Water-Soluble Sulfonated Amino-Formaldehyde Resins. III. Effect of Reaction Conditions on Stability

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Synopsis

Several preparations of water-soluble sulfonated amino-formaldehyde resins were prepared under different reaction conditions. The stability of these solutions was studied after accelerated aging at 60°C for 2 weeks. Viscosity and pH changes were monitored with storage time. The results showed that our four-step reaction procedure produces more stable products than the three-step reaction procedure. The four steps of reaction are: hydroxymethylation, sulfonation, low-pH condensation, and high-pH rearrangement. The three-step process discussed in the literature combines hydroxymethylation and sulfonation as one step followed by low-pH condensation and high-pH rearrangement. It was found that the more stable products of the four-step process are affected slightly by the F/M molar ratio and the concentration of reactants in contrast with the three-step process in which these variables affect stability drastically. In general, the pH, temperature, and time of reaction of the fourth step are the main controlling factors for product stability. An attempt was made to explain the stability behavior of these solutions in terms of their molecular weight distribution curves.

INTRODUCTION

The stability of water-soluble sulfonated amino-formaldehyde resins used in various applications is of major importance since these polymers must function at moderate temperatures for a relatively long time. The stability problem becomes more acute if the resins are to be stored in a hot, arid climate such as that of the Arabian Gulf. In general, the chemical and thermal stability of almost all water-soluble polymers is limited. This limitation in stability is determined by the free volume, which is the sole parameter determining the rate of molecular rearrangements and such transport phenomena as diffusion and viscosity, which depend on them.[1]

Stability can also be limited by temperature. The underlying concept is that material functions depend on temperature because they rely on free volume.[1,2] The stability of concentrated polymeric solutions after aging depends, to a large extent, on their internal structure in terms of entanglement coupling intensity. The adherence of the polymer molecules at specific loci forms a temporary cross link. Aging of polymeric systems and other materials can be treated mathematically as a zero-order chemical reaction following the Arrhenius equation.[3] The stability of polymeric solutions during aging can be shown by measuring the changes in their viscometric functions as a function of aging time. This is possible because any molecular transformation, whether chemical or physical, influences the viscometric functions of the polymer

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TABLE I
Reaction Conditions for Preparation of Water-Soluble Sulfonated Amino–Formaldehyde Resins

Sample no.	Urea (%)	F/M + U	Step 1, hydroxymethylation			Step 2, sulfonation			Step 3, low pH condensation			Step 4, high pH condensation			Concentration of solids in solution before dilution (%)	Viscosity of 20% solid at 20°C (cP)
			pH_1	T_1 (°C)	t_1 (min)	pH_2	T_2 (°C)	t_2 (min)	pH_3	T_3 (°C)	t_3 (min)	pH_4	T_4 (°C)	t_4 (min)		
1	0.0	4.0	11.35	50	15	11.35	80	60	3.5	50	90	7.0	80	60	24	4.56
2	0.0	4.0	11.35	50	15	11.35	80	60	3.5	50	110	7.0	90	180	24	3.54
3	0.0	4.0	11.35	50	15	11.35	80	60	3.5	50	110	8.0	90	60	24	3.86
4	0.0	4.0	11.35	50	15	11.35	80	60	3.5	50	110	9.0	90	60	24	3.80
5	0.0	4.0	11.35	50	15	11.35	80	60	3.5	50	110	7.0	90	60	24	3.50
6	0.0	4.0	11.35	50	15	11.35	80	60	3.5	50	110	7.0	100	60	24	3.41
7	0.0	4.0	11.35	50	15	11.35	80	60	3.5	50	110	9.0	80	60	24	5.01
8	0.0	4.0	11.35	50	15	11.35	80	60	3.5	50	110	9.0	100	60	24	3.41
9	0.0	4.0	11.35	50	15	11.35	80	60	3.5	50	110	9.0	80	120	24	4.56
10	0.0	4.0	11.35	50	15	11.35	80	60	3.5	50	110	9.0	80	180	24	4.48
11	0.0	3.0	11.35	50	15	11.35	80	60	3.5	50	90	7.0	80	60	24	4.09
12	0.0	3.0	11.35	50	15	11.35	80	60	3.5	50	90	8.0	80	60	24	4.56
13	0.0	3.0	11.35	50	15	11.35	80	60	3.5	50	90	9.0	80	60	24	5.01
14	0.0	3.0	11.35	55	15	11.35	80	60	3.5	55	70	7.0	80	60	24	3.87
15	0.0	3.0	11.35	75	30	—	—	—	3.5	50	90	8.0	80	60	24	3.86
16	0.0	3.0	11.35	75	30	—	—	—	3.5	50	45	7.0	80	60	32	3.75
17	0.0	3.0	11.35	50	15	11.35	80	60	3.5	50	35	7.5	80	60	31	3.94
18	0.0	4.0	11.35	50	15	11.35	80	60	3.5	50	10	7.0	80	60	40	3.43
19	0.0	4.0	11.35	75	30	—	—	—	3.5	50	105	7.0	80	60	24	5.60
20	0.0	4.0	11.35	55	15	11.35	80	60	3.5	55	85	7.0	80	60	24	4.69

