CHAPTER 14

PHENOL–, UREA–, AND MELAMINE–FORMALDEHYDE POLYMERS

14.1 Introduction

Phenol (**1**), urea (**2**), and melamine (**3**) are three compounds of seemingly disparate structure; yet they are related in terms of how they react with formaldehyde, as well as in the processing and applications of the resultant polymers.

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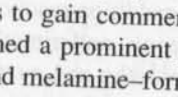

$$H_2N-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2$$

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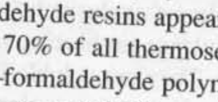

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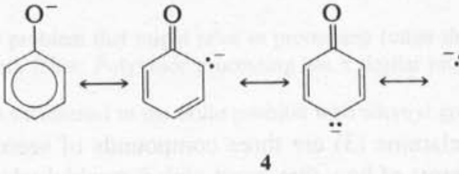
Phenol–formaldehyde condensation polymers, often referred to as *phenolic resins*, were the first true synthetic polymers to gain commercial acceptance. This occurred early in this century, and they have maintained a prominent position in the polymer market to the present time. Urea–formaldehyde and melamine–formaldehyde resins appeared a few years later (in the early 1920s and 1930s, respectively). About 70% of all thermosetting polymers produced is made up of phenol–, urea–, and melamine–formaldehyde polymers, with phenolics enjoying the lion's share. Because the three polymer types exhibit some similarities in their chemistry, but more important, because their processing and end-use applications are related, they are treated together in this chapter.

Phenol–formaldehyde resins$^{1-6}$ are normally prepared by two different methods. One involves a base catalyst with an excess of formaldehyde over phenol. The initially formed product (called a *resole*) can be cured to a thermosetting polymer simply by heating; as such, it constitutes a one-component system. The other method utilizes an excess of phenol over formaldehyde in the presence of an acidic catalyst. In this case, the initial product, called a *novolac* (also spelled *novolak*), requires the addition of more formaldehyde to effect curing. The chemistry of these two processes is discussed below.

Phenolic resins are widely used as lacquers and varnishes, molding compounds, laminates (particularly for decorative wall panels and table tops), and adhesives (notably for plywood and particle board).[7] Flameproof fibers based on crosslinked novolacs (Carborundum trade name Kynol) are used for thermal insulation and protective clothing.[8] Urea and melamine resins[7,9,10] (often referred to as *amino resins*) are used in similar applications and also in the treatment of textiles for improved crease and shrink resistance and for improving the wet strength of paper. Phenolic polymers are sometimes used as ion-exchange resins when other functional groups are present.

14.2 Phenol–Formaldehyde Polymers: Resoles

Resoles are the product of the reaction between phenol and excess formaldehyde in the presence of base. Under these conditions phenol is present as the resonance-stabilized anion (**4**).



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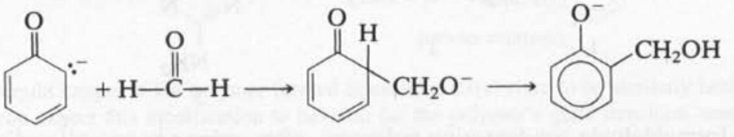
The first step in the polymerization involves addition of the anion to formaldehyde to give *ortho*- and *para*-substituted methylolphenols. This is shown (reaction 14.1) for the *ortho* product.* (Although reactions involving the *ortho* positions only are given below, it is understood that analogous reactions also occur at *para* positions.)



(14.1)

Because phenol is very reactive, simple monoaddition reactions seldom occur; instead, a mixture of monomethylolphenols, dimethylolphenols, and trimethylolphenols is formed with substitution occurring almost exclusively at the *ortho* and *para* positions. The initially formed methylolphenols condense on heating to give *resoles*, which are, in effect, low-molecular-weight prepolymers. They are soluble in base and contain a large number of free methylol groups. Resoles are, of course, complex mixtures of compounds, but a representative structure (**5**) is given. The methylene bridges linking the benzene rings result from condensation between methylolphenols and available *ortho* or *para* positions, either by direct S_N2 displacement of the hydroxyl group (14.2) or by Michael addition (14.4) to an *ortho* or

