Investigations of the Chemical Structure of Sulfonated Amine–Formaldehyde Resins. 3. Intermediate Chemical Structures

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ABSTRACT: ^{13}C NMR was used to characterize the chemical structure of species produced after each of the three reaction steps used in preparing sulfonated amino–formaldehyde resins. It was found that, after the urea–formaldehyde addition step, monomethylol- and dimethylolurea were predominantly formed. During the sulfonation step, all of the sodium metabisulfite added reacted with the methylol groups. Finally, the condensation step resulted in the formation of oligomers. Methylene bridges and not dimethylene ether linkages were almost exclusively found in the structure of the sulfonated urea–formaldehyde resins. The effects of reactant ratio on the chemical structure of these resins were also studied and analyzed.

Introduction

In the first part of this series,[1] it was shown that ^{13}C nuclear magnetic resonance can be used for determining the chemical structure of sulfonated urea–formaldehyde resins. On the basis of a number of model compounds and model reactions, the authors were able to identify the signals of the main structural units. When a semiquantitative approach was used, the relative concentrations of different structural units were calculated and a preliminary analysis on the effect of the monomer composition on the structure of the final resin was given. It was pointed out that, for a more detailed insight into the urea–formaldehyde–sulfite reaction, the investigation of the individual steps of the resin preparation was necessary.

According to the literature,[2,3] sulfonated urea–formaldehyde (SUF) resins are prepared in a multistep procedure. The first step is a reaction between urea and formaldehyde in the presence of a basic catalyst to form a mixture of different methylolureas. In the second step sodium metabisulfite is added and the reaction between the methylol groups and bisulfite ions is carried out under basic or acidic conditions. This step is followed by a low-pH condensation step, which includes the formation of higher molecular weight oligomers and, depending on the reaction conditions, of cross-linked products. Following the literature on preparation of the sulfonated malamine–formaldehyde resins,[2] the first and the second steps (addition and sulfonation) may be combined in a single step. Another variation of the preparation procedure is the reversal of the order of the second and third steps. Occasionally a fourth step, consisting of a high-pH "rearrangement", is added to the procedure[2,3] to stabilize the resin against further condensation and gelation.

Unfortunately, most of the previous investigations on the synthesis of the SUF resins followed an empirical and not a fundamental approach. No information is available on the chemical changes in the reaction product after each of the reaction's three or four steps as a function of the monomer ratios and the reaction conditions. Therefore, it is the objective of the present paper to contribute to a better understanding of the chemical changes, occurring in the SUF reaction, by using one of the most powerful tools in polymer characterization: ^{13}C NMR. This paper will discuss the changes in chemical structures of SUF resins prepared according to a protocol made of three steps: addition, sulfonation, and condensation. The next paper will compare the chemical species found by this protocol and another one where the order of the sulfonation and condensation steps is reversed. It will also discuss differences in chemical structure when the addition and sulfonation steps are combined in a single step.

Experimental Section

NMR Measurement. ^{13}C NMR spectra were obtained on a Bruker AM-300 NMR spectrometer, operating at 75.369 MHz for ^{13}C NMR, equipped with an ASPECT-3000 computer system. For the standard experiments the broad-band noise decoupling technique was used and the experimental conditions were as follows: sweep width, 200 ppm; spectrum size, 64K words; pulse width, 6 μs; relaxation delay, 15 s; number of pulses, 3000–10 000; sample temperature, 25 °C. The samples were taken directly from the reaction mixture with 1 drop of D_2O added for internal lock. All samples were measured in 10-mm tubes.

In order to confirm the validity of the quantification procedure, a number of samples were measured by using the inverse-gated decoupling technique. The experimental conditions were as follows: spectrum size, 64K words; sweep width, 200 ppm; pulse width, 6 μs corresponding to an 80° pulse; relaxation delay, 120 s, number of pulses, 1000–10 000, sample temperature, 25 °C. As the solvent, water was used, with 1 drop of D_2O added for deuterium internal lock.

Synthesis of the Samples. The resin samples were prepared according to the method described in part 1 of this series.[1] Briefly, a sulfonated urea–formaldehyde resin with a formaldehyde to urea ratio (F/U) of 3.0 and a sulfite to urea ratio (S/U) of 1.0 is prepared by the following method: 262 g of a 24% formalin solution were heated to 80 °C, and the pH was adjusted to 10.0; 40 g of urea and 198 g of water were added. After 20 min, 313 g of sodium metabisulfite as a 20% solution was added. After 60 min, the pH was lowered to 3.0 and the reaction mixture was left at 80 °C for 60 min. Then the solution's pH was adjusted to 9.0. The solution was cooled and filtered, and the solid content was determined. Other SUF resins with different F/U and S/U ratios were prepared similarly. After the end of each step 5 mL of solution was taken, cooled to room temperature, and then subjected to NMR measurements.

