

CONCLUSIONS

The stochastic model of the solid state polymerization presented here is based on several simple assumptions and in spite of their simplicity the process is described quite satisfactorily. The two facts which should be emphasized are (1) that the results of the computation experiments are the consequence of the precisely defined mechanism of the process, without any additional assumptions being made, which are necessary in the formal kinetics. (2) That the proposed model enables us to achieve a fuller description of the polymerization. It is possible to watch the course of micro- and macroprocesses and to obtain consistent information even for those processes which are difficult to achieve by direct experimentation.

Both the above mentioned attributes of the computational model described here permit us to use it as a semi-empirical method to predict the results of real polymerization processes.

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The acid catalysed condensation of phenol-4-sulphonic acid with formaldehyde

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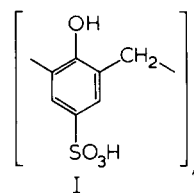
The reaction products formed when phenol-4-sulphonic acid reacts with formaldehyde have been investigated using ^1H and ^{13}C nuclear magnetic resonance. It is shown that the reaction does not proceed readily at high phenol-4-sulphonic acid: formaldehyde ratios. As the ratio is decreased evidence of reaction is observed and further decreases lead to crosslinking. The crosslinking reaction is explained in terms of desulphonation and electrophilic substitution of the sulphonic acid group by a hydroxymethylene carbonium ion.

Keywords Phenolsulphonic acid; formaldehyde; condensation reaction; acid catalysis; nuclear magnetic resonance

INTRODUCTION

The resinous reaction products of phenol sulphonic acids with formaldehyde are well known, particularly in the formation of synthetic tanning agents¹ for use in the leather industry and also in the formation of cation exchangers². In general synthetic tanning agents are water soluble materials whilst ion exchange resins are of course insoluble.

Many papers and patents have reported the polycondensation of sulphonated phenol with formaldehyde. These investigations have been mainly concerned with the manufacture and final properties of the products which may give them commercial importance. However, very little work has been carried out on the chemistry of the condensation reaction of phenol sulphonic acid and formaldehyde under acid catalysed conditions. The many references to patents³ claim that the polycondensation will yield a sulphonated polymer which depending on the reaction conditions may be either soluble or insoluble in water. Since the sulphonation of phenol gives predominantly *p*-phenol sulphonic acid it would be normally expected that the resulting product could be represented as (I), i.e. a sulphonated novolak. However, as it is well known that insoluble materials can be formed under appropriate conditions it was decided to investigate the reaction between *p*-phenol sulphonic acid and formaldehyde in dilute solution under acid conditions.



EXPERIMENTAL

Materials

All of the phenolic compounds used in this work were of analytical reagent grade purchased from Aldrich Chemical Co. Inc. Formaldehyde was used in the form of an aqueous solution 39–41% w/v.

*Synthesis of phenol-4-sulphonic acid*⁴

Phenol (53 g) was sulphonated with concentrated sulphuric acid (98%) at 120°C as described by Coffey. Yield 82.75 g. The ^{13}C spectra (Figure 1) shows the existence of only four different carbon atoms as would be expected in the symmetrical *p*-isomer.

Reaction between phenol-4-sulphonic acid and formaldehyde

The appropriate weight of phenol sulphonic acid was

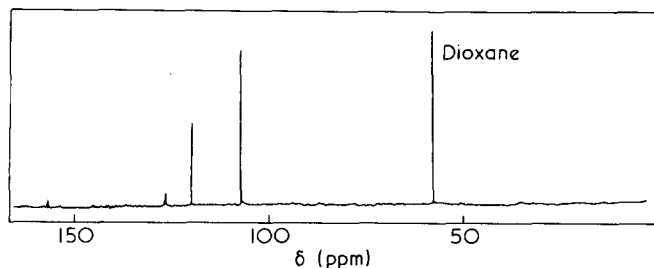


Figure 1 250 MHz ^{13}C spectrum of phenol-4-sulphonic acid, (solvent $\text{D}_2\text{O}/\text{NaOH}$, dioxane reference)

dissolved in distilled water (25 ml) containing sulphuric acid (0.5 ml) to give a pH value of 2.0. The required amount of formaldehyde in the form of an aqueous solution (40%) was added and the mixtures reacted at 100°C for 18 hours. This reaction was repeated using phenol sulphonic acid: formaldehyde ratios of 1:0.5, 1:0.75, 1:1, 1:1.5 and 1:2 respectively.