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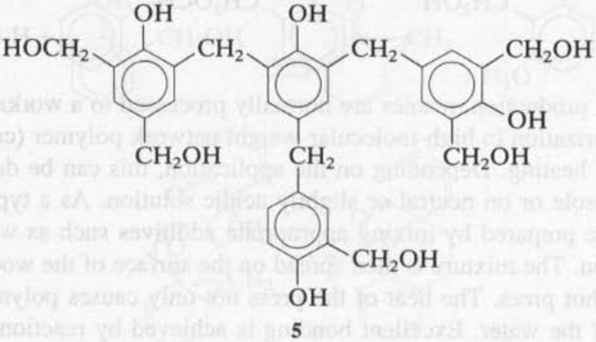
*Addition does not occur at the oxygen atom because the product, a hemiacetal, is unstable. Furthermore, the Cannizzaro reaction of formaldehyde to give methanol and formate ion is not a significant side reaction because the rate is much lower than that of formaldehyde with phenolate anion.

para quinone methide structure that might be present in equilibrium (14.3) with the methylol anion.



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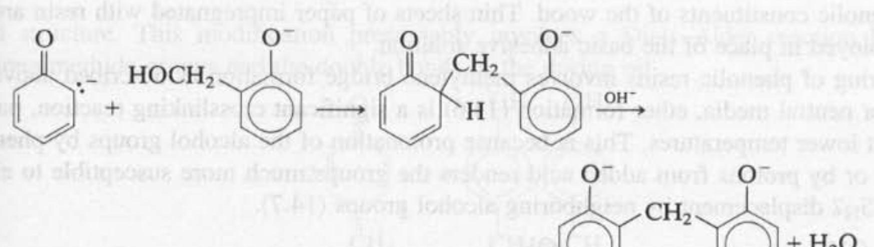

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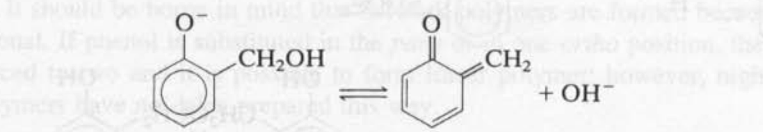
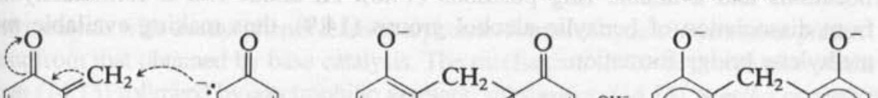
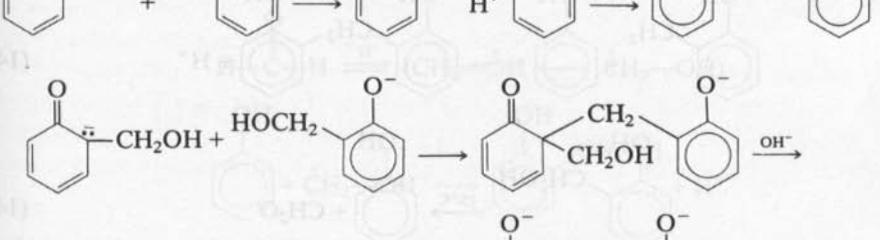


(14.3)

Studies with model compounds such as *o*-hydroxybenzyl alcohol (also known as saligenin) show that formaldehyde is also evolved in methylene bridge formation, suggesting that initially the bridge can occur at a carbon bearing a methylol group (14.5).

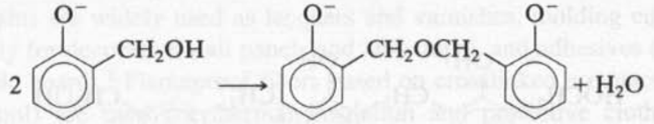


(14.4)



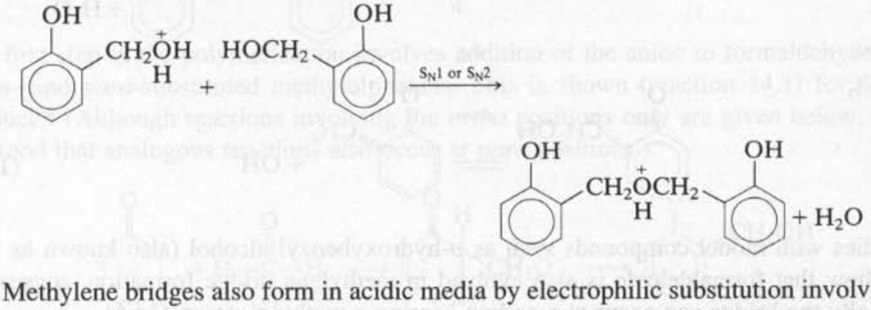
(14.5)

Ether linkages may also form (14.6), if the solution is very weakly basic or neutral.

