

# Synthesis of Formaldehyde Polymers from Benzene-1,2-diol, Phenolic Alkane-1,2-diol, and Phenolic Alkane-1,3-diol as Immobilized Chelatants for Borate Anion

John H. P. Tyman, Peter B. Payne

Department of Chemistry, Brunel University, Uxbridge, Middlesex UB8 3PH, United Kingdom

Received 6 September 2006; accepted 22 November 2006

DOI 10.1002/app.26004

Published online 27 March 2007 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** A variety of phenolic aryl-1,2- and 1,3-diols have been condensed with formaldehyde to form polymers serving as immobilized chelatants for borate anions. In this way, polymers from 1,2-dihydroxybenzene, 2-hydroxymethylphenol, and a 3-methyl derivative (saligenins) and 2-(4-hydroxyphenyl)propane-1,3-diol have been converted into formaldehyde polymers with an increasing level of conformational mobility in the diol moiety of the polymer. The extraction of borate from alkaline solutions with three types of polymers has been examined, and the polymer

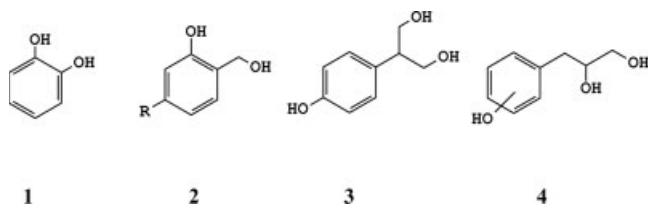
containing planar 1,2-dihydroxybenzene has been found to be superior to a saligenin- and 2-(4-hydroxyphenyl)propane-1,3-diol-derived polymer. This suggests that conformational mobility is not an important structural feature. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 420–423, 2007

**Key words:** aromatic diol; formaldehyde polymer; immobilized chelatant; borate

## INTRODUCTION

The interaction between boric acid and alcohols, notably 1,2- and 1,3-diols, is well known from the classical research of Boesekin<sup>1</sup> and others.<sup>2,3</sup> Industrially, there has been great interest in the solvent extraction of boric acid and borates from natural sources.<sup>4–6</sup> Additionally, although boron is an essential trace element in natural growth, in some areas irrigation water is not suitable if it contains boron in excess of 2–3 ppm. However, through the impact of green chemistry, it is appropriate to avoid water-immiscible organic solvents. The feasibility of concentrating aqueous systems has encouraged the employment of water-insoluble immobilized chelatants, which were first examined for the recovery of metal ions.<sup>7–10</sup> As far as we know, the recovery or removal of anions by this means has not previously been studied. Other technical applications of chelating polymers<sup>11</sup> have been investigated.<sup>12,13</sup> In this work, following earlier work,<sup>14,15</sup> we have synthesized polymeric structures through the reaction of pheno-

lic monomeric 1,2- and 1,3-diols with formaldehyde to obtain immobilized chelatants for the complexation of borate/boric acid. At the outset, we had little information of either the molar ratios of phenolic diol to borate involved in complexation or the potential conformational requirements of the phenolic diol monomer used for borate complexation. Accordingly, we examined essentially a planar system in readily available 1,2-dihydroxybenzene (catechol **1**), salicyl alcohol **2** (R = H) with one flexible bond, and C-methyl substituted salicyl alcohol **2** (R = Me) specifically to potentially influence the position of methylene substitution in formaldehyde polymerization with two flexible bonds [2-(4-hydroxyphenyl)propane-1,3-diol (**3**)] and three isomers [3-(*x*-hydroxyphenyl)propane-1,2-diol (**4**)]. Monomers **1–4** were prepared as previously described.<sup>15</sup>



This article is part 41c of *Long Chain Phenols*; for part 41b, see ref. 15.

Correspondence to: J. H. P. Tyman (jhptyman@hotmail.com).

Contract grant sponsor: Macphersons, Ltd.