The products were isolated by one of two general methods depending on the solubility of the reaction product. For water-soluble products calcium carbonate was added to neutralize the sulphuric acid catalyst. After filtering hot the filtrate was allowed to stand and any solid material obtained was converted to the sodium salt by the addition of sodium sulphate. In the case of water-insoluble materials the resins were neutralized with sodium hydroxide and washed repeatedly with distilled water.

Desulphonation studies

Phenol-4-sulphonic acid (0.05 mole) was dissolved in distilled water (25 ml) and refluxed for 18 hours at pH 2.0 (adjusted with hydrochloric acid). Barium nitrate solution was added to the sample in large excess. The resulting milky solution was filtered through a pre-weighed sintered glass crucible and washed several times with distilled water. The crucible and its contents were dried to constant weight and the percentage desulphonation determined. The procedure was repeated in the presence of formaldehyde (0.05 mole).

Synthesis of 2,6-dimethyl-phenol-4-sulphonic acid⁵

2,6-Dimethylphenol (210 g) was heated at 110°C in an oil bath for 6 hours with concentrated sulphuric acid (25 g). The product was neutralized with barium carbonate to pH 5.0 and the barium sulphate removed by filtration. The barium phenol sulphonate was recrystallized once from water and converted to the sodium salt by the addition of sodium sulphate. This solution was concentrated and recrystallized twice from water. Yield 33 g. Sulphonation in the 4 position was confirmed by ^1H n.m.r. showing only one aromatic proton (Figure 2).

Synthesis of 4,4'-dihydroxy-3,5,3',5'-tetramethyl-diphenyl methane (II)

2,6-Dimethylphenol (12.2 g 0.1 mole) was dissolved in ethanol (30 ml) containing hydrochloric acid (5 ml). Formaldehyde (5 ml 40% aqueous solution) was added dropwise with stirring and the reaction was allowed to proceed for 12 hours. The resulting mixture was cooled and the solid product collected by filtration. The crude material was recrystallized from ethanol. Yield 11.8 g. The structure was confirmed using i.r., ^1H and ^{13}C spectroscopy (Figures 3 and 4).

Reaction of 2,6-dimethyl-phenol-4-sulphonic acid with formaldehyde

2,6-Dimethyl-phenol-4-sulphonic acid (13.3 g) was dissolved in distilled water (25 ml) containing formaldehyde (0.75 g 40% aqueous) at pH 2.0 adjusted with concentrated sulphuric acid (0.5 ml), and refluxed for 18 hours. The insoluble reaction material was washed with distilled water and dried under vacuum. This material was further examined using i.r., ^1H and ^{13}C spectroscopy.

Infra-red spectra and nuclear magnetic resonance studies were carried out using a Perkin-Elmer i.r. spectrophotometer 398 and a Bruker WH-250 FT spectrophotometer respectively.

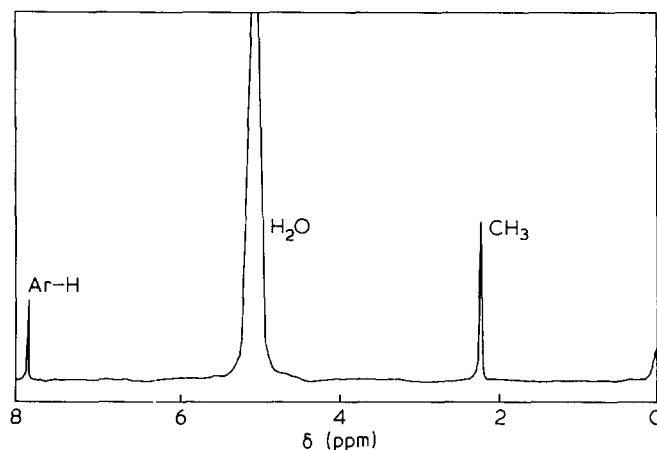


Figure 2 250 MHz ^1H spectrum of 2,6-dimethyl-phenol-4-sulphonic acid (solvent $\text{D}_2\text{O}/\text{NaOD}$ ref. TMS)

