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Strategic Synthesis of Model Novolac Resins

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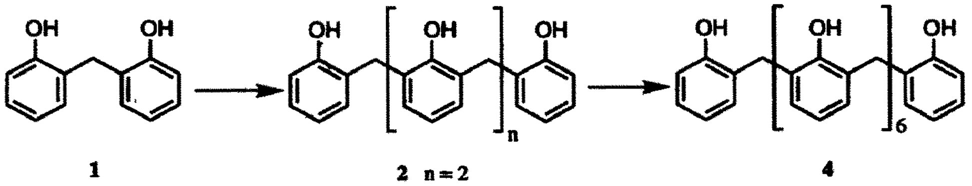
Keywords: Novolac Resin; Hexamethylenetetramine; Phenol-Formaldehyde Resin; Curing.

Abstract: Model novolac resins which contain the maximum number of free *ortho* positions for reaction with the curing agent hexamethylenetetramine (HMTA) have been prepared. The key transformation was the ion assisted *ortho*-specific phenol-formaldehyde oligomerization of suitably protected precursors.

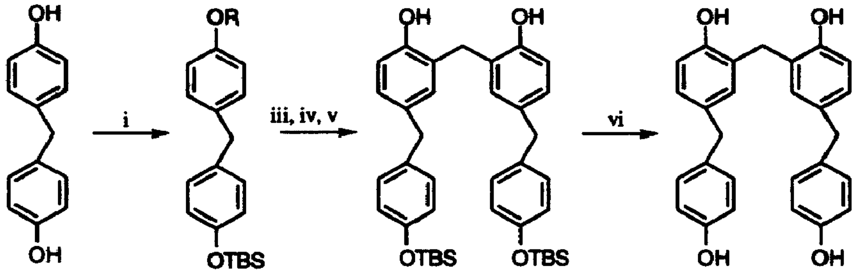
Since the pioneering work by Baekeland,[1] in 1907, phenol-formaldehyde resins have become one of the most versatile synthetic polymers with a large range of commercial applications. Many of the physical and mechanical properties that enable these resins to be widely utilised can be directly related to the curing process. Hence, over the years phenol-formaldehyde resins have been extensively studied in an effort to identify the reaction mechanisms and reactive intermediates that occur during curing. However, due to the complexity of these systems, there still exists a great deal of uncertainty with regard to the overall process. In an attempt to understand these complicated systems we, along with several other groups,[2-11] have examined the chemistry of curing of simple novolac model compounds such as the xylenols and cresols with hexamethylenetetramine (HMTA). These studies have shown that the curing process proceeds through a range of intermediates which include benzoxazines, tribenzylamines and azomethines. Our investigations, on these monomeric model systems, indicate that the various pathways are determined by whether the curing agent, HMTA, reacts initially at a position *ortho* or *para* to the hydroxyl substituent on the phenolic ring. This study has now been extended to include higher model systems consisting of novolac resins of between 2-8 units. This communication describes the methodology developed for the strategic synthesis of model novolac resins, consisting of 4 or 8 phenolic units, which contain the maximum number of free *ortho* positions.



1　　**2** n = 2　**3** n = 4　　**4**

Scheme 1

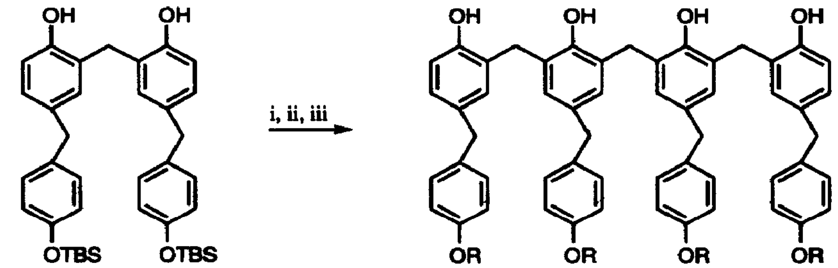
The synthetic scheme for the preparation of the model resins is based on the reported ion assisted *ortho*-specific phenol-formaldehyde oligomerization developed by Casiraghi and co-workers[12] for the selective synthesis of the phenolic systems **1-4**, which contain the maximum number of free *para* positions. It was anticipated that the synthesis of the series of model oligomers containing the maximum number of free *ortho* positions would be somewhat more complex than the all *ortho*-linked homologues (**1-4**). The synthesis starts with the commercially available *para*-linked dimer **5**. Coupling of this system with paraformaldehyde would result in the formation of the desired tetramer **9**, however further coupling is complicated due to the fact that there are two different types of *ortho* sites in **9**, which both have the potential to react, resulting in a complex non-selective mixture of products. Therefore, protection/deprotection procedures had to be developed in order to control the regioselectivity of the coupling reaction to generate oligomers higher than 4 units.