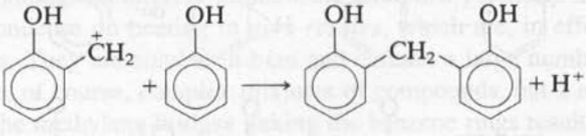

(14.6)

In commercial production, resoles are normally processed to a workable viscosity; then subsequent polymerization to high-molecular-weight network polymer (called *resite*) can be effected simply by heating. Depending on the application, this can be done directly on the base solution of resole or on neutral or slightly acidic solution. As a typical example, plywood adhesives are prepared by mixing appropriate additives such as wood flour with the basic resole solution. The mixture is then spread on the surface of the wood veneers prior to placing them in a hot press. The heat of the press not only causes polymerization to occur but also steams off the water. Excellent bonding is achieved by reaction between the resin and phenolic constituents of the wood. Thin sheets of paper impregnated with resin are often employed in place of the basic adhesive solution.

Curing of phenolic resins involves methylene bridge formation as described above. In acidic or neutral media, ether formation (14.6) is a significant crosslinking reaction, particularly at lower temperatures. This is because protonation of the alcohol groups by phenolic protons or by protons from added acid renders the groups much more susceptible to either S_N1 or S_N2 displacement by neighboring alcohol groups (14.7).


(14.7)

Methylene bridges also form in acidic media by electrophilic substitution involving benzylic carbocations and available ring positions (14.8). At about 150°C formaldehyde is evolved from dissociation of benzylic alcohol groups (14.9), thus making available more sites for methylene bridge formation.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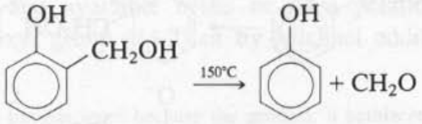
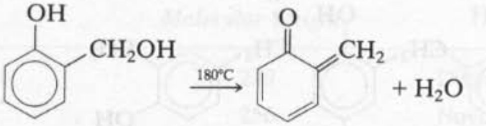
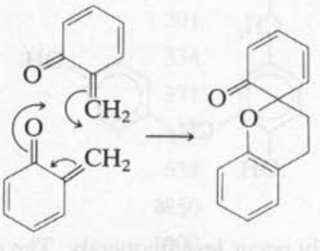

(14.9)

A reaction that occurs at about 180°C and that contributes to crosslinking is dehydration to form the highly reactive *ortho* or *para* quinone methides (14.10), which undergo a variety of reactions including cycloaddition with other quinone methides to give chroman groups

(14.11) or dimerization to give unsaturated linkages (14.12). Phenolic resins have been modified by reaction with drying oils to incorporate some flexibility into the otherwise very

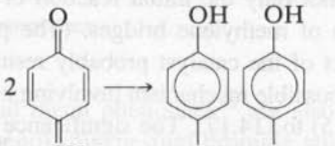


(14.10)



(14.11)

rigid structure. This modification presumably involves a Diels–Alder reaction between quinone methide groups and the double bonds of the drying oil.

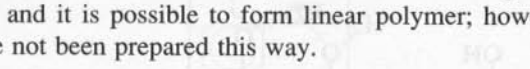


(14.12)

It is apparent, then, that high-molecular-weight phenolic resins have extremely complex structures. It should be borne in mind that network polymers are formed because phenol is polyfunctional. If phenol is substituted in the *para* or in one *ortho* position, the functionality is reduced to two and it is possible to form linear polymer; however, high-molecular-weight polymers have not been prepared this way.