solution. Therefore, the measurement of the viscosity of the polymeric solution against aging time at any accelerated aging temperature would be an acceptable parameter for determining the stability of these water-soluble polymers. The viscometric functions of these polymer solutions and their molecular structure are greatly influenced by the chemical reaction procedure and conditions.

One of the main objectives of this paper is to show the extent to which these water-soluble resins are thermally stable as a function of reaction conditions and procedure. An attempt will be made to explain the results obtained from a molecular view point. Of course, the stability of this group of polymers can be enhanced by storing them in their solid form, but this is rather costly.

EXPERIMENTAL

Materials

The raw materials used in this study are those described in the first part of this series: melamine, sodium metabisulfite, and paraformaldehyde in addition to sulfuric acid, sodium hydroxide, and calcium hydroxide. Twenty samples were prepared for this study according to the reaction conditions shown in Table I.

Procedure

Preparation of the Resins. The samples were prepared according to the four-step process discussed in Part 1 of this series. Some samples were also prepared according to the three-step process described in the patent literature.[4]

Accelerated Aging. Samples were stored in air-tight glass containers and placed in an air-circulating oven held at 60°C. Each sample was divided into seven parts. The viscosity and pH of these fractions were measured every 2 days for 14 days. Some samples were aged at room temperature for 6 months and their viscosity and pH were monitored periodically.

Viscosity and pH Measurements. Viscosity was measured at 20°C using a Haake rotational viscometer Model CV-100 with sensor system ME-30. pH was measured with a pH meter.

Molecular Weight Determination. Molecular weights and molecular weight distribution of some samples were done by gel permeation chromatography (GPC). The tests were done by Mikroanalytisches Labor Pascher, Bonn, West Germany. The analysis was done at 50°C using distilled water as eluant and silica gel (10 μm) with pore sizes 6–100 nm as separating materials.

RESULTS

The effect of eight reaction variables on the stability of sulfonated urea–melamine–formaldehyde solutions after aging was investigated. Factors tested are urea percentage in the resin, formaldehyde to melamine molar ratio (F/M), the fourth step reaction conditions [i.e., pH, temperature (T), and time (t)], concentration of the reaction mixture, the storage pH of the final

TABLE II
Effect of Formaldehyde to Melamine Ratio on the Stability of Solutions After Accelerated Aging at 60°C for 2 Weeks

Sample no.	F/M	Initial[a] viscosity at 20°C (cP)	Final viscosity at 20°C (cP)	Drop in viscosity (%)	Initial pH	Final pH	Drop in pH (%)
1	4	4.42	3.47	21.5	9.3	7.65	17.7
		3.92	3.20	18.4	10.4	7.75	25.4
11	3	3.91	3.20	18.2	9.05	8.10	10.5
		4.09	3.20	21.8	11.31	8.20	27.5

[a]Viscosities are measured for 20% solid content solutions.

product before aging, and the reaction procedure adopted (i.e., patent literature procedure vs. the procedure developed in our laboratory).

Effect of Formaldehyde to Melamine Molar Ratio. The effect of the F/M ratio on the molecular weight distribution will be discussed later, but it was found that larger ratios lead to wider distributions, with large fractions of low and high molecular weight species. On aging, this distribution gets narrower, resulting in a more stable product. Low F/M ratios result also in narrow distributions that are not altered significantly upon storage. Thus, samples 1 (F/M = 4) and 11 (F/M = 3) showed drops in viscosity of 18.4 and 21.8%, respectively, and drops in pH of 25.4 and 27.5%, respectively, when they were stored at a pH of approximately 11. However, at a lower storage pH (approximately 9), the samples showed a decrease in viscosity of 21.5 and 18.2% and in pH of 17.7 and 10.5%, respectively. Two conclusions can be drawn. First, better stability is obtained with low F/M. Second, the lower the storing pH, the better the stability (Table II).