*Journal of Applied Polymer Science*, Vol. 105, 420–423 (2007)  
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The formaldehyde polymerization of catechol **1** does not appear to have been studied, and the nearest approach is the reaction of catechin with hexamethylenetetramine.<sup>17</sup> Saligenin **2** (R = H) and 3-methylsaligenin **2** (R = Me) were prepared from

aldehyde/formaldehyde precursors by a modification of a described procedure<sup>18</sup> and then reduction with sodium borohydride. The polymerization of **3** and of **4** was effected under acidic conditions, and the polymeric products were characterized spectroscopically. A phenol/formaldehyde polymer was synthesized as a reference compound.

## EXPERIMENTAL

### Materials

The chemicals were obtained from Aldrich Chemical Co. (Gillingham, Dorset, UK).

### Chromatography

Thin-layer chromatography (TLC) was carried out with glass plates precoated with silica gel 60A and visualizations with iodine or under ultraviolet light. Column and flash chromatography was carried out on Merck Kieselgel 60 (Merck Chemicals, Ltd., Nottingham, UK) (230–400 mesh; American Society for Testing Materials), and dry flash chromatography was performed on Kieselgel 60H and Kieselgel 60GF.

### Spectroscopy

Infrared spectra were recorded on a PerkinElmer 1420 instrument (Beaconsfield, UK) as KBr discs or as films for liquids. <sup>1</sup>H-NMR spectra were taken on a Varian CFT-20 (Walton, Surrey, UK) or a JEOL JNM-FX200 instrument (Welwyn Garden City, Herts, UK) in deuterated solvents with tetramethylsilane as an internal standard. Mass spectra were recorded on a modified MS 902 AEI instrument.

### Extraction studies

Buffers were prepared with deionized water. pH measurements were performed with a Corning 240 instrument (Corning Instruments, Ltd., Halstead, Essex, UK). Carbonate buffer solutions were prepared with the appropriate volumes of 0.1M sodium carbonate (750 cm<sup>3</sup>) and 0.1M sodium bicarbonate (250 cm<sup>3</sup>).

The appropriate amount of NaB(OH)<sub>4</sub> in the buffer solution was agitated with the respective polymer in a polythene bottle for 20 h. The polymer was then filtered, and the amount of borate in the filtrate was determined by atomic absorption with a PerkinElmer 2380 spectrophotometer with a PRS-10 printer sequencer. The experiments were duplicated.

### 1,2-Dihydroxybenzene(catechol)/formaldehyde polymer

To a stirred mixture of catechol (24.9 g, 226 mM) and 37% formaldehyde (21 cm<sup>3</sup>, 260 mM) in water (9 cm<sup>3</sup>) was added dropwise hydrochloric acid (1 cm<sup>3</sup>, 9 mM)

over 1 h. The mixture was then heated and maintained at 60°C for 2 h, during which a dark red, viscous liquid formed. After this time, the heating was reduced to keep a temperature of 30°C for 24 h. The resultant red solid was filtered, washed with water, and dried *in vacuo* at 80°C for 16 h to afford a solid block (yield = 26.7 g). This was crushed, washed with water, dried at 80°C, and, after cooling to the ambient temperature, crushed to a 20-μm particle size in a ball mill.

### Reference phenol/formaldehyde polymer

This phenol/formaldehyde resin was prepared from phenol (40 g, 426 mM) and a 37% formaldehyde solution (40 cm<sup>3</sup>, 430 mM) at 40°C by the dropwise addition of 3M hydrochloric acid (2.4 cm<sup>3</sup>, 7 mM) over 1 h followed by refluxing for 3 h (TLC monitoring). The reaction was then complete, and the volatile material was steam-distilled to leave, upon cooling, a red solid.

### Salicyl aldehyde/formaldehyde polymer

#### Sodium hydroxide catalyst

To a stirred, heated mixture of salicyl aldehyde (40 cm<sup>3</sup>, 328 mM) and 37% formaldehyde (35 cm<sup>3</sup>, 432 mM) was added dropwise 10M sodium hydroxide (2 cm<sup>3</sup>, 20 mM), and refluxing was maintained for 5 h. The viscous mass (TLC monitoring) was washed with water until it was neutral, and this resulted in a brown precipitate, which was filtered, dissolved in dimethylformamide, and reprecipitated with water. The resultant solid was filtered, washed with water, and dried at 150°C to give 17 g.