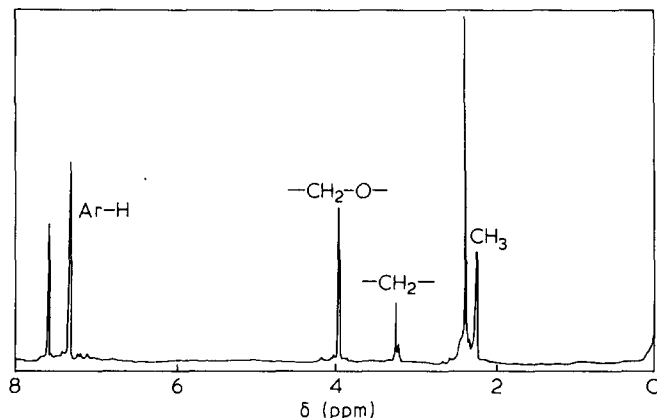


Figure 3 250 MHz ^1H spectrum of 4,4'-dihydroxy-3,5,3',5'-tetramethyl-diphenyl methane (solvent CD_3CO , ref. TMS)

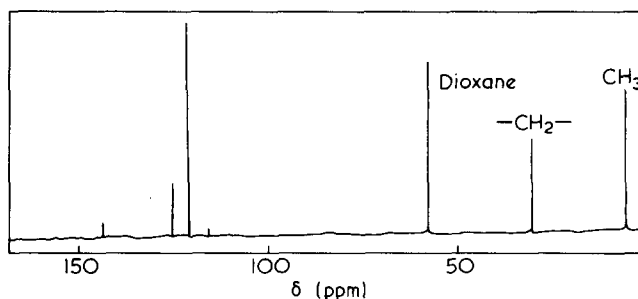


Figure 4 250 MHz ^{13}C spectrum of 4,4'-dihydroxy-3,5,3',5'-tetramethyl-diphenyl methane (solvent dimethyl sulphoxide, ref. dioxane)

RESULTS AND DISCUSSION

Reaction between phenol-4-sulphonic acid and formaldehyde

All reaction products were examined using i.r. and n.m.r. spectroscopy where possible. The materials obtained ranged from apparently no reaction to highly crosslinked resins. The results are summarized in *Table 1*.

The i.r. spectra failed to show any significant differences between the reaction products and the starting material. However ^1H and ^{13}C n.m.r. spectroscopy made it possible to detect the existence of additional groups indicating that reaction had occurred viz. methylol (CH_2OH), methylene and ether links (CH_2OCH_2). All of these groups have been detected in the study of the reaction between phenol and formaldehyde⁶. In the case of PSA:F ratios 1:0.5 and 1:0.75 no such groups could be detected, there was however a distinct pink colouration which is often observed in phenol/formaldehyde reactions⁷. Clearly in the case of the crosslinked resins n.m.r. studies could not be employed.

In any discussion of the reaction of *p*-phenol sulphonic acid with formaldehyde it is perhaps useful to compare the reaction with that between other *p*-substituted phenols such as *p*-cresol and *p*-chlorophenol with formaldehyde. These two materials should yield linear, entirely σ - σ' substituted novolaks⁸. These reactions occur quite quickly under conditions similar to those employed in this work. However in the case of phenol-4-sulphonic acid, only at PSA:F ratios of 1 and less can any reaction be detected. Unlike *p*-cresol and *p*-chlorophenol, decreasing the PSA:F ratio further results in crosslinking. The lack of reactivity at high PSA:F ratios may be due to the influence of the sulphonic acid group on the reactivity of the phenol sulphonic acid in the electrophilic substitution reaction between phenol and formaldehyde. In the reaction between phenol and formaldehyde under acid conditions the attacking species is the carbonium ion $+\text{CH}_2\text{OH}$. When this group enters the aromatic nucleus the electronic structures of the carbocations formed show that the σ and *p* substituted species are most stable. This is found for aromatic ring systems substituted with electron donating groups viz. hydroxy, amino, alkyl and alkoxy.

