

# $^{13}\text{C}$ n.m.r. characterization of sulphonated urea-phenol-formaldehyde resins

Harald Pasch\*

Academy of Sciences of the GDR, Central Institute of Organic Chemistry,  
Rudower Chaussee 5, Berlin-1199, GDR

and Issam S. Dairanieh

Products Department, Petroleum, Petrochemicals and Materials Division,  
Kuwait Institute for Scientific Research, Safat, 13109, Kuwait  
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The chemical structure of sulphonated urea-phenol-formaldehyde resins prepared in a three-step synthesis protocol was determined by  $^{13}\text{C}$  n.m.r. Separate resonance regions for each monomer were obtained and signals of most of the functional groups of urea and phenol entities were separated except for the methylene sulphonate group. Formaldehyde was mostly bound to phenol as *ortho*-methylol groups. However, no phenol-urea methylene bridges were detected. The effect of increasing the phenol percentage in the resin was studied. It was found that variations in the phenol/(phenol + urea) ratio did not affect the resin's degree of condensation. However, it was shown that decreasing this ratio led to an increase in the amount of sulphonate groups attached to the monomers.

(Keywords: sulphonated urea-phenol-formaldehyde resins;  $^{13}\text{C}$  n.m.r.; chemical structure)

## INTRODUCTION

The use of sulphonated amino-formaldehyde resins as drilling mud additives was recently patented<sup>1</sup>. It was found that sulphonated urea-formaldehyde and sulphonated urea-melamine-formaldehyde resins can be effectively used as additives for drilling fluids. A further improvement in the performance of these resins was observed when phenol was added to the reaction mixture. Therefore, interest developed for investigating the structure of the sulphonated urea-phenol resins and for conducting an n.m.r. study comparable to earlier investigations on the chemical structure of sulphonated urea-formaldehyde resins<sup>2-4</sup>.

Condensation products of a wide variety of amino and phenolic compounds with formaldehyde are produced in large scale for different applications. Co-condensed resins between phenol and urea or melamine have been used as adhesives for plywood<sup>5</sup>. However, despite their industrial importance the knowledge about the chemistry of this type of resins is limited. The question of whether genuine copolymers or mixtures of homopolymers are formed during the condensation reaction is still not clearly answered. In the system phenol-melamine-formaldehyde it was found, that copolymers of phenol and melamine were not formed in either the precondensate or in the crosslinked resin<sup>6-8</sup>.

The simultaneous condensation of urea, melamine and formaldehyde was studied using chromatographic and spectroscopic methods<sup>6</sup>. A controllable reaction involving all monomers was possible only in neutral and basic media. Certain indications of the formation of copolymers were obtained from acetone dilutability and turbidimetric measurements but further verification was desirable. The

co-condensation between resols and amino resins was investigated using  $^{13}\text{C}$  n.m.r.<sup>10</sup>. Applying an additive relationship, the chemical shift of methylene bridges characteristically for copolymers were calculated:

$-\text{NH}-\text{CH}_2-\textit{ortho}(\text{Ph})$	38.7 ppm
$-\text{NH}-\text{CH}_2-\textit{para}(\text{Ph})$	44.1 ppm
$>\text{N}-\text{CH}_2-\textit{ortho}(\text{Ph})$	44.8 ppm
$>\text{N}-\text{CH}_2-\textit{para}(\text{Ph})$	50.3 ppm

In order to determine the suitable conditions for producing co-condensates, three model reactions were carried out: the reaction of methylolphenol and methylolurea; the reaction of methylolurea and phenol itself; and the reaction of methylolphenol and urea itself. Only in the third reaction could co-condensation be confirmed by the presence of the signal at 44.2 ppm characteristic of the  $-\text{NH}-\text{CH}_2-\textit{para}(\text{Ph})$  unit.

So far no information is available about the chemical structure of sulphonated urea-phenol-formaldehyde reaction products. In order to characterize this type of resins (SUPF), samples were prepared in accordance with a previously described procedure<sup>2</sup> and analysed by  $^{13}\text{C}$  n.m.r. spectroscopy.

