributions of selected samples of prepared resins were determined using gel permeation chromatography (GPC). The elution curves are shown in Figure 3. These results should be assessed in relative terms since no calibration standards of known molecular structure and weight similar to these resins are known. Table V shows the apparent weight average molecular

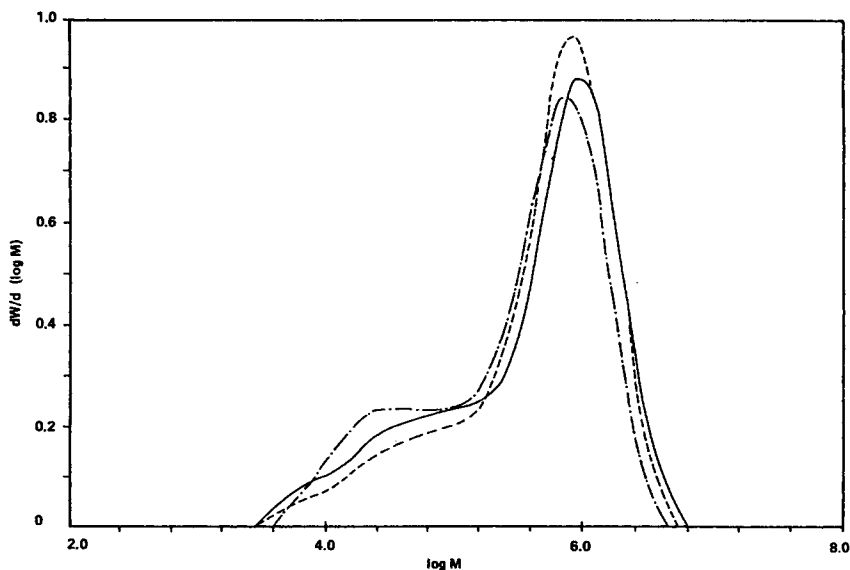


Fig. 3. Molecular weight distribution of resin 1 (—), resin 1 after aging (---), and resin 28 (-.-).

TABLE V
Apparent Molecular Weight Distribution of Selected Resin Samples

| Resin ^a no. | Viscosity at 20°C (cP) | Apparent wt avg molecular weight (\bar{M}_w) | Apparent no. avg molecular weight (\bar{M}_n) | Poly dispersity (\bar{M}_w/\bar{M}_n) |
|---------------------------|------------------------------|--|---|---|
| 1 (fresh) | 4.3 | 844,000 | 76,400 | 10.99 |
| 1 (aged) ^b | 3.4 | 815,000 | 106,000 | 7.69 |
| 28 | 3.9 | 644,000 | 74,100 | 8.69 |

^aFor detailed reaction conditions of resins see Table III.

^bSample was aged at 60°C for 2 weeks.

weight \bar{M}_w , the apparent number average molecular weight \bar{M}_n , and the polydispersity of some of these resins.

Results show that resin 1 prepared with F/M = 4.0 has a higher weight average molecular weight than resin 28 with F/M = 3.0 (Table V), but the number averages are almost equal. This was anticipated since resin 1 is formed from a predominantly tetramethylol monomer with one group blocked by sulfonation leaving three active centers for polycondensation, where as resin 28 is formed from a trimethylol monomer with only two active centers. Aging of the resin results in fragmenting some of the higher molecular weight species as well as in polymerizing some of the smaller molecules, causing polydispersity to drop from 10.99 to 7.69. The results correlated with the properties of these resins as dispersants, as will be discussed in a future paper of this series.

This research has been supported in part by a grant from the Kuwait Foundation for Advancement of Sciences (KFAS) under Grant Number 84-12-02 and the Kuwait Melamine Industries Company. This is Publication No. KISR 2091, Kuwait Institute for Scientific Research, Kuwait.

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Received September 9, 1986

Accepted November 3, 1986