Effect of pH, Temperature, and Time of the Fourth Step and Solution pH Before Storage. The effect of fourth step pH on stability is evident from data on samples 1, 3, 5, and 7. Samples 1 and 7 were prepared with fourth step pH 7 and 9, respectively; the drop in viscosity and pH upon storage at a pH of approximately 11 were 18.4 and 25.4% for sample 1 and 27 and 23.6% for sample 7, respectively. Samples 5 and 3 were prepared at a fourth step pH of 7 and 8, respectively. The drops in viscosity and pH upon storage were 8.3 and 29.9% for sample 5 and 10.6 and 29% for sample 3, respectively.

The temperature also seems to have a significant effect. Samples 1, 5, and 6 were prepared at fourth step temperatures of 80, 90, and 100°C, respectively. Tests were conducted on two samples with different storage pH had conclusive results. At a storage pH of approximately 11, the viscosity drop for samples 1, 5, and 6 were 18.4, 8.3, and 5.8% and the pH drops were 25.4, 29.9, and 30%, respectively. At a storage pH of 8–9, the viscosity drops were 21.5, 13.5, and 6.7%, but the pH drop was significantly lower at 17.7, 6.9, and 8.3%, respectively, for 1, 5, and 6. Again, a conclusion can be drawn on the effect of pH and temperature in the fourth step: The higher the reaction temperature and the lower the storage pH, the more stable the product.

The effect of reaction time is apparent in samples 5 and 2, which were both prepared at 90°C, for 1 and 3 h, respectively. The viscosity drops were 8.3 and

TABLE III
Effect of pH, Temperature and Time of the Fourth Step on Stability of Solutions after Accelerated Aging at 60°C for 2 Weeks

Sample no.	Fourth step reaction conditions			Initial[a] viscosity (cP)	Final viscosity (cP)	Drop in viscosity (cP)	Initial pH	Final pH	Drop in pH (%)
	pH	T (°C)	t (min)						
1	7.0	80.0	60	4.42	3.47	21.5	9.30	7.65	17.7
				3.92	3.20	18.4	10.40	7.75	25.4
5	7.0	90.0	60	3.85	3.33	13.5	8.11	7.55	6.9
				3.62	3.22	8.3	11.05	7.82	29.9
6	7.0	100.0	60	3.56	3.32	6.7	8.11	7.43	8.3
				3.39	3.20	5.8	11.05	7.75	30.0
2	7.0	90.0	180	3.41	3.24	4.4	11.27	8.00	30.8
7	9.0	80.0	60	4.80	3.50	27.0	10.60	8.10	23.6
9	9.0	80.0	120	4.34	3.50	20.0	10.87	7.90	27.3
10	9.0	80.0	180	4.42	3.55	18.0	11.30	8.10	28.3
3	8.0	90.0	60	3.58	3.20	10.6	10.88	7.80	29.0

[a]Viscosities were measured for 20% solid content solutions.

4.4%, respectively, when storage pH was approximately 11. The same was observed for samples 7, 9, and 10 prepared at 80°C for 1, 2, and 3 h; they show viscosity drops of 27, 20, and 18%, respectively. Therefore, the higher the reaction time, the more stable the product.

Conclusions on reaction conditions in the fourth step are: More stable products can be obtained if the reaction temperature and reaction time are high and the pH is low, and if the resin's final pH before storage is as low as possible. More specifically, a fourth step temperature of 90–100°C, a reaction time of 1–3 h, and a pH of 7 give a very stable product (Table III).

Effect of Total Reactant Concentration in solution. The effect of total solid concentration in the solution during preparation of the condensate strongly affects the kinetics of the reaction. The effect of concentration on final product stability was studied in several samples. Samples 11 and 17 were prepared at concentrations of 24 and 31%, respectively, and F/M = 3 : 1. The corresponding drops in viscosity after aging were 21.8 and 22%, respectively.

TABLE IV
Effect of Total Reactant Concentration on the Stability of Solutions After Accelerated Aging at 60°C for 2 Weeks

Sample no.	F/M	Reactant concentration solid in solution (%)	Initial[a] viscosity at 20°C (cP)	Final viscosity at 20°C (cP)	Drop in viscosity at 20°C (%)	Initial pH	Final pH	Drop in pH (%)
1	4	24	3.92	3.20	18.4	10.4	7.75	25.4
11	3	24	4.09	3.20	21.8	11.31	8.2	27.5
17	3	31	3.94	3.06	22.0	10.05	8.78	12.7
18	4	40	3.41	2.65	22.2	9.36	7.65	18.2

[a]Viscosities are measured for 20% solid content solutions.