Results and Discussion

The chemical structure of the sulfonated urea–formaldehyde resin is influenced by the reactant ratios (F/U and S/U) and the reaction conditions (T, t, and pH of

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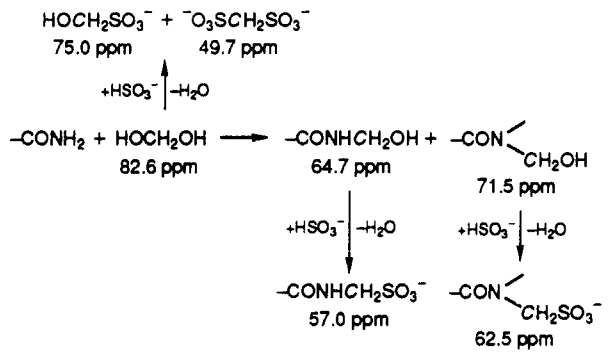
Table I
Reactant Ratios of Various SUF Resins

expt	F/U	S/U	expt	F/U	S/U
1	3.0	0.0	4	2.0	0.0
2	3.0	0.5	5	2.0	0.5
3	3.0	1.0	6	2.0	1.0

each of the three steps). Preliminary investigations indicated that the reactant ratios had a more pronounced effect on the SUF chemical structure than the reaction conditions. Consequently, this paper will be limited to showing the effects of changing the F/U and S/U ratios on the chemistry of the SUF reaction. Table I shows the SUF resins studied in this work. In all cases, after the final step clear solutions were obtained as the reaction product except for experiment 4 in which the resin precipitated after the sulfonation step.

The signals appearing in the ^{13}C NMR spectra of sulfonated urea–formaldehyde resins can be divided into two groups, i.e., signals belonging to structural units of ordinary urea–formaldehyde resins and signals appearing as a result of the sulfonation reaction. As for the first group, the signal assignments were based on literature data[4-6] and confirmed by conducting measurements on model compounds [methylolureas and methyleneureas] and resins.[1] Regarding the structural units attached to sulfonate groups, model reactions were carried out and incremental methods were used.[1] By reacting formaldehyde and methylolureas with the sulfite and characterizing the reaction products by ^{13}C NMR, we were able to assign all signals appearing in the spectra and to establish the following reaction scheme:



After the chemical shift regions for the model compounds and resins were established, a comparison with the chemical shifts obtained for the SUF resins under study was carried out. It was found that, for the actual SUF resins, the same chemical shifts (to within ±0.02 ppm) were obtained, and therefore it was assumed that the peak assignments made for model compounds and resins are valid for the actual resins as well.

It is known that the quantification of ^{13}C NMR spectra in most cases is complicated due to the nuclear Overhauser effect (NOE) and spin relaxation phenomena. To overcome these effects, inverse-gated decoupling and the addition of relaxation reagents are used. However, in our case inverse-gated decoupling would be very time consuming, because long pulse delays have to be used in order to compensate the long relaxation times (T_1) and to suppress the NOE of the carbonyl groups. According to Slonim et al.,[5] the T_1 values for all types of methylene groups (-CH_2OH, -CH_2OCH_2-, -OCH_2O-, -CH_2-) are of the same magnitude, and therefore it was assumed that these groups can be quantified when a sufficient pulse delay is applied. On the other hand, if the T_1 values for the different carbonyl groups are comparable, these groups could be quantified separately. In order to prove the validity of this approach, a number of samples were measured with inverse-gated decoupling and a pulse delay of 120 s and compared with results obtained with broad-band noise decoupling and a pulse delay of 15 s. The quantification is demonstrated for one sample in Table II and it was found that the differences in the relative numbers of structural units are within the error of the experiment. That means that the ratios of the intensities of the carbonyl and methylene groups determined separately for each group are equal for both techniques. Accordingly, it is justifiable to use broad-band noise decoupling for obtaining relative concentrations of structural units.

Table II
Concentration of Functional Groups in a SUF Resin (F/U = 3.0; S/U = 1.0) Obtained by Using Different ^{13}C NMR Techniques

assignt	inverse-gated decoupling	broad-band decoupling
-NHCONH-	0.12	0.10
-NHCON< and -NHCONHCH2SO3-	0.45	0.42
-NHCON(CH2SO3-)<	0.30	0.34
-CO- cyclic	0.13	0.14
-OCH_2OH	0.10	0.09
$HOCH_2OH$	0.38	0.37
-CH_2OCH_2- cyclic	0.22	0.25
>NCH_2O-	0.10	0.06
>NCH_2OH	0.33	0.35
-$NHCH_2O$	0.02	0.03
>NCH_2OH cyclic	0.21	0.24
-$NHCH_2OH$	0.33	0.38
>$NCH_2SO_3^-$	0.14	0.10
>$NCH_2SO_3^-$ cyclic	0.10	0.07
-NH-$CH_2SO_3^-$	0.93	0.90
>NCH_2NH-	0.04	0.05
-$NHCH_2NH$-	0.10	0.11