14.3 Phenol–Formaldehyde Polymers: Novolacs

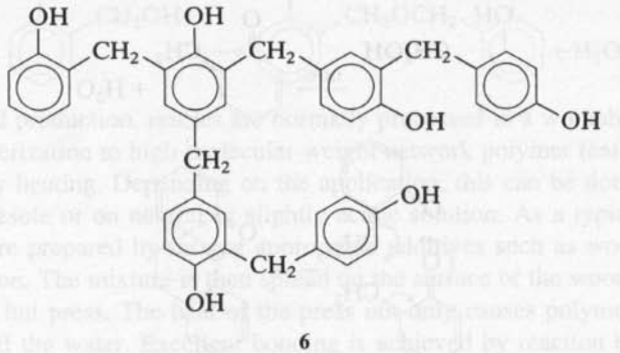
Acid catalysis with excess phenol leads to a phenol–formaldehyde condensation product quite different from that obtained by base catalysis. The mechanism involves protonation of the carbonyl group (14.13) followed by electrophilic aromatic substitution (14.14) at *ortho* or *para* positions.



$$\mathrm{H-\overset{\displaystyle O}{\overset{\|}{C}}-H} \overset{H^+}{\rightleftharpoons} (\mathrm{CH_2{=}\overset{+}{O}H} \longleftrightarrow \mathrm{\overset{+}{C}H_2{-}OH}) \quad (14.13)$$

(14.14)

Under acidic conditions further reaction occurs to give methylene bridges as discussed in the preceding section (reactions 14.7 and 14.8). The net result is the formation, in the early stages of polymerizaton, of complex mixtures of low-molecular-weight polymers (for example, **6**) characterized by having random *para–para*, *ortho–ortho*, or *ortho–para* methylene linkages. It has been shown, again with model compounds, that the *para* position is more reactive with strong acid catalysts at pH less than 3 (the usual condensation conditions); hence



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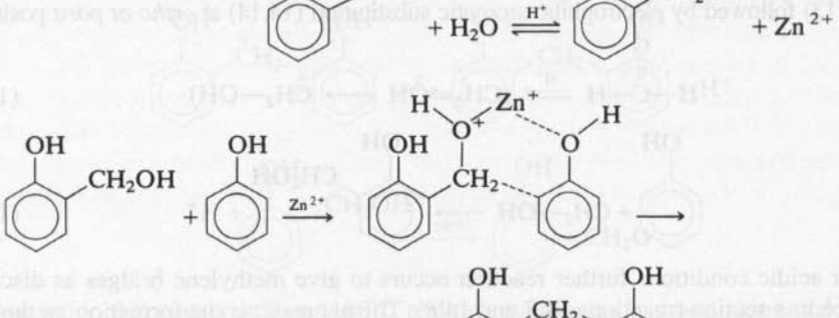
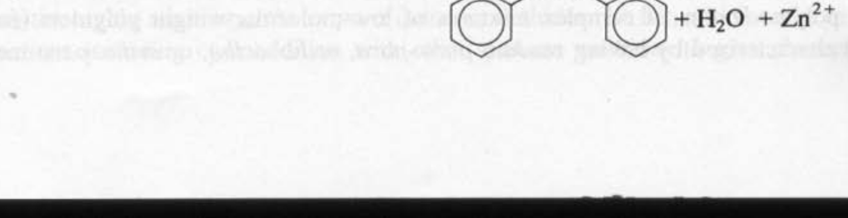
ortho–ortho linkages undoubtedly occur less frequently. The opposite is the case at pH 4.5 to 6 where condensation at *ortho* positions predominates. The use of divalent metal catalysts facilitates *ortho* condensation—not only the initial reaction of phenol with formaldehyde, but also the subsequent formation of methylene bridges. (The products are referred to as *o,o'*-novolacs.) This directive effect of the catalyst probably results from chelation involving the phenolic hydroxyl group.[11] A possible mechanism involving hydrated formaldehyde and a zinc salt is given in reactions (14.15) to (14.17). The significance of having substitution predominantly in the *ortho* positions is that curing (described below) occurs more rapidly because the more reactive *para* positions remain available for crosslinking.

$$Zn^{2+} + HOCH_2OH \rightleftharpoons {}^{+}ZnOCH_2OH + H^{+} \qquad (14.15)$$



(14.16)



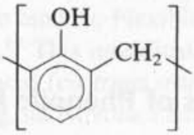
(14.17)

TABLE 14.1. Effect of Reactant Ratio on Molecular Weight[a]

Moles Formaldehyde/10 Moles Phenol	*Average Molecular Weight*	*Resin Type*
1	229	Dihydroxydiphenylmethane
2	256	Novolac
3	291	Novolac
4	334	Novolac
5	371	Novolac
6	437	Novolac
7	638	Novolac
8	850	Novolac
9	1000	Novolac
12	—	Resite

[a] From Carswell,[6] courtesy of Wiley-Interscience.