TABLE V
Effect of Reaction Procedure on the Stability of Solutions After Accelerated Aging at 60°C for 2 Weeks

Sample no.	F/M	Reaction procedure	Reactant concentration solid in solution (%)	Initial[a] viscosity at 20°C (cP)	Final viscosity at 20°C (cP)	Drop in viscosity (%)	Initial pH	Final pH	Drop in pH (%)
1	4	Four-step	24	3.92	3.20	18.4	10.40	7.75	25.4
18	4	Four-step	40	3.41	2.65	22.2	9.36	7.65	18.2
11	3	Four-step	24	4.09	3.20	21.8	11.31	8.20	27.5
17	3	Four-step	31	3.94	3.06	22.0	10.05	8.78	12.7
15	3	Three-step	24	3.86	3.40	11.7	9.40	8.55	9.0
16	3	Three-step	32	3.75	2.74	27.7	9.20	8.55	7.0
19	4	Three-step	24	5.27	3.41	35.3	8.46	7.60	9.0

[a]Viscosities are measured for 20% solid content solutions.

Also, samples 1 and 18 were prepared at concentrations of 24 and 40%, respectively, and F/M = 4:1. The corresponding drops in viscosity after aging were 18.4 and 22.2%, respectively, and the drops in pH were 25.4 and 18.2%. Therefore, we can conclude that reactant concentration has no effect on stability provided that the degree of polymerization is almost equal. Concentration only affects the kinetics of the reaction and thus the cycle time. This is only true if a four-step reaction procedure such as the one adopted by the authors is used. However, we shall see later that concentration of reactants could affect the solution stability if another procedure, such as the three-step process described in the patent literature is adopted. The effect of concentration on stability using the four-step procedure is shown in Table IV.

Effect of Reaction Procedure. As pointed out earlier, the reaction procedure plays a significant role in the stability of final products (Table V). As will be explained later, this significant effect comes as a result of the molecular rearrangement of the final product being affected by the reaction procedure. Samples 1, 18, 11, and 17 were all prepared by the four-step process, and samples 15, 16, and 19 were prepared by the three-step process; all other variables were the same as shown in Table I.

The drop in viscosity after accelerated aging of samples 1, 18, 11, and 17 ranges from 18.4 to 22.2% despite the difference in F/M ratio and reactant concentrations. But if one examines the drop in viscosity of samples 15, 16, and 19 (prepared according to the three-step process), the difference is more noticeable. For example, samples 15 and 16 were prepared with an F/M ratio of three and with reactant concentrations of 24 and 32%, respectively, and their respective drops in viscosity after accelerated aging was 11.7 and 27.7%. This shows that the reactant concentration plays a more significant role in the stability of products of three-step process than in that of the products of the four-step process, which remain stable. This conclusion is significant because preparation of this class of polymers at higher concentrations reduces the costs tremendously in terms of shorter cycle time. Whether prepared at 20% solid concentration or 40% solid concentration, the resins are marketed and used as solutions with 20% solid content. That is, the preparation of a batch at 40% solid concentration will result in doubling the productivity for the same cycle time of production. Therefore, it is necessary to produce these

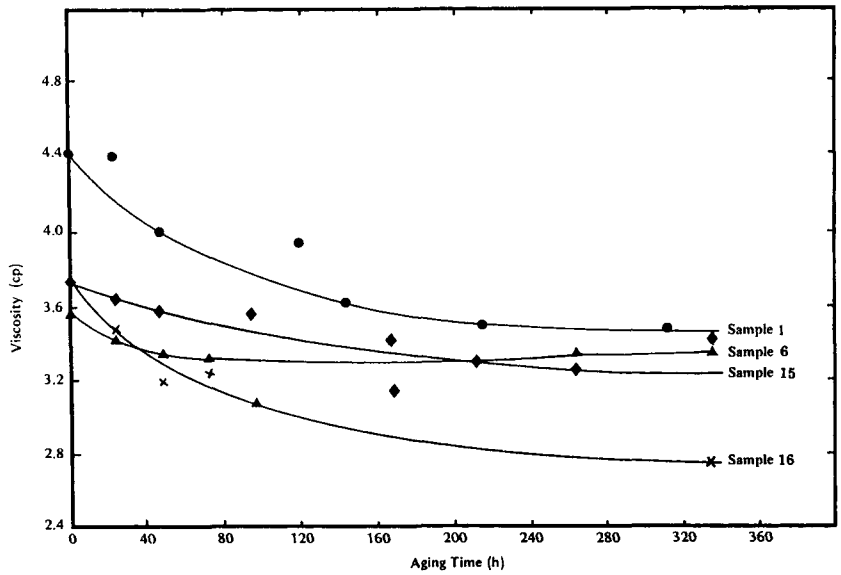

Fig. 1. Viscosity drop after accelerated aging at 60°C of several samples. (Samples 1 and 6 were prepared by the four-step process, and samples 15 and 16 were prepared by the three-step procedure.)

products at the highest concentration possible provided the major properties of these products don't change appreciably. One of these properties is, of course, stability after accelerated aging. Figure 1 is a graphic representation of the viscosity drop after accelerated aging of samples prepared according to both procedures.