For the calculation of the relative numbers of different structural units, the ^{13}C NMR spectrum was divided into two separate regions: the carbonyl group region (155–165 ppm) and the methylene group region (47–92 ppm). The summed area of all signals in the carbonyl region was normalized to 1.0, and the summed area of all signals in the methylene region was normalized to 2.0 (F/U = 2) or 3.0 (F/U = 3), respectively. The relative amount of each single structural unit (X_n) was then calculated from the summed area of all signals (A_o) and the area of the appropriate signal (A_n) as follows:

carbonyl region $X_n = 1.0 \times (A_n/A_o)$

methylene region $X_n = (2.0)(3.0) \times (A_n/A_o)$

Urea–Formaldehyde Addition Step. As mentioned earlier, the addition reaction between urea and formaldehyde results in a mixture of different methylolureas. It is expected that after the addition step similar reaction products are obtained for experiments 1 and 2 and experiments 5 and 6. Table III shows the results of the ^{13}C NMR determination of the functional groups present in the reaction mixture after the first step. The assignment of the functional groups and calculation of concentrations were discussed in detail in the first part of this series.[1] Table III shows that within the experimental errors (random errors in resin preparation and errors due to NMR computations) there is a good agreement in the results obtained for the same F/U ratio. The average error was 11% for the F/U ratio of 3.0 and 9% for the F/U ratio of 2.0.

Table III
Concentration of Functional Groups in the Reaction Mixture after the Addition Step

		F/U = 3.0			F/U = 2.0		
δ, ppm	assignt	S/U = 0	S/U = 0.5	av	S/U = 0.5	S/U = 1.0	av
162.0	NH_2CONH–	0.17	0.12	0.14	0.31	0.36	0.33
160.2	–NHCONH–	0.40	0.47	0.43	0.48	0.49	0.48
159.8	–NHCON<	0.14	0.11	0.12	0.09	0.09	0.09
156.3–155.4	–CO– cyclic	0.30	0.30	0.30	0.12	0.06	0.09
86.7	$-OCH_2OH$	0.04		0.02			
82.5	$HOCH_2OH$	0.30	0.38	0.34	0.12	0.10	0.11
78.5–78.0	$-CH_2OCH_2-$ cyclic	0.74	0.57	0.65	0.31	0.27	0.29
75.0	$>NCH_2O-$	0.09	0.07	0.08	0.06	0.08	0.07
71.2	$>NCH_2OH$	0.26	0.26	0.26	0.13	0.13	0.13
69.0	$-NHCH_2O-$	0.14	0.20	0.17	0.11	0.17	0.14
68.3–68.0	$>NCH_2OH$ cyclic	0.62	0.52	0.57	0.21	0.21	0.21
64.7	$-HNCH_2OH$	0.80	1.00	0.90	1.07	1.04	1.05

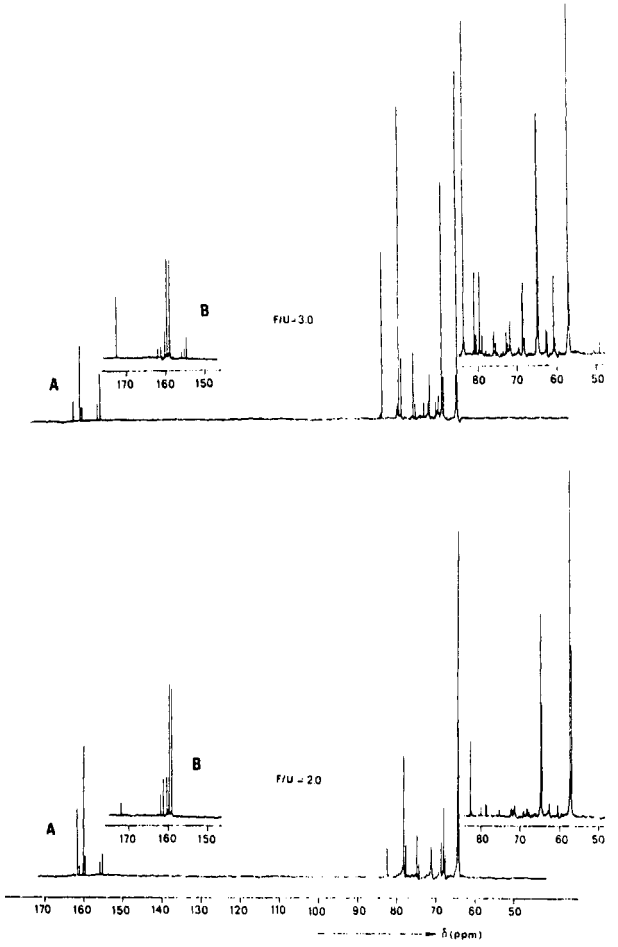
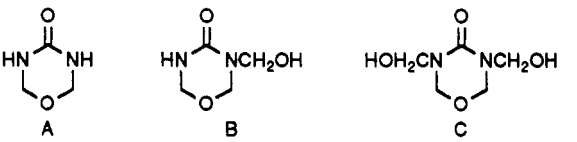


Figure 1. ^{13}C NMR spectra of SUF resins after the addition (A) and after the sulfonation (B) step; reaction order A–S–C; S/U = 1.