## EXPERIMENTAL

$^{13}\text{C}$  n.m.r. Fourier transform spectra were obtained on a Bruker AM-300 n.m.r. spectrometer operating at 75.369 MHz for  $^{13}\text{C}$ . The spectrometer was equipped with an Aspect-3000 computer system. The inverse gated decoupling technique was used, experimental conditions were: memory capacity for data acquisition 64K words, sweep width 250 ppm, pulse width 6  $\mu\text{s}$ , relaxation delay 10-15 s, number of pulses 1000-10000 and sample

\* To whom correspondence should be addressed

**Table 1** Composition of the reaction mixtures investigated using  $^{13}\text{C}$  n.m.r.

Resin	F/(U+P) <sup>a</sup>	S/(U+P) <sup>b</sup>	P/(U+P) <sup>c</sup>
1	3.0	0.2	1.0
2	3.0	0.2	0.8
3	3.0	0.2	0.5
4	3.0	0.2	0.2

<sup>a</sup> Molar ratio of formaldehyde to urea and phenol

<sup>b</sup> Molar ratio of sodium bisulphite to urea and phenol

<sup>c</sup> Molar ratio of phenol to urea and phenol

temperature 25°C. As the solvent, water was used with one drop of deuterium oxide added for deuterium internal lock.

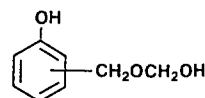
The resin samples were prepared according to a previously described procedure<sup>2</sup>. Briefly, 262 g of a 24% formalin solution were heated to 80°C and the pH was adjusted to 10. Water, (250 g), urea (20 g) and phenol (31 g) were added (step 1). After 20 min, 63 g of a 20% sodium metabisulphite solution were added and the mixture was stirred for 60 min (step 2). The pH was lowered to 3 and the mixture was heated for 60 min, then it was cooled and its pH raised to 9.0 (step 3). For this resin F/(U+P) was 3.0, S/(U+P) was 0.2 and P/(U+P) was 0.5 where F, U, P and S are respectively, the number of moles of formaldehyde, urea, phenol and sulphite. Resins with different P/(U+P) ratios were prepared similarly (Table 1).

## RESULTS AND DISCUSSION

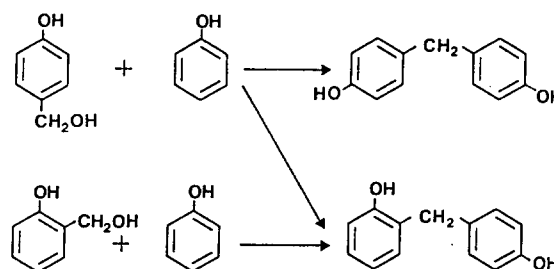
Prior to investigating the structure of sulphonated urea-phenol-formaldehyde resins (SUPF), it is necessary to obtain information about the spectroscopical behaviour of the appropriate 'homopolymers', i.e. sulphonated urea-formaldehyde resins (SUF) and sulphonated phenol-formaldehyde resins (SPF). As for SUF, complete information was obtained in previous investigations<sup>3,4</sup>. Signals were assigned and a semi-quantitative procedure

for calculating concentrations of various chemical structures was presented<sup>2,3</sup>. The most important chemical shifts obtained for phenol-formaldehyde resins are known<sup>11,12</sup>. In order to compare these chemical shifts with those obtained for the SPF resins, a resin with a P/(U+P) ratio of 1.0 was prepared (experiment 1) and subjected to  $^{13}\text{C}$  n.m.r.

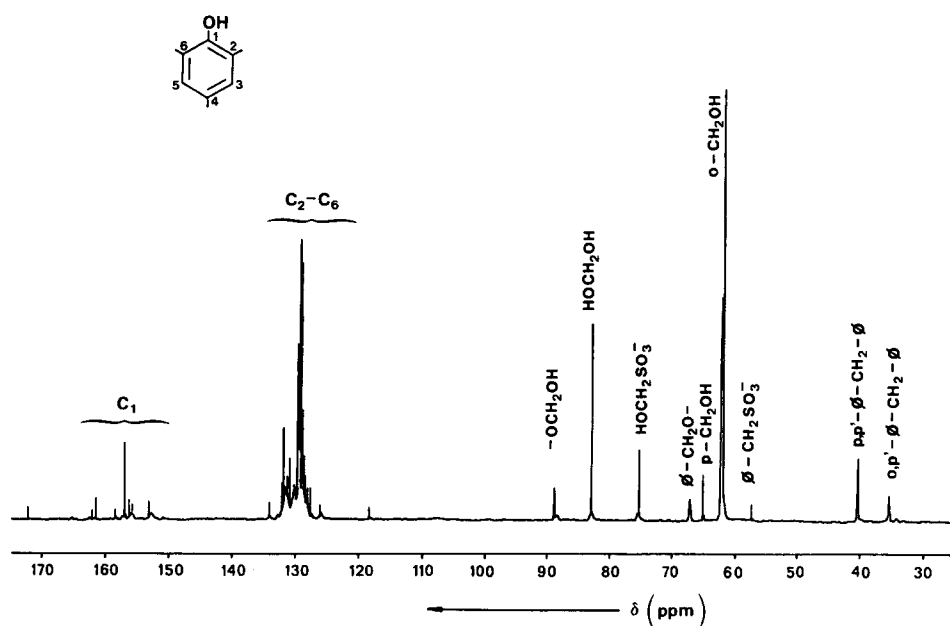
The  $^{13}\text{C}$  n.m.r. spectrum and full assignment of the signals are presented in Figure 1. During the three-step procedure *ortho*- and *para*-methylol groups were formed, about 10% of the initial formaldehyde remained unreacted. A certain amount of hemiformals was obtained, having the following average structure