Room Temperature Stability. Two samples (19 and 1) were stored at room temperature for six months at pH 11. Sample 19 was prepared by the three-step process, and sample 1 was prepared by the four-step process. The drop in viscosity and pH after 6 months were 14 and 7.2%, respectively, for sample 19 and 2.3% and 10.1% respectively, for sample 1 when the storage pH was approximately 11 (Table VI).

Judging from room temperature stability data and accelerated temperature data (Fig. 1), it appears that 1 day of aging at 60°C is almost equivalent to 6 months of storage at room temperature. Therefore, stability testing at 60°C for 2 weeks is sufficient to predict the stability of these products for their life storage time.

TABLE VI
Room Temperature Stability of Some Samples

Sample no.	Preparation procedure	Initial[a] viscosity at 20°C (cP)	Final viscosity at 20°C (cP)	Drop in viscosity (%)	Initial pH	Final pH	Drop in pH (%)
1	Four-step	4.70	4.59	2.3	11.12	10.00	10.1
19	Three-step	5.27	4.53	14.0	11.20	10.39	7.2

[a]Viscosities are measured for 20% solid content solution.

TABLE VII
Apparent Average Molecular Weight ($\overline{M}_w$), Apparent Number Average Molecular Weight ($\overline{M}_n$), and Polydispersity of Some Samples

Sample no.	Apparent weight average molecular weight ($\overline{M}_w$)	Apparent number average molecular weight ($\overline{M}_n$)	Polydispersity ($\overline{M}_w/\overline{M}_n$)	Basic features in reaction conditions
1	1,040,000	101,000	10.3	Standard four-step process
5	1,040,000	86,100	12.1	Like sample 1 except $T_4 = 90°C$
6	1,050,000	105,000	10.0	Like sample 1 except $T_4 = 100°C$
11	965,000	83,900	11.5	Like sample 1 except F/M = 3
15	1,010,000	64,900	15.6	Prepared according to literature three-step procedure
18	1,130,000	100,000	11.3	Like sample 1 except high concentration (40%) of resin

Effect of Reaction Conditions on Molecular Weight Distribution. Uncalibrated molecular weight distributions of some preparations of water-soluble sulfonated melamine–formaldehyde resins were determined. The weight average molecular weight ($\overline{M}_w$) and the number average molecular weight ($\overline{M}_n$) are almost the same for samples 1, 5, 6, and 18 for the four samples prepared according to the four-step process developed by the authors and with an F/M ratio of 4 : 1 (Table VII). Samples 11 and 15 were prepared by the four-step process and three-step process, respectively; both have a formaldehyde to melamine ratio of 3 : 1. As was pointed out in the first part of this series, the F/M ratio influences the number average molecular weight but not the weight average molecular weight (Table VII). Table VII also shows the high polydispersity of sample 15, which was prepared by the three-step process. It should be noted that these molecular weights should be evaluated in relative terms and not as absolute numbers since no standards are available for calibration.

DISCUSSION

As we pointed our earlier, the effect of reaction conditions influence the stability of water-soluble amino-formaldehyde resin solutions after aging through their influence on the molecular rearrangement of these polymeric

solution systems. We chose viscosity as the function that reflects the molecular rearrangement after accelerated aging. This choice is valid since the frictional characteristics of polymer molecules in dilute solutions, as manifested in solution viscosity, and diffusion rates depend directly on the size of the molecular domain. Thus, these properties are closely related to the molecular configuration including the linear dimensions of the molecule.[5] Therefore, the basic property that changes during aging is segmental mobility, which is reflected in solution viscosity. At any temperature, segmental mobility depends primarily on the free volume remaining. Segmental mobility, free volume, and hence frictional characteristics of polymer molecules, or simply solution viscosity, are all governed by the molecular configuration of these systems.