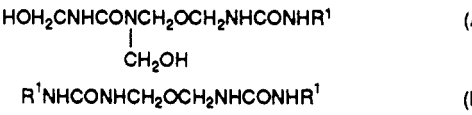
As expected, in the addition step mainly methylolureas are formed. In the ^{13}C NMR spectra signals of high intensity were obtained at 71.2 and 64.7 ppm (Figure 1), belonging to methylol groups bonded to tertiary and secondary nitrogen atoms, respectively. In addition, functional groups characteristic for dimethylene ethers and urons are present. Signals for methylene bridges, indicating condensation reactions, and oxymethylene units ($-CH_2O-$, $-OCH_2OH$), indicating formation of hemiformals $-N(H)(CH_2O)_nCH_2OH$, were not present in the spectra in all cases (see Figure 1). Free formaldehyde, existing as methylene glycol (82.5 ppm), was found in the reaction mixture in an amount that varied with the F/U ratio.

It can be seen from Table III, that dimethylene ether structures (signals at 75.0 and 69.0 ppm in Figure 1) are present in the reaction mixture in minor amounts. Surprisingly, there is no increase in the concentration of these bridges, when the F/U ratio increases from 2 to 3. This is in agreement with the finding that the concentration of methylol groups ($>NCH_2OH$ + $-NHCH_2OH$) does not increase significantly when the F/U ratio is increased.

In agreement with previous results,[1] it was found that significant amounts of cyclic structure "urons" are formed during the urea–formaldehyde reaction. They can be present as uron itself (A) and mono- (B) and dimethyloluron (C), but the relative concentration of the different



functional groups ($-CO-$, $-CH_2OCH_2-$, $-CH_2OH$) indicates that mainly C is present in the reaction mixture. From the data for cyclic structures, the concentrations of CO (155.4–156.3 ppm), CH_2OCH_2 (78.0–78.5 ppm), and CH_2OH (68.0–68.3 ppm) were 0.30, 0.65, and 0.57, respectively. Therefore, the relative concentration is 1 to 2 to 2, which is that of structure C. As for the dimethylene ethers it can be assumed that their formation is controlled by the reaction temperature rather than the F/U ratio or the concentration of methylol groups. Therefore, it is unlikely that highly branched molecules ($>NCH_2OCH_2N<$) are formed. Assuming that only dimeric units are formed, the dimethylene ethers should have the following chemical structure:



Since the average concentration of $>NCH_2O-$ groups is 0.07 and 0.08 for F/U = 2 and 3, respectively (Table III), then an amount of A-type ethers of 0.07–0.08 per urea unit can be expected. Accordingly B-type ethers should be present in a concentration of 0.03–0.04 per urea unit. These numbers were arrived at by considering the average concentration of the $-NHCH_2O-$ groups (0.14 and 0.17 for F/U = 2 and 3, respectively) and subtracting from them the average concentrations of the NCH_2O- groups, thus leaving the contribution solely due to the B-type ethers. Tetramethylolurea is not present in the reaction mixture, as can be concluded from the absence of signals characteristically for >NCON< units. Therefore, the concentration of trimethylolurea can be calculated as

follows:

	F/U = 2	F/U = 3
>NCH_2OH	0.13	0.26
bonded in (A)	−0.07	−0.08
	0.06	0.018

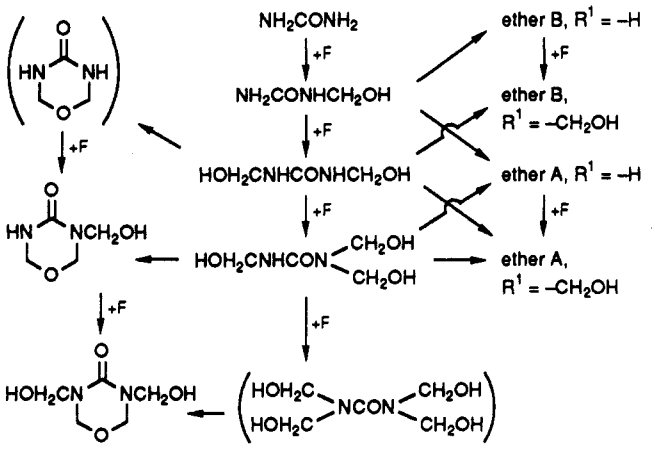
Accordingly trimethylolurea is present in a concentration of 0.03 (F/U = 2) and 0.09 (F/U = 3) in the reaction mixture after the addition step. (Recall, there are two >NCH_2OH groups per trimethylolurea unit.) The amounts of mono- and dimethylolurea can now be calculated from the appropriate concentrations of NH_2CONH–, –NHCONH–, and –$NHCH_2OH$ for the two possible cases.