5 | **6** R = H, **7** R = TBS (ii) | **8** | **9**

Scheme 2. *Reagents and Conditions*: i, TBSCl (1.2 eq.), imidazole, DMF, 25 °C, 5 h (**6** 47 %, **7** 42 %); ii, TBAF, THF, 0 °C, 30 min (40 %); iii, Mg (1 eq.), EtBr (1 eq.), Et_2O, 25 °C, 30 min; iv, **6**, Et_2O, 25 °C, 30 min, then benzene, 25 °C to 80°C; v, paraformaldehyde (0.5 eq.), 80°C, 20 h (72 %); vi, TBAF, THF, 0 °C, 30 min (70 %).

Treatment of the *para*-linked dimer **5** with *tert*-butyldimethylsilyl chloride (TBSCl) and imidazole in anhydrous DMF[13] at room temperature gave a mixture of products. Preparative chromatography afforded the desired mono *tert*-butylsilyl protected dimer **6** in 47 % yield. The remainder of the mixture was identified as the bis *tert*-butyldimethylsilyl product **7** which could be converted by selective deprotection to afford **6**, as well as the dihydroxy starting material **5** (Scheme 2). The mono silylated dimer **6** was found to be susceptible to silyl migration at room temperature resulting in formation of three products resembling the original reaction mixture prior to chromatography. Therefore the dimer **6** was only stored at -18°C, for short periods of time. The metal phenoxide of the mono-silylated dimer **6** was generated by treatment with ethyl magnesium bromide and subsequent coupling using paraformaldehyde in refluxing benzene for 20 h selectively gave the *ortho-ortho* linked bis-silylated tetramer **8** in 72% yield. The site selectivity of the coupling reaction was evident by the appearance of a signal at δ 30.9 in the ^{13}C NMR spectrum which is characteristic of a *ortho-ortho* methylene bridge.[14, 15] This is distinct from the *para-para* methylene bridge (δ 40.1) present in the starting dimer **5**.

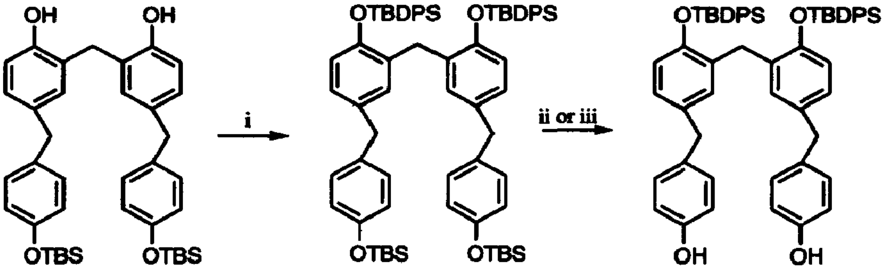


8 | **10** R = TBS, **11** R = H (iv)

Scheme 3. *Reagents and Conditions*: i, Mg (2 eq.), EtBr (2 eq.), Et_2O, 25 °C, 30 min; ii, **8**, Et_2O, 25 °C, 30 min, then benzene, 25 °C to 80°C; iii, paraformaldehyde (0.5 eq.), 80°C, 20 h (92 %); iv, TBAF, THF, 0 °C 10 min (83 %).

Compound 8 was a key intermediate in the synthesis of both linear and branched model octamers containing only free *ortho* positions. The tetramer 8 could be conveniently deprotected using tetrabutylammonium fluoride (TBAF)[13] to afford the first of the model resins, tetramer 9 (Scheme 2). The preparation of tetramer 9 can also be carried out in one step from the *para*-linked dimer 5 by coupling using the ethyl magnesium bromide conditions, however, this material cannot be converted regioselectively to the desired octamers 11 and 15, due to the reasons discussed earlier.