Apart from being influenced by intermolecular interaction between segments belonging to different polymer molecules or intramolecular interaction between segments of the same molecule that might be entangled through entanglement couplings or might be crosslinked, the viscometric function expressed by the solution viscosity reflects a great deal about the molecular weight distribution of these systems. The molecular weight distribution curve provides data on the weight average molecular weight and number average molecular weight. According to Flory,[5] weight average molecular weights are sensitive to the presence of larger species whereas the number average molecular weight is sensitive to the proportion by weight of smaller molecules. Consequently, the number average molecular weight is rather insensitive to small proportions by weight of constituents larger than the average molecular size.

In view of this discussion, we shall examine some of the molecular weight distribution curves obtained on these polymeric solutions relative to each

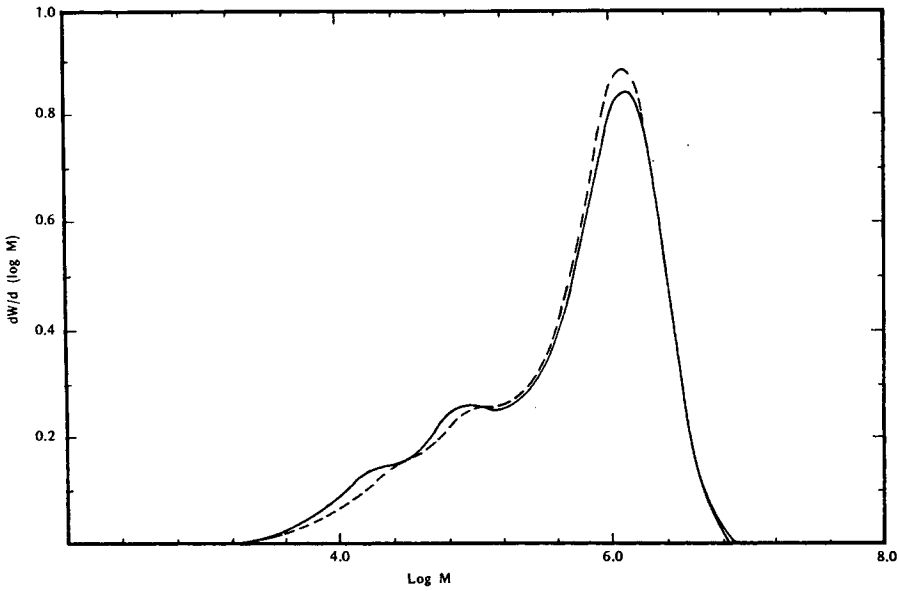

Fig. 2. Effect of formaldehyde to melamine ratio on molecular weight distribution: sample 11 (—) with F/M = 3 and sample 1 (---) with F/M = 4.

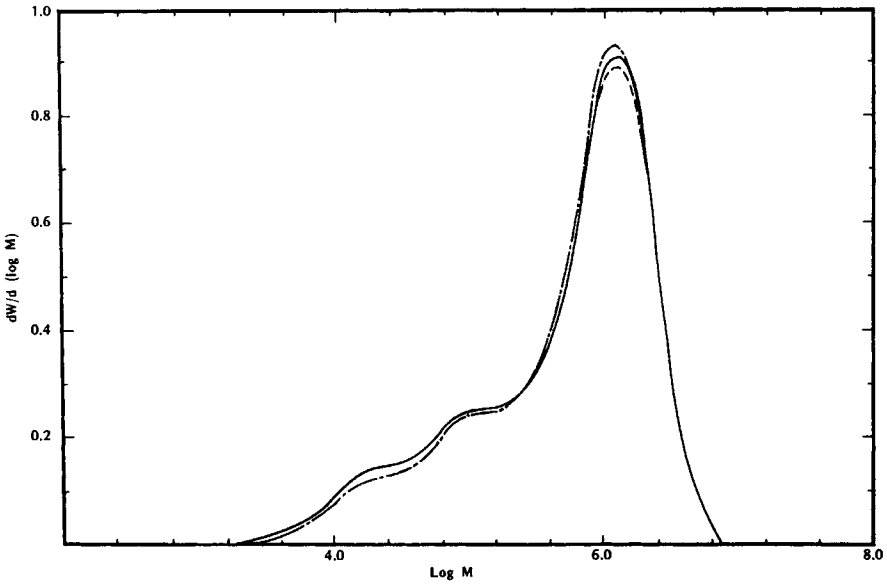

Fig. 3. Effect of fourth step temperature on molecular weight distribution: sample 1 (---), sample 5 (—), and sample 6 (· · ·).

other and try to explain the stability characteristics of these solutions. It is worth mentioning that the various molecular weight distribution curves are only relative, and an absolute value of $\overline{M}_w$ and $\overline{M}_n$ could not be obtained due to the lack of a standard sample for this type of polymeric solutions.