		F/U = 2	F/U = 3
R^1 = –H	UF[a]	0.19	
	UF_2[b]	0.39	0.41
R^1 = –CH_2OH	UF	0.33	0.14
	UF_2	0.25–0.34	0.26

[a] UF = monomethylolurea. [b] UF_2 = *N,N'*-dimethylolurea.

To illustrate how these numbers were obtained, consider the average concentrations of the NH_2CONH– group (i.e., the case where R^1 = H). For F/U = 2 and 3 the concentrations are 0.33 and 0.14, respectively (Table III). One has to subtract from these values the concentration of this group appearing in the A-type ether (0.07 and 0.08 for F/U = 2 and 3, respectively) and the concentration of this group appearing in the B-type ether (0.07 and 0.08 for F/U = 2 and 3, respectively). Thus, for F/U = 2, the concentration of the NH_2CONH– (or monomethylolurea) becomes 0.33 − 0.08 − 0.07 = 0.19, and for F/U = 3 the concentration is 0.14 − 0.08 − 0.08 = 0. As for the case where R^1 = CH_2OH, no NH_2 groups are possible in either the A- or B-type ethers, and, consequently, the concentration of monomethylolurea will be 0.33 and 0.14 for F/U = 2 and 3, respectively. The remaining numbers in the above listing can be obtained by similar arguments.

It can be concluded that in the urea–formaldehyde reaction under the conditions of the present experiment urea is bonded mainly in the form of mono- and dimethylolureas and mono- and dimethylolurons. Since it was expected that significant amounts of higher methylolated ureas (tri- and tetramethylolurea) are formed during the reaction, it is postulated that these products favorably form urons. The following reaction scheme can be proposed:



Sulfonation Step. After the formation of the oligomer mixture, the sulfonation reaction is carried out under basic conditions by adding sodium metabisulfite. For the purpose of our investigations, sulfite to urea ratios (S/U) of 0.5 and 1.0 were used. A similar reaction was carried out for comparison without adding sulfite. The relative concentrations of functional groups, derived from ^{13}C NMR, are summarized in Table IV.

To ensure that the sulfonation reaction is not interfered with by other reactions (for example condensation), a sulfonation step was carried out without adding sulfite (experiment 1). With comparison of the data for this experiment after the addition step (see Table III) with that after the sulfonation step (see Table IV), it could be seen that no significant changes occurred in the reaction mixture. Accordingly, the sulfonation step consists exclusively of reactions involving or due to the sulfite.

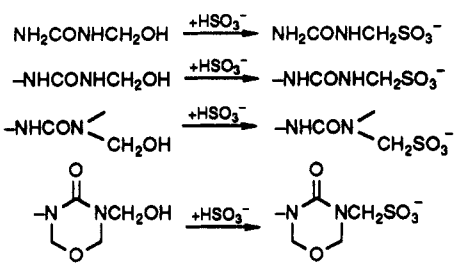
Comparison of the ^{13}C NMR spectra of a sulfonation product (experiment 3) with that of the mixture without sulfite (experiment 1), it is obvious that a number of reactions occurred due to the presence of sulfite (see Figure 2). First, the concentration of dimethylene ethers and urons decreased remarkably, and in the case of experiment 6, the concentration dropped to zero. Second, the concentration of methylene glycol increased most probably due to the establishment of a new equilibrium between formaldehyde and the different methylolureas. Third, new signals appeared in the ^{13}C NMR spectra as a result of the reaction of bisulfite ions with methylol groups, leading to a significant decrease of the amount of methylol groups. As can be seen from Figure 2, in the carbonyl region signals at 161.3, 159.5, and 159.0 ppm are obtained, indicating that three different types of sulfonate group–neighbored carbonyl groups are formed. A difference in the chemical shift between the old and the newly formed signals of about 0.7 ppm in all cases leads to the conclusion that the signals belong to the following units:

161.3 ppm: $NH_2CONHCH_2SO_3^-$
(NH_2CONH–, 162.0 ppm, Δ = 0.7 ppm)

159.5 ppm: –$NHCONHCH_2SO_3^-$
(–NHCONH–, 160.2 ppm, Δ = 0.7 ppm)

159.0 ppm: –NHCON(<)$CH_2SO_3^-$
(–NHCON(<), 159.8 ppm, Δ = 0.8 ppm)

The following reactions are likely to occur:



In addition to these reactions, the decrease of the ether concentration indicates that an ether cleavage takes place in the presence of bisulfite ions, and it can be assumed