$\nu_{\max}$  (cm<sup>-1</sup>, KBr disc): 1650 (C=O).  $\delta_H$  (CDCl<sub>3</sub>): 3.87 (2H, s, ArCH<sub>2</sub>Ar), 6.80–7.28 (3H, m, HAr), 9.74 (1H, s, CHO), 11.12 (1H, s, HO, exchange).

#### Sulfuric acid catalyst

To the same heated quantities, 3M sulfuric acid (285 cm<sup>3</sup>, 855 mM) was added, and the mixture was refluxed for 50 h, at which point TLC monitoring indicated that the reaction was complete. The mixture was steam-distilled to remove the volatile material and cooled to afford a brown solid, which was filtered, washed with water, heated in air at 150°C, washed again with water, dissolved in dimethylformamide, and reprecipitated with water. The light brown solid was dried in air at 150°C to give 12 g with spectral properties identical to those of the base-catalyzed product.

### Saligenin/formaldehyde polymer

To a salicyl aldehyde/formaldehyde polymer (10 g) suspended in 3M sodium hydroxide at 0°C, sodium borohydride (4 g, 10 mol of propn.) was added in

small portions over 1 h. The mixture was allowed to warm to the ambient temperature and stirred for 2 h, acidified with dilute sulfuric acid, filtered, washed with water, and dried at 100°C *in vacuo* to give 8.2 g.

$\nu_{\max}$  ( $\text{cm}^{-1}$ , KBr disc): 3500 (OH).  $\delta_{\text{H}}$  [ $(\text{CD}_3)_2\text{CO}$ ]: 3.10 (1H, s, HO), 3.73 (2H, s,  $\text{ArCH}_2\text{Ar}$ ), 4.65 (2H, s,  $\text{ArCH}_2\text{OH}$ ), 6.71–7.05 (3H, m, HAr), 8.25 (1H, s, HOAr).

### 2-Hydroxy-4-methylbenzaldehyde/formaldehyde polymer

To a stirred mixture of 2-hydroxy-4-methylbenzaldehyde (10 g, 74 mM) and 37% formaldehyde (8  $\text{cm}^3$ , 99 mM), 3M sulfuric acid (55  $\text{cm}^3$ ) was slowly added, and the mixture was then refluxed for 50 h, at which point TLC monitoring indicated that the reaction was complete. The product was worked up as for the salicyl aldehyde analogue to afford finally 3.50 g.

$\nu_{\max}$  ( $\text{cm}^{-1}$ , KBr disc): 1655(C=O).  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ): 2.35 (3H, s, Me), 3.86 (2H, s,  $\text{ArCH}_2\text{Ar}$ ), 6.82–7.26 (3H, m, HAr), 9.73 (1H, s, CHO), 11.05 (1H, s, HO).

### 2-Hydroxymethyl-5-methylphenol/formaldehyde polymer

To a 2-hydroxy-4-methylbenzaldehyde polymer (3 g) suspended in 3M sodium hydroxide (30  $\text{cm}^3$ ) at 0°C, sodium borohydride (1.50 g) was added slowly, and the reaction was allowed to proceed as for the salicyl aldehyde polymer. The workup afforded 2.50 g of a light brown solid after drying *in vacuo* at 100°C.

$\nu_{\max}$  ( $\text{cm}^{-1}$ , KBr disc): 3480 (OH).  $\delta_{\text{H}}$  [ $(\text{CD}_3)_2\text{CO}$ ]: 2.20 (3H, s, Me), 2.95 (1H, s, OH), 3.71 (2H, s,  $\text{ArCH}_2\text{Ar}$ ), 4.64 (2H, s,  $\text{ArCH}_2\text{OH}$ ), 6.73–7.12 (3H, m, HAr).