Following the semi-quantitative procedure used for the SUF resins, the estimation of the amount of different functional groups (see Table 2) indicates that most of the formaldehyde is bound to phenol as *ortho*-methylol groups (1.68 of theoretically possible 2.0). The condensation reaction involved mostly the *para*-positions, which is documented by the formation of *p,p'*- and *o,p'*-methylene bridges.



This is in agreement with the expected higher reactivity of the *para*-methylol group and the *para*-proton towards condensation<sup>13,14</sup>.

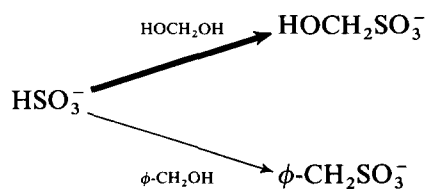


**Figure 1**  $^{13}\text{C}$  n.m.r. spectrum of a sulphonated phenol-formaldehyde resin, F/(U+P)=3.0, S/(U+P)=0.2, P/(U+P)=1.0

**Table 2** Relative concentrations of functional groups in the SUPF reaction; F/(U + P) = 3.0, S/(U + P) = 0.2;  $\phi$  = phenol

Chemical shift $\delta$ (ppm)	Structural unit	P/(U + P) = 1.0 (Resin 1)	P/(U + P) = 0.8 (Resin 2)	P/(U + P) = 0.5 (Resin 3)	P/(U + P) = 0.2 (Resin 4)
88.4–86.3	–OCH <sub>2</sub> OH (U + P)	0.18	0.22	0.20	0.15
82.5	HOCH <sub>2</sub> OH	0.33	0.53	0.67	0.68
78.4	>NCH <sub>2</sub> O–cycl. (U)	–	0.04	0.20	0.42
75.0	HOCH <sub>2</sub> SO <sub>3</sub> <sup>–</sup> + >NCH <sub>2</sub> O– (U)	0.18	0.06	0.04	0.04
71.3	>NCH <sub>2</sub> OH (U)	–	0.08	0.18	0.26
68.2	>NCH <sub>2</sub> OH cycl. (U)	–	0.04	0.13	0.32
67.0	$\phi$ -CH <sub>2</sub> O– (P)	0.14	0.20	0.17	0.05
64.5	–NHCH <sub>2</sub> OH (U) + <i>p</i> -CH <sub>2</sub> OH (P)	0.09	0.17	0.21	0.23
61.6	<i>o</i> -CH <sub>2</sub> OH (P)	1.68	1.14	0.65	0.19
57.0	–CH <sub>2</sub> SO <sub>3</sub> <sup>–</sup> (U + P)	0.04	0.15	0.18	0.20
53.4	>NCH <sub>2</sub> NH– (U)	–	negligible	0.08	0.20
50.5	>NCH <sub>2</sub> N< cycl. (U)	–	negligible	0.02	0.05
47.0	–NHCH <sub>2</sub> NH– (U)	–	negligible	0.06	0.11
40.0	<i>p,p'</i> -CH <sub>2</sub> (P)	0.26	0.20	0.11	0.02
35.0	<i>o,p'</i> -CH <sub>2</sub> (P)	0.09	0.18	0.09	0.02
	$n = 1/(1 - [\text{CH}_2])$	1.54	1.61	1.56	1.64

As for the sulphonation reaction the conversion was 100% (0.22 of theoretically possible 0.2). However, most of the sulphite reacted with methylene glycol (0.18) instead of the methylol groups (0.04).