Organotin compounds[12] and metal phenolates[13] are also effective in promoting *ortho* substitution. The reaction of phenoxymagnesium bromide with formaldehyde, for example, results in low-molecular-weight linear novolacs (**7**). The reaction of phenol with paraformaldehyde in anhydrous xylene at 190°C yields similar products.[14]



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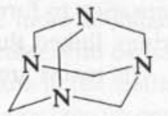
Unless excess phenol is used, the condensation reaction proceeds to high-molecular-weight infusible resin (resite), so in practice less than an equivalent of formaldehyde is reacted with phenol. The resultant product, a novolac, is fusible and has an average molecular weight dependent in large measure on the phenol/formaldehyde ratio, as shown in Table 14.1. Novolacs can also be prepared under basic conditions, but the reaction is complicated by a tendency toward chain branching and gelation. In the presence of divalent metal compounds, *ortho* condensation is preferred, as described above.

The basic difference between resoles and novolacs is that the latter contain no hydroxymethyl groups for all practical purposes and hence cannot be converted to network high polymer simply by heating. Crosslinking is brought about by adding additional formaldehyde or, more commonly, by adding paraformaldehyde or hexamethylenetetramine (**8**), a



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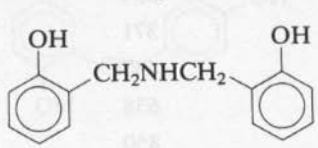
high-melting (>230°C) solid having an interesting cage structure that is obtained by the reaction of formaldehyde with ammonia. Formaldehyde is released from these compounds under the influence of heat and pressure, as in a molding operation, and crosslinking occurs again by formation of methylene bridges. Some benzylamine linkages (**9**) are also formed when hexamethylenetetramine is used. Other types of additives commonly used as reinforcers or extenders in molding formulas include wood flour, chopped rags, and glass fibers. Asbestos, once commonly used as a reinforcer, is now out of favor because of health concerns. Pigments are also added, as are stearates or oils to facilitate releasing from the mold. Phenolic resins are sometimes blended with synthetic rubber to enhance flexibility.



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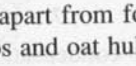
Commercial production of both resoles and novolacs involves two basic steps. The monomers and catalyst are reacted in aqueous solution to a relatively low viscosity; then water is removed under vacuum, and the solid product is ground to a powder. At this point the polymer is of relatively low molecular weight, soluble, and fusible. It is referred to as the A-stage. (As described earlier, aqueous solutions of resoles, with appropriate additives, are used directly as plywood glues or for impregnating paper.) The A-stage resin is mixed with additives (including hexamethylenetetramine or paraformaldehyde in the case of novolacs), then heated further to a higher-molecular-weight B-stage. The polymer is converted to resite (C-stage) in a final molding operation.

14.4 Chemical Modifications of Phenolic Resins

The only aldehyde of any significance, apart from formaldehyde, of use in phenolic resins is furfural (**10**), obtainable from corncobs and oat hulls. It is frequently used in the preparation of molding resins because it improves the polymer's flow properties. Some other aldehydes that have been studied are acrolein, acetaldehyde, and butyraldehyde, although reactions of the latter two are complicated by their tendency to undergo aldol condensations, particularly under basic conditions. Starch hydrolysates, which undergo dehydration to form 5-hydroxymethylfurfural (**11**) under acidic conditions, have also been investigated as a partial replacement for formaldehyde.[15] Related to **10** and **11** is furfuryl alcohol (**12**), which undergoes acid-catalyzed condensation to form chemically resistant polymers called *furan resins*,[16] which contain furan rings linked through methylene groups and thus are structurally related to phenolic resins. The resins are used as tank and vat linings in chemical plants.



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