### 2-(4-Hydroxyphenyl)-propane-1,3-diol/formaldehyde polymer

To a stirred mixture of 2-(4-hydroxyphenyl)-propane-1,3-diol (0.50 g, 3 mM) and a 37% formaldehyde solution (0.30  $\text{cm}^3$ , 4 mM), 2M sulfuric acid was slowly added, and the heating was maintained until the reaction was complete (TLC monitoring) after 6 h of refluxing. The mixture was worked up as before for the salicyl and methyl salicyl aldehyde polymers to give a pale brown solid, which was dried at 100°C *in vacuo* and finally washed with ethyl acetate and with light petroleum (40–60°C).

$\nu_{\max}$  ( $\text{cm}^{-1}$ , KBr disc): 3550 (OH).

## RESULTS AND DISCUSSION

### Polymerization of the diols

The reactions of the various diols generally proceeded to moderate-to-good yields by either base or

acid catalysis to give solid products that were comminuted into powders with 20- $\mu\text{m}$  particles.

The polymeric saligenins were prepared by the reduction of the respective polymeric precursor salicyl aldehyde to retain the *o*-hydroxymethyl group for subsequent chelation.

The condensation of formaldehyde took place at *o*- and *p*-positions to the phenolic hydroxyl group. In the case of catechol **1**, four such positions are available. With salicyl aldehyde, only two positions are probably available on account of the deactivating influence of the formyl group; for 2-hydroxy-4-methylbenzaldehyde, probably only two positions are available for methylene group introduction, one being sterically hindered. Compound **3** has two *o*-positions available for condensation. The structures of the formaldehyde polymers of diols **1** and **2** (R = H or Me) and **3** are depicted as **5**, **6**, **7**, and **8**:

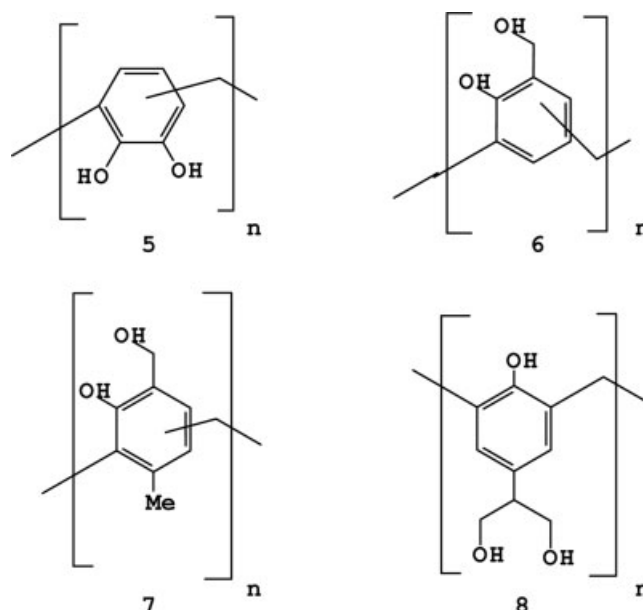


TABLE I  
Chelation of Borate by Phenolic Diol Polymers

Polymer (with HCHO)	Amount (mg)	Removed boron (mg)	Removal (%)
Catechol	0.50	2.80	60
	1.0	6.0	
Saligenin	0.50	2.6	54
	1.0	5.4	
Methyl saligenin	0.50	2.5	48
	1.0	4.8	
2-(4-Hydroxyphenyl)-propane-1,3-diol <sup>a</sup>	0.10	0.9	45
Phenol	0.50	0.20	2
	1.0	0.40	

<sup>a</sup> Twenty milligrams of  $\text{NaB}(\text{OH})_4$  was used in a 200- $\text{cm}^3$  buffer.