Two explanations are possible. The reactivity of the phenolic methylol group towards sulphonation is low compared to the reactivity of the urea methylol group.

Alternatively there exists a deficit of methylol groups available for sulphonation due to a low velocity of the hydroxymethylation reaction (addition step).

In order to prove the validity of the explanations, a similar experiment was carried out, where the S/(U + P) ratio was increased to 1.0 and each single step was investigated by n.m.r. The results, summarized in Table 3 show, that under the conditions of the experiment, after the addition step only 30% of the total formaldehyde was reacted; 70% still existed as free formaldehyde or its oligomers. At this high excess of formaldehyde, it has to be expected that in the sulphonation step a mostly sulphite-formaldehyde reaction takes place. In fact only 20% of the sulphite reacted with methylol or methylene ether groups to form  $\phi$ -CH<sub>2</sub>SO<sub>3</sub><sup>–</sup> groups. At the same time the formation of methylol groups continues during the sulphonation step.

The <sup>13</sup>C n.m.r. spectra of SUPF resins with different P/(U + P) ratios are presented in Figure 2. It can be seen that for each monomer mainly separate resonance regions were obtained. The aromatic carbons of the phenolic nuclei (C<sub>2</sub>–C<sub>6</sub>) appeared at 115–135 ppm, whereas the carbonyl signals of urea together with the C<sub>1</sub> signals of the phenol were obtained at 155–164 ppm. All functional groups of urea are well separated from the functional groups of phenol, except the –NHCH<sub>2</sub>OH (urea) and the *para*-CH<sub>2</sub>OH (phenol) groups which overlapped at 64.5 ppm. Only one signal of methylene sulphonate groups –CH<sub>2</sub>SO<sub>3</sub><sup>–</sup> was obtained, regardless of its link to urea or phenol.

**Table 3** Relative concentrations of functional groups in the SPF reaction. F/(U + P) = 3.0; S/(U + P) = 1.0; P/(U + P) = 1.0;  $\phi$  = phenol

Structural unit	A <sup>a</sup>	S <sup>a</sup>	C <sup>a</sup>
–OCH <sub>2</sub> O–	0.37	–	–
–OCH <sub>2</sub> OH	0.57	–	–
HOCH <sub>2</sub> OH	1.31	0.07	–
HOCH <sub>2</sub> SO <sub>3</sub> <sup>–</sup>	–	0.80	0.77
$\phi$ -CH <sub>2</sub> OCH <sub>2</sub> - $\phi$	0.20	–	–
$\phi$ -CH <sub>2</sub> O–	0.25	–	–
<i>p</i> -CH <sub>2</sub> OH	0.20	0.52	0.39
<i>o</i> -CH <sub>2</sub> OH	0.39	1.47	1.22
$\phi$ -CH <sub>2</sub> SO <sub>3</sub> <sup>–</sup>	–	0.24	0.26
$\phi$ -CH <sub>2</sub> - $\phi$	–	–	0.30

<sup>a</sup> Sample after addition (A), sulphonation (S) and condensation (C)

The methylene bridges linking urea units were well separated from those linking phenolic nuclei, however signals characteristic of the phenol-urea linkages were not obtained. The relative concentrations of the functional groups in SUPF resins were summarized in Table 2. It was obvious, that the amount of sulphonate groups, linked to one of the monomers, increased significantly with decreasing P/(U + P) ratio.

The degree of condensation in this type of condensation resins can be obtained from the concentration of the ether or the methylene linkages in the oligomers. Because only methylene bridges could be detected in the products, the degree of condensation can be directly related to the concentration of methylene bridges (i.e. [CH<sub>2</sub>]) through the formula 1/1 – [CH<sub>2</sub>]. From Table 2 it can be seen that the degree of condensation (*n*) of the SUPF resins was not influenced by the P/(U + P) ratio.