The stability studies show that four main factors in the reaction conditions influence stability: formaldehyde to melamine ratio (F/M), the fourth step reaction conditions (i.e., pH, temperature and time), reactant concentration in the solution, and reaction procedure (i.e., four-step process vs. three-step process). We shall now examine the effect of these factors on the molecular weight distribution of these solutions.

Figure 2 shows the effect of the formaldehyde to melamine ratio for two samples, prepared according to the four-step process; one has F/M = 4 (sample 1) and the other F/M = 3 (sample 11). The difference in the portion of low molecular weight species is slightly less in sample 11 than it is in sample 1, that is, the number average molecular weight of sample 1 is slightly higher. This slight difference in $\overline{M}_w$ and $\overline{M}_n$ is not expected to influence stability (Table II).

Figure 3 shows the effect of the fourth step temperature on the molecular weight distribution of three samples prepared according to the four-step process with T_4 ranging from 80 to 100°C. Again, the molecular weight distribution for these samples are almost the same, which indicates that complete polymerization has taken place resulting in almost the same $\overline{M}_w$ and $\overline{M}_n$. As was pointed out earlier in Table III, however, the drop in viscosity after aging was significantly different among the three samples. The only explanation we can provide is that additional energy input in the fourth step (i.e., by increasing the temperature) reduces the degree of entanglement coupling and the intermolecular interaction between segments of different

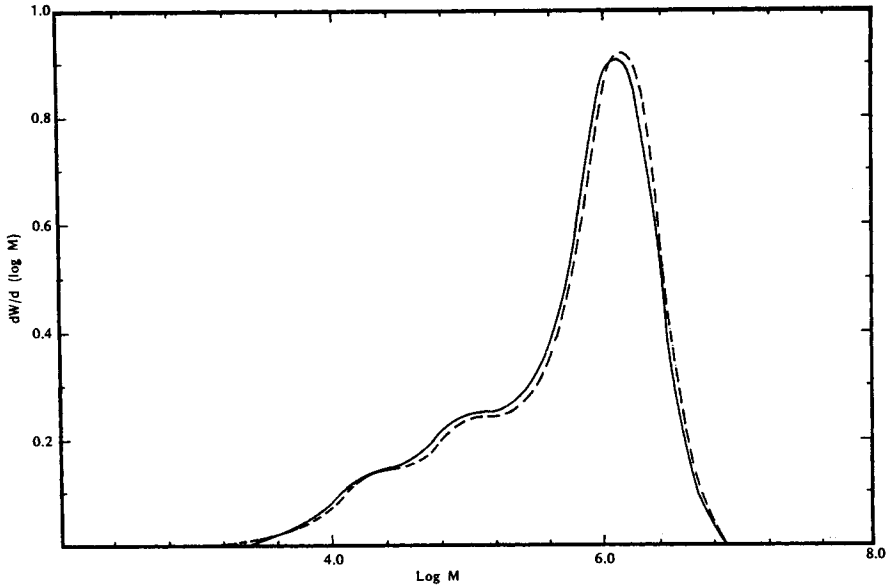

Fig. 4. Effect of reactant concentration on molecular weight distribution: sample 1 (---) and sample 18 (—).

molecules without influencing the $\overline{M}_w$ and $\overline{M}_n$, resulting in a more relaxed and stable molecular configuration.

Figure 4 shows the effect of reactant concentration on the molecular weight distribution of two samples prepared according to the four-step process but with different concentrations. Sample 1 has a concentration of 24% and