However, the sulphonic acid group possesses a relatively large dipole moment and consequently an electron withdrawing effect. This tends to deactivate the nucleus, resulting in low reactivity towards electrophiles. The above consideration possibly explains the fact that reaction with formaldehyde only takes place at low PSA:F ratios.

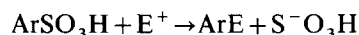
The most unusual feature of this reaction is the formation of water-insoluble materials, particularly if one considers the linear products obtained with *p*-chlorophenol by Burke⁹. In the acid condensation of phenol-4-sulphonic acid with formaldehyde two possible

reactions may be involved in the crosslinking reaction, namely reactions at the meta position relative to the hydroxy group or desulphonation followed by reaction with formaldehyde. Reaction at the meta position involves the electrophilic attack of a hydroxymethylene carbonium ion with subsequent condensation to form branched chains and crosslinks. Studies of the reaction of 2,4,6-tri-methyl-phenols with formaldehyde by Finn and Musty¹⁰ showed that reaction only occurred at high acid concentrations and elevated temperatures ($150^\circ\text{--}200^\circ\text{C}$). Considering in addition the bulkiness of the sulphonic acid group it is unlikely that reaction occurs at the meta position.

The second mechanism for crosslinking would require the removal of a sulphonic acid group to yield a suitable reaction site for the hydroxymethylene carbonium ion. In order to study the desulphonation process under pH conditions similar to those employed in the reaction, hydrochloric acid was used so that the acid catalyst would not interfere with the test procedure. In addition the extent of desulphonation in the presence of acid and formaldehyde is greater than in acid alone, the percentage desulphonations were found to be 32% and 18.6% respectively. It is therefore clear that considerable desulphonation occurs during the reaction. In fact the presence of formaldehyde appears to increase the amount of desulphonation. Desulphonation can be regarded as an electrophilic substitution of the sulphonic acid group, protodesulphonation.

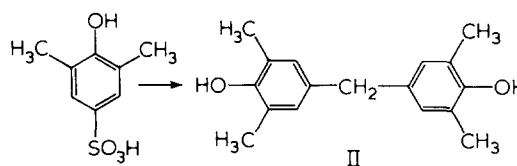
This desulphonation in the presence of formaldehyde should lead, when the low reactivity of phenol-4-sulphonic acid is considered, to the production of unsulphonated novolaks at high PSA:F ratios. This was not particularly apparent except that a distinct red-brown colouration was observed. Such coloured products are associated with phenol-formaldehyde resins.

The fact that the presence of formaldehyde enhanced the desulphonation reaction is considered to be evidence that desulphonation may also proceed *via* an electrophilic substitution reaction viz.



rather than the conventional protodesulphonation. This type of reaction has been extensively studied in the nitration of phenol sulphonic acid^{11,12,13}. The replacement of an alkyl group by the sulphonium cation is also well known in the Jacobsen reaction.

With the possibility of electrophilic desulphonation in mind, it was decided to study the reaction between 2,6-dimethylphenol-4-sulphonic acid and formaldehyde. This reaction which can be considered to be analogous to the reaction between segments of a fully $-\sigma-$ linked polyphenolsulphonic acid should produce the compound (II)

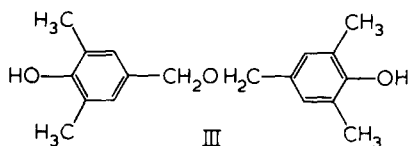


Both the dimethylphenolsulphonic acid and the dimer were synthesized and the n.m.r. spectra can be seen in

Table 1 Phenol sulphonic acid reaction products pH 2.0 100°C

PSA : F	Reaction product
1 : 0.5	Phenol sulphonic acid
1 : 0.75	Phenol sulphonic acid
1 : 1	Water soluble resin
1 : 1.5	Water soluble resin
1 : 2	Water insoluble resin

Figures 2, 3 and 4. From the spectra it is concluded that the sulphonic acid is essentially pure but the dimer shows a structure containing ether links suggesting that it is contaminated with a compound of possible structure (III).