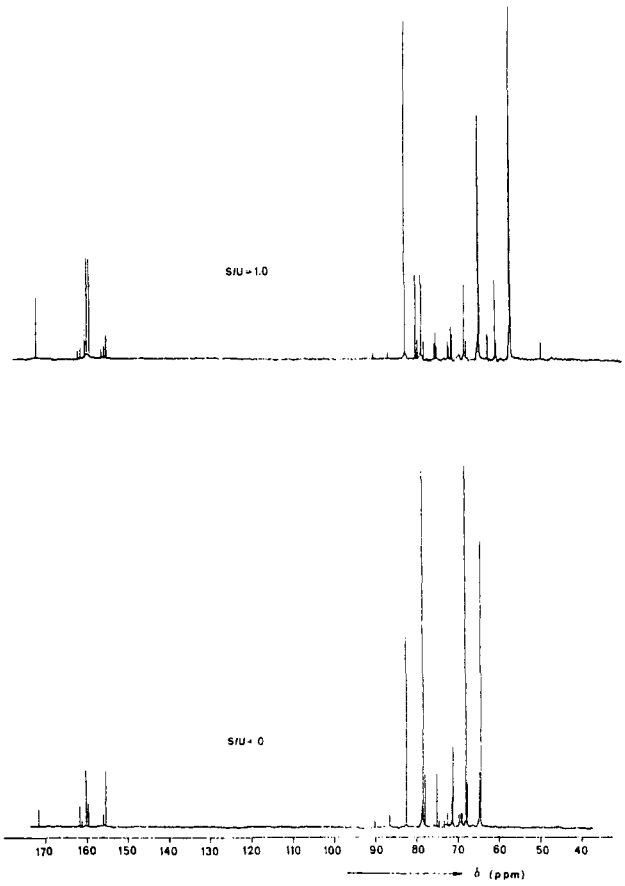
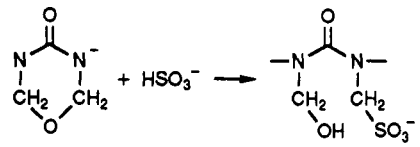


Figure 2. ^{13}C NMR spectra of SUF resins after the sulfonation step; F/U = 3.

that additional sulfonate groups are formed.

$$-NHCH_2OCH_2NH- + HSO_3^- \rightarrow -NHCH_2SO_3^- + HOCH_2NH-$$

This would be in agreement with the sharp decrease of the uron concentration, where a similar reaction could take place.



With comparison of the relative concentration of the functional groups after the sulfonation step, it was found that the amount of sulfonate groups is very close to the initial concentration of the sulfite in the reaction mixture, supporting the findings in the first part of this series[1] that sulfonation takes place quantitatively. The results on the sulfonation step can be summarized as follows:

1. The main reaction is the formation of sulfonate groups from methylol groups and bisulfite ions. All types of methylol groups are involved, but the reactivity of methylol groups bonded to a secondary nitrogen appears to be higher than that of those bonded to a tertiary nitrogen.
2. In the presence of sulfite ions a cleavage of dimethylene ether units takes place, most likely yielding sulfonate and methylol groups.
3. Urons are unstable in the sulfonation step, and ether cleavage occurs.

Condensation Step. During the condensation step, reactions characteristic of all amino–formaldehyde resins[7] occurred. The dimethylene ether units are unstable in acidic medium, and therefore ether cleavage takes place and methylene bridges are formed. Under the conditions of the experiment the cyclic ethers (urons) are stable. Compared to the sulfonation step, the concentration of free methylene glycol increases due to changes in the formaldehyde–methylolurea equilibrium and additionally due to the formation of formaldehyde in the ether cleavage.

$$-NHCH_2OCH_2NH- \xrightarrow{H^+} -NHCH_2NH- + CH_2O$$

The number of methylol groups decreases sharply and new signals in the region of 47–55 ppm appear, indicating that methylene bridges are formed.

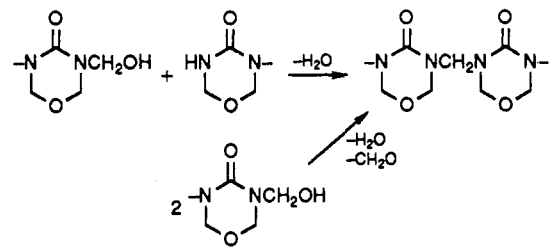
$$-NH-CH_2OH + NH_2- \xrightarrow[-H_2O]{} -NH-CH_2-NH-$$

$$>N-CH_2OH + NH_2- \xrightarrow[-H_2O]{} >N-CH_2-NH-$$

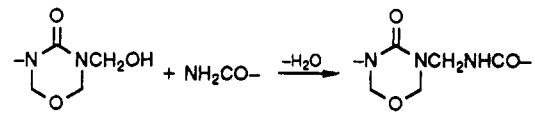
$$-NH-CH_2OH + HN< \xrightarrow[-H_2O]{} -NH-CH-N<$$

Accordingly, the number of NH_2CONH- units decreases to zero and the concentration of $-NHCON<$ units increases.

A new signal appears in the NMR spectrum at 50.3 ppm, and at the same time the number of uron-bonded methylol groups decreases. It is assumed that this signal is due to the formation of methylene bridges between uron units

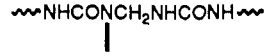


or between uron and linear units.



The latter seems to be more likely because of steric reasons.