## CONCLUSIONS

Sulphonated urea-phenol-formaldehyde resins were prepared according to a three-step procedure and the <sup>13</sup>C n.m.r. spectra of a number of resins were analysed. It was shown that separate resonance regions were obtained for each monomer. Most of the functional groups of urea and phenol were separated except for the methylene sulphonate group (–CH<sub>2</sub>SO<sub>3</sub><sup>–</sup>). No signals for the urea-phenol methylene linkage were detected. The effect of variations in the reactant ratios was briefly studied. It

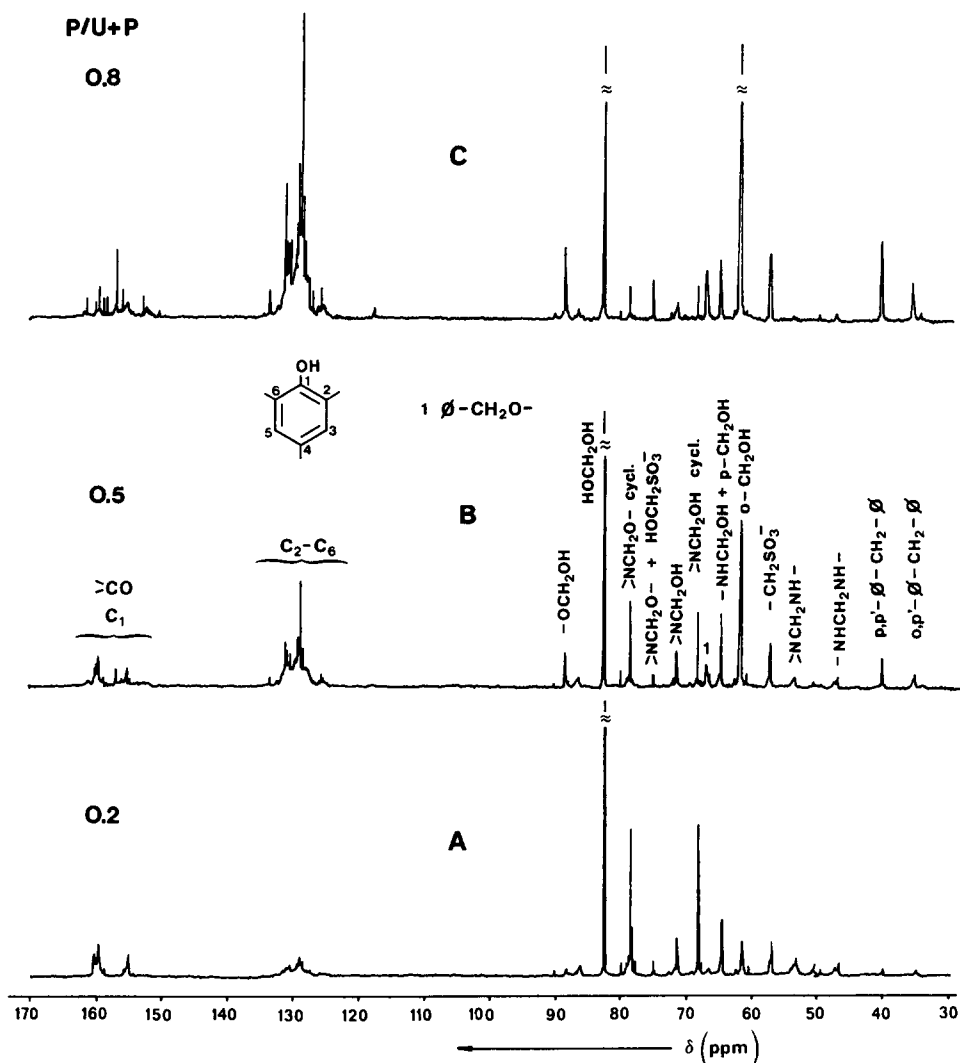


Figure 2  $^{13}\text{C}$  n.m.r. spectra of sulphonated urea-phenol-formaldehyde resins with different P/(U + P) ratios: (a) 0.8, (b) 0.5, (c) 0.2. F/(U + P) = 3.0, S/(U + P) = 0.2

was found that increasing the P/(U + P) (i.e. the phenol percentage in the resin) led to decreased amount of sulphonate groups linked to none of the monomers. Two values for the S/(U + P) ratios were utilized in this study to explain the observation that most sulphite groups reacted with methylene glycol rather than methylol groups. By examining the chemical structure of the reaction mixture after each of the three reaction steps, it was concluded that the deficit in methylol groups led to the formation of sulphonated formaldehyde.

Further work is needed to examine the effect of the F/(U + P) ratio on the chemical structure of SUPF resins and to study the reaction conditions where a urea-phenol methylene bridge is formed.

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