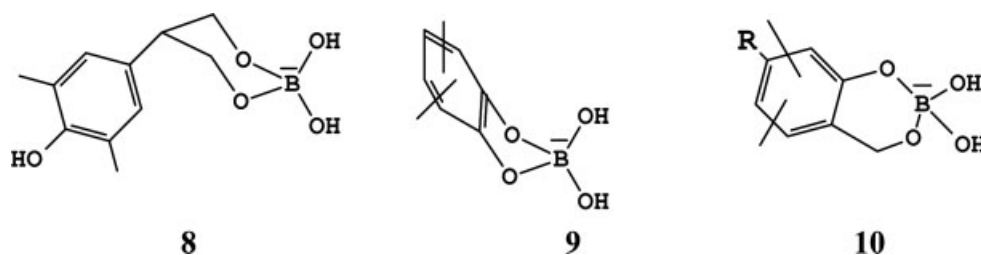


Figure 1 Probable structures of the diol-tetraborate complexes.

### Extraction of borate by phenolic diols

The amount of boron removed with the polymer (0.5 and 1.0 g) by  $\text{NaB}(\text{OH})_4$  (92 mg, containing 10 mg of boron) in a buffer solution (200  $\text{cm}^3$ ) at pH 10.40 was examined with the four phenolic diol/formaldehyde polymers studied. Thus, the results obtained with the formaldehyde polymer systems from catechol, saligenin, and methyl saligenin and from 2-(4-hydroxyphenyl)-propane-1,3-diol are given in Table I.

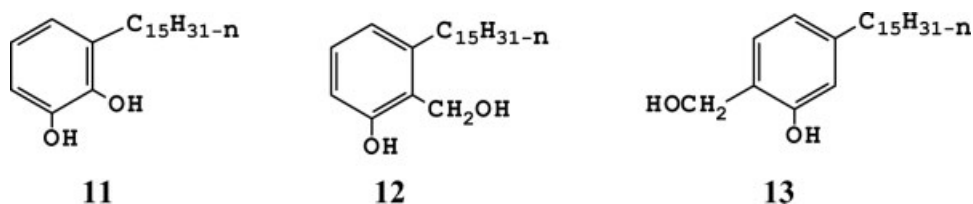
The results show that the formaldehyde/diol polymers have a complexing ability toward borate and that polymerization does not impair chelation. It can be concluded that the polymers from **1** and **2** ( $R = \text{H}$ ) and **2** ( $R = \text{Me}$ ) have removed 18, 16, and 15 ppm boron, respectively, from a buffered solution containing initially 27 ppm boron. The polymer from **3** has removed 4.5 ppm boron from a solution initially containing 10 ppm boron. By contrast, the phe-

nol/formaldehyde polymer does not take up the borate anion. Probable structures **8**, **9**, and **10** for the polymeric borate complexes from **3** (six-membered chair), **1** (five-membered), and **2** ( $R = \text{H}$  or  $\text{Me}$ ), respectively, are shown in Figure 1 (the bonds to the formaldehyde polymer are depicted as unattached).

The more planar (aryl-1,2-dioxy) structure in **9** appears to result in more effective chelation than those in **8** (chair) and **10** (semichair). Generally, the flexible conformations in the original diols, **2** ( $R = \text{H}$  or  $\text{Me}$ ) and **3**, do not appear to confer more facile chelation than that in **1**.

As in the carbocyclic series, a five-membered ring containing boron is likely to be more stable than a six-membered ring.

In solvent-extraction studies with monomeric systems, Tyman and Mehet<sup>4</sup> found that the catechol structure in 2,3-dihydroxypentadeca(enyl)benzene (urushiol **11**) was superior to the saligenin structures in anacardic (**12**) and isoanacardic alcohols (**13**):



With simple aliphatic 1,2- and 1,3-diols, a progression was found<sup>19</sup> from a 1 : 1 diol/borate complex to a 2 : 1 diol/borate complex; our results (to be described elsewhere), determined with a spectrophotometric method and <sup>11</sup>B-NMR, with these more complex monomeric phenolic diols support a 1 : 1 structure in solution. For the diols in a polymeric form with formaldehyde, a 1 : 1 diol/borate ratio would appear to be more feasible than a 2 : 1 structure. Unfortunately, polymers from diol **4** could not be examined for borate complexation. Additionally, the regeneration or recovery of borate or boric acid from the polymers remains to be investigated.

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