During the condensation reaction branching points formed, but it cannot be decided whether these branching points bear methylol or methylene groups. Taking into consideration that units of the type $>NCH_2N<$ are not formed during the condensation, it can be assumed that the oligomer molecules are mainly linear.



Structure of the SUF Resins. The final composition of the SUF resins after a three-step preparation procedure is summarized in Table V. In terms of structural units it can be summarized that in all cases products are obtained, containing mainly metholol and sulfonate groups and methylene bridges. This is very obvious in the case of low F/U and high S/U ratios (for example, experiment 6). In Figure 3, S/U = 1.0, in the methylene region only four signals of higher intensity at 82.5, 64.1, 57.0, and 47.0 ppm were obtained, belonging to free formaldehyde, $-NHCH_2OH$ and $-NHCH_2SO_3^-$ groups and methylene bridges of the type $-NHCH_2NH-$, respectively. These signals account for about 76% of the overall formaldehyde. All products contain significant amounts of free formal-

Table IV
Concentration of Functional Groups in the Reaction Mixture after the Sulfonation Step

		F/U = 2		F/U = 3		
δ, ppm	assignt	S/U = 0.5 (expt 5)	S/U = 1 (expt 6)	S/U = 0 (expt 1)	S/U = 0.5 (expt 2)	S/U = 1 (expt 3)
162.0	NH_2CONH–	0.15	0.08	0.18	0.08	0.02
161.3	$NH_2CONHCH_2SO_3^-$	0.11	0.13		0.08	0.05
160.2	–NHCONH–	0.25	0.13	0.38	0.24	0.11
159.8	–NHCON<	0.31	0.36	0.12	0.29	0.40
159.5	$-NHCONHCH_2SO_3^-$					
159.0	$-NHCON<^{CH_2SO_3^-}$	0.11	0.31		0.12	0.30
156.3–155.4	–CO– cyclic	0.08		0.31	0.18	0.12
86.7	$-OCH_2OH$			0.01		
82.5	$HOCH_2OH$	0.16	0.15	0.28	0.48	0.44
78.5–78.0	$-CH_2OCH_2-$ cyclic	0.13		0.77	0.45	0.22
75.0	$>NCH_2O-$	0.02		0.10	0.09	0.07
71.2	$>NCH_2OH$	0.09	0.10	0.26	0.20	0.16
69.0	$-NHCH_2O-$	0.07	0.03	0.18	0.05	0.04
68.3–68.0	$>NCH_2OH$ cyclic	0.12		0.65	0.39	0.22
64.1	$-NHCH_2OH$	0.84	0.52	0.83	0.78	0.61
62.5	$>NCH_2SO_3^-$		0.05		0.05	0.06
60.4	$>NCH_2SO_3^-$ cyclic	0.02	0.01		0.02	0.12
57.0	$-NHCH_2SO_3^-$	0.49	0.98		0.46	0.93

Table V
Concentration of Functional Groups in SUF Resins after a Three-Step Preparation Procedure (Addition–Sulfonation–Condensation)

	F/U = 2		F/U = 3	
assignt	S/U = 0.5 (expt 5)	S/U = 1 (expt 6)	S/U = 0.5 (expt 2)	S/U = 1 (expt 3)
NH_2CONH–	0.3	0.04		
$NH_2CONHCH_2SO_3^-$	0.03	0.06		
–NHCONH–	0.31	0.17	0.30	0.13
–NHCON<	0.49	0.47	0.51	0.56
$-NHCONHCH_2SO_3^-$				
$-NHCON<^{CH_2SO_3^-}$	0.12	0.26	0.12	0.28
–CO– cyclic	0.05	0.02	0.07	0.03
$-OCH_2OH$			0.08	0.04
$HOCH_2OH$	0.25	0.16	0.64	0.54
$-CH_2OCH_2-$ cyclic	0.18	0.06	0.58	0.31
$>NCH_2O-$		0.02	0.05	0.02
$>NCH_2OH$	0.13	0.10	0.26	0.22
$-NHCH_2O-$				
$>NCH_2OH$ cyclic	0.04	0.03	0.34	0.13
$-NHCH_2OH$	0.23	0.20	0.37	0.24
$>NCH_2SO_3^-$	0.06	0.08	small	0.11
$>NCH_2SO_3^-$ cyclic	0.03	0.02	small	0.10
$-NHCH_2SO_3^-$	0.51	0.98	0.51	0.88
$>NCH_2NH-$	0.28	0.15	0.10	0.16
$>NCH_2<$ cyclic	0.05	0.01	0.05	0.07
$-NHCH_2NH-$	0.22	0.18	0.12	0.13
$n = 1/(1 - [CH_2])$	2.2	1.5	1.4	1.5

dehyde. Hemiformal structures are not present, and dimethylene ether bridges are only present in a minor amount in the final resins. This means that all SUF oligomers under the conditions of our experiment are bridged nearly exclusively by methylene bridges and not by dimethylene ether bridges. In the case of high F/U ratios the final resins contain significant amounts of cyclic structures. The concentration of cyclic carbonyl groups is almost equal to the concentration of methylene bridges bonded to cyclic structures, and thereby it can be assumed that the uron units are present in the final resins in the oligomeric rather than the monomeric form.