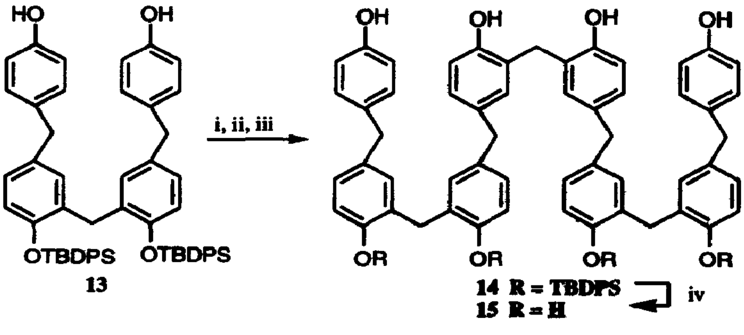
The synthesis of the branched system was carried out in two steps from tetramer 8 (Scheme 3). Coupling of the magnesium bromide salt of bissilylated tetramer 8, using the standard conditions, afforded the carbon skeleton 10 required for the branched octamer in an excellent yield (92 %). The branched model resin 11 was obtained after removal of the *tert*-butyldimethylsilyl protecting group using TBAF in tetrahydrofuran, at room temperature.



8 12 13

Scheme 4. *Reagents and Conditions*: i, TBDPSCl (4.5 eq.), imidazole (6 eq.), DMF, 60 °C, 10 h (67 %); ii, HF-pyridine, pyridine, THF, 0 °C, 10 min, then 25 °C, 4.5 h (80 %); iii, BF_3Et_2O, $CHCl_3$, 0 °C, 10 min, then 25 °C, 3 h (96 %).

The preparation of the analogous linear system was more complex as it required a further protection step followed by a selective deprotection to unmask the terminal hydroxy group of the tetramer, necessary to direct the *ortho*-specific coupling reaction. Masking of the remaining hydroxy groups required the use of a more robust protecting group so as to facilitate the selective deprotection later in the synthesis (Scheme 4). Therefore the tetramer 8 was treated with *tert*-butyldiphenylsilyl chloride[16] (TBDPSCl) at 60 °C to afford the fully protected compound 12. The selective deprotection of tetramer 12 was unsuccessful using TBAF under a variety of conditions with one or both of the TBDPS groups also being cleaved. However, use of either HF-pyridine[17] or boron trifluoride etherate[18] afforded the bis *tert*-butyldiphenylsilyl protected system 13 in good yield in both cases.



13

Scheme 5. *Reagents and Conditions*: i, Mg (2 eq.), EtBr (2 eq.), Et_2O, 25 °C, 30 min; ii, 13, Et_2O, 25 °C, 30 min, then benzene, 25 °C to 80°C; iii, paraformaldehyde (0.5 eq.), 80°C, 20 h (45 %); iv, TBAF, THF, (97 %).

Coupling of **13** under the usual conditions afforded the octamer **14** which was fully deprotected by treatment with TBAF to give the desired linear octamer **15** (Scheme 5). The *ortho*-specific coupling reaction of **13** proceeded in 45 %, which compares with the reported literature values for the preparation of the *ortho*-linked tetramer **2** and octamer **4** (32 and 24 % respectively). However, the yield for the coupling reaction of **13** was disappointing considering the good yields obtained earlier in the silylated series to prepare tetramer **8** and octamer **10** (72 and 92 % respectively).

Model resins **9**, **11** and **15** were prepared using methodology that was based on the ion assisted *ortho*-specific phenol-formaldehyde procedure.[19] The synthesis of these three systems provides the opportunity to investigate the role the structure of the novolac resin plays in determining the properties of the cured system. The protection/deprotection methodology developed for the preparation of these compounds will be extended to the synthesis of other model resins differing in the *ortho*:*para* ratio and degree of branching which would increase the variety of compounds that could be included in the curing studies.

Acknowledgements

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19. Model resins **9**, **11** and **15** exhibited spectroscopic (^{1}H and ^{13}C NMR) and analytical (combustion analysis or high resolution MS) data in accord with the assigned structure.

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