This is particularly apparent from the proton spectra, Figure 3. The ^{13}C spectra, Figure 4, does not illustrate this behaviour, possibly because the chemical shift of the ether link is close to the chemical shift for the reference material, dioxane, Figures 5 and 6 show the ^1H and ^{13}C spectra for the product of reaction between the dimethyl-phenol-sulphonic acid and formaldehyde. These spectra are very similar to those obtained for the dimeric compound. This is considered to be evidence to support the idea that in the crosslinking reaction observed when phenol-4-sulphonic acid is reacted with formaldehyde, crosslinking occurs not only by desulphonation but also by the electrophilic replacement of the sulphonic acid group by a hydroxymethylene cation.

CONCLUSIONS

In dilute acid, phenol-4-sulphonic acid does not readily react with formaldehyde at high PSA:F ratios. However as the ratio decreases some reaction appears to take place resulting eventually in a crosslinked product. This behaviour is unusual in the sense that as the *para* position of the aromatic nucleus is blocked, only linear water soluble products would be expected. There is some evidence that aromatic desulphonation takes place which would give rise to reactive crosslinking sites. Crosslinks may also occur *via* an electrophilic replacement of the sulphonic acid group by a hydroxymethylene group which may undergo further condensation. This type of reaction has been observed by other workers¹⁴, where the reaction between 2,4-dimethyl-3-carbomethoxy-5- and 2,4-dimethyl-5-carbomethoxy-3-pyrrole sulphonic acid and formaldehyde give the substituted di-5-pyrrolymethane and di-3-pyrrolymethane respectively.

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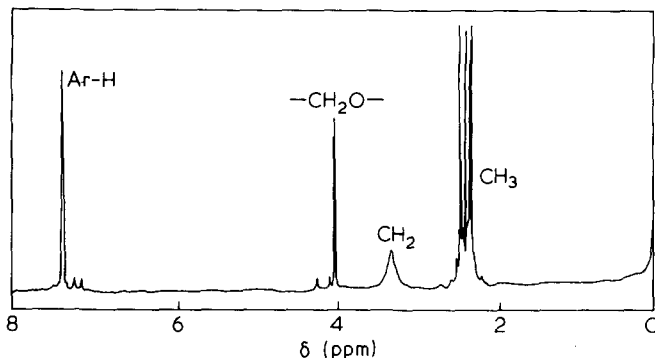


Figure 5 250 MHz ^1H spectrum of reaction product of 2,6,-dimethylphenol-4-sulphonic acid with formaldehyde (solvent CD_3CO , ref. TMS)

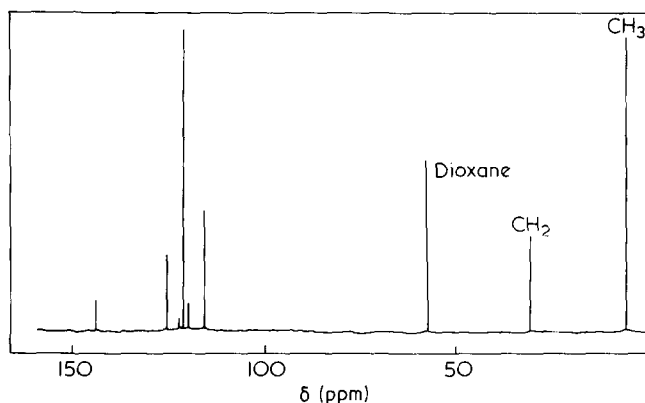


Figure 6 250 MHz ^{13}C spectrum of reaction product of 2,6,-dimethylphenol-4-sulphonic acid with formaldehyde (solvent dimethyl sulphoxide, ref. dioxane)

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