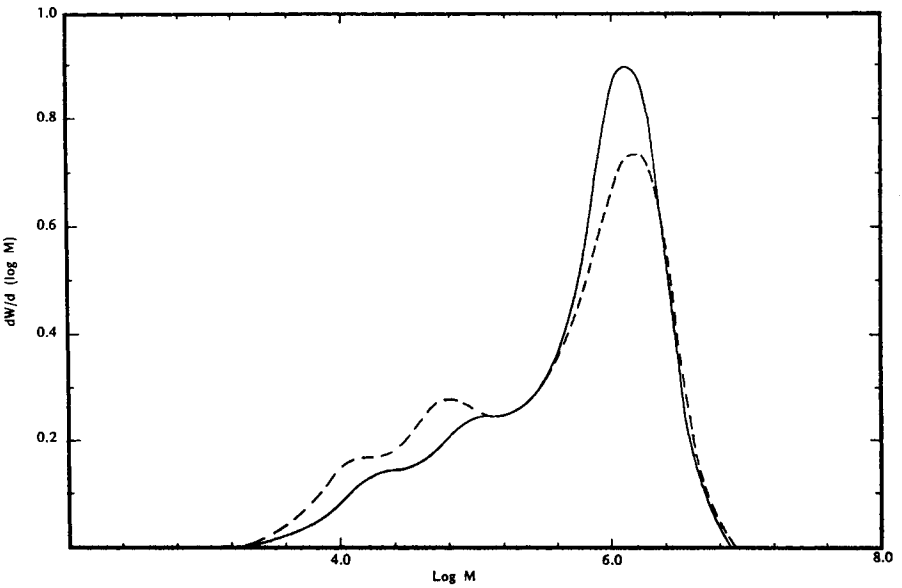

Fig. 5. The effect of reaction procedure on molecular weight distribution: sample 1 (—) four step process; sample 15 (---) three step process.

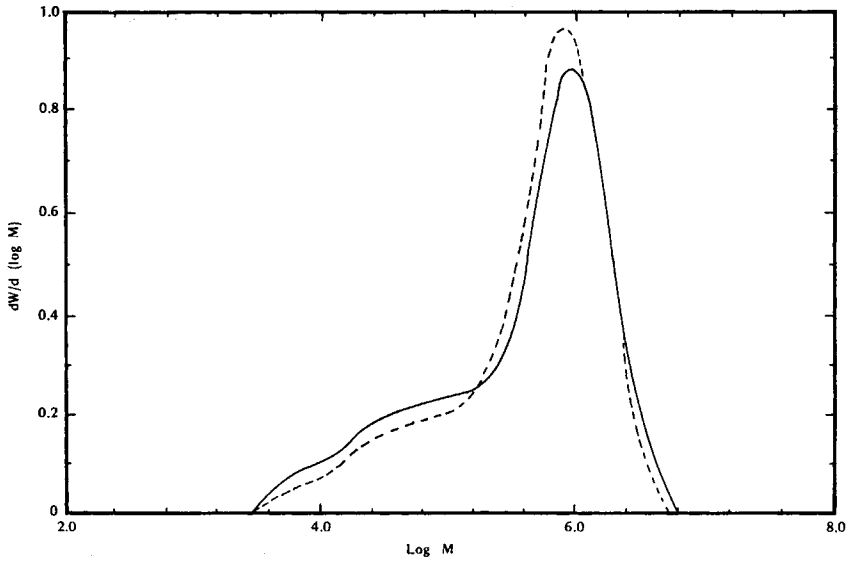

Fig. 6. Molecular weight distribution of sample 3: before aging (—); after aging (---).

sample 18 has a concentration of 40%. Obviously, the molecular weight and the stability are almost the same (Table IV). When polymers are prepared by the three-step process, however, their stability is greatly affected by reactant concentration. This may be one of the advantages of the four-step process.

Figure 5 shows the effect of reaction procedure on the molecular weight distribution of two samples. Sample 11 was prepared by the four step process and sample 15 by the three-step process. Sample 11 has a much lower proportion by weight of low molecular weight species than sample 15 ($\overline{M}_n$, 83,900 and 64,900, respectively). In addition, sample 15 has a higher polydispersity (15.6) than sample 11 (11.5). Since sample 15 has a higher proportion by weight of low molecular weight segment, further aging will tend to polymerize these fractions into a high molecular weight fraction, resulting in a more stable product. This is in agreement with the results (Table V). Finally, Figure 6 shows the effect of aging on the molecular weight distribution of sample 3. The sample was aged at 60°C for 2 weeks. After aging, the proportion by weight of the low molecular weight species is reduced as a result of further polymerization. The same can be accomplished if the temperature of the fourth step was increased (Fig. 3).

CONCLUSIONS

It can be concluded from this study that reaction conditions influence the stability of water-soluble polymers. The stability of sulfonated melamine–formaldehyde resins can be improved if they are prepared in the four distinct steps hydroxymethylation, sulfonation, low pH condensation, and a high pH rearrangement. The reaction conditions of the fourth step are the major controlling factor for the stability of these polymers. Stability is improved if the pH in the fourth step is low (~ 7) the temperature of reaction is high (80–100°C), and the reaction time is high (~ 1–3 h). Stability improves

slightly with a lower F/M ratio. Concentration of reactants influence stability slightly if a four-step procedure is followed, but if a three-step procedure is followed, the concentration influences stability drastically with higher concentrations leading to a less stable product. It is believed that, in the four-step procedure, more entanglement couplings and crosslinks are formed than in the three-step process. This gives rise to the interaction between segments that influence the solution viscosity.

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