In all cases sulfonate groups of the type $>NCH_2SO_3^-$ are formed in minor concentrations. This indicates that methylol groups bonded to a secondary nitrogen exhibit a much higher reactivity in the sulfonation reaction.

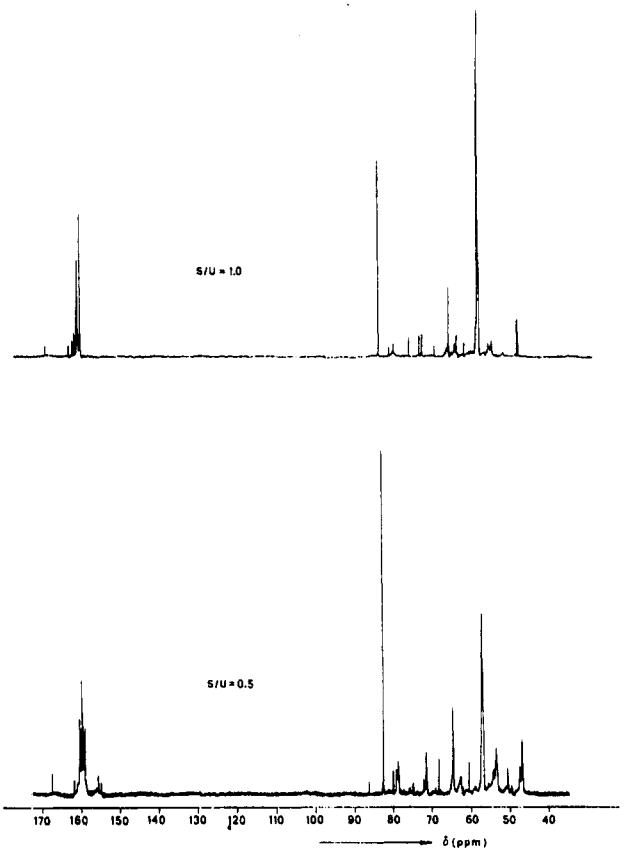


Figure 3. ^{13}C NMR spectra of final SUF resins after addition, sulfonation, and condensation; F/U = 2.

Conclusions

The chemical species formed after each of the three reaction steps followed in the synthesis of sulfonated urea–formaldehyde resins were characterized by using ^{13}C NMR. Resins with various F/U and S/U ratios were used in the study. After the addition step between urea and formaldehyde, it was shown that (a) mono- and dimethylolureas constituted 40–60% of the species in the reaction mixture, (b) about 5–10% free formaldehyde was detected, (c) 10–30% of cyclic structures (urons) were also formed, and (d) no hemiformals were present in the reaction mixture. In the sulfonation step methylol groups were substituted by

SO_3H groups. Additionally, ether cleavage and a drop in uron concentration were detected during this step. Finally in the third step, condensation, oligomers formed through methylene and not ether linkages. While both types of linkages are theoretically possible, oligomers with predominantly methylene bridges were identified.

The effects of reactant ratios on the chemical structure of SUF resins were also studied. It was found that increasing the F/U ratio from 2 to 3 resulted in the formation of larger amounts of cyclic structures (Table V). The degree of condensation was found to be a function of both F/U and S/U ratios. Although the amount of methylene bridges, formed in the course of the reaction, is relatively low (therefore, the accuracy of this quantification will be low too), a first estimation of the degree of condensation (n) can be obtained from the amount of methylene bridges [CH_2] by $n = 1/(1 - [CH_2])$. The degree of condensation in experiment 5 (F/U = 2, S/U = 0.5) is about 2.2, which is significantly higher than 1.5 calculated for experiment 6 (F/U = 2, S/U = 1.0). This is obviously due to a decrease of methylol groups available for condensation that occurred as a result of increasing the S/U ratio. Increasing the F/U ratio from 2 to 3 is not expected to increase the degree of condensation, which is measured by the concentration of [CH_2] groups. Recall that a reaction between an amine and a methylol group leads to the formation of a methylene bridge. Since the amount of amine groups is decreased (by increasing F/U from 2 to 3), then n is not expected to increase with F/U. Table V shows that this is the case. For experiment 2 (F/U = 3, S/U = 0.5), experiment 3 (F/U = 3, S/U = 1.0), and experiment 6 (F/U = 2, S/U = 1.0), n is 1.4, 1.5, and 1.5, respectively. What remains to be explained is the fact that, for F/U = 3.0, the degree of condensation is not a function of S/U. This is straightforward if one recalls that in this case n is limited (controlled) by the amine and not the methylol groups. Since the number of amino groups available for condensation is not affected by the S/U ratio, n is not affected either.

Obviously, there are other factors affecting the chemical structure of the SUF resins including switching the order of the sulfonation and condensation steps. This will be the subject of the next paper.

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References and Notes

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