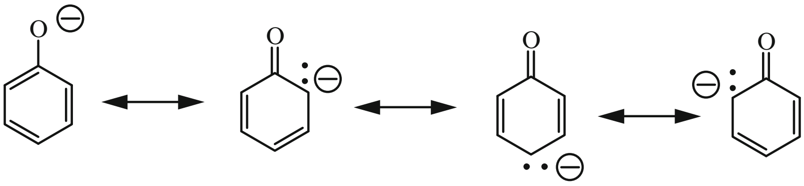
7.12 Phenol-Formaldehyde Resins

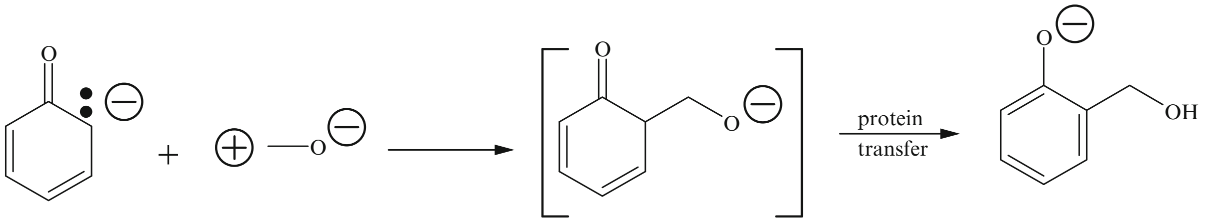
The phenolic resins are condensation products of phenol and formaldehyde [144–146, 148]. These materials were among the earliest commercial synthetic plastics. Two different methods [144–146] are used to prepare them. In the first one, the condensations are base catalyzed, while in the second one, they are acid-catalyzed. The products formed with basic catalysts are called *resols* and with acidic ones *novolacs*. Phenolic resins are used widely in coatings and laminates. The pure resins are too friable for use as structural materials by themselves. They become useful plastics, however, when filled with various fillers.

7.12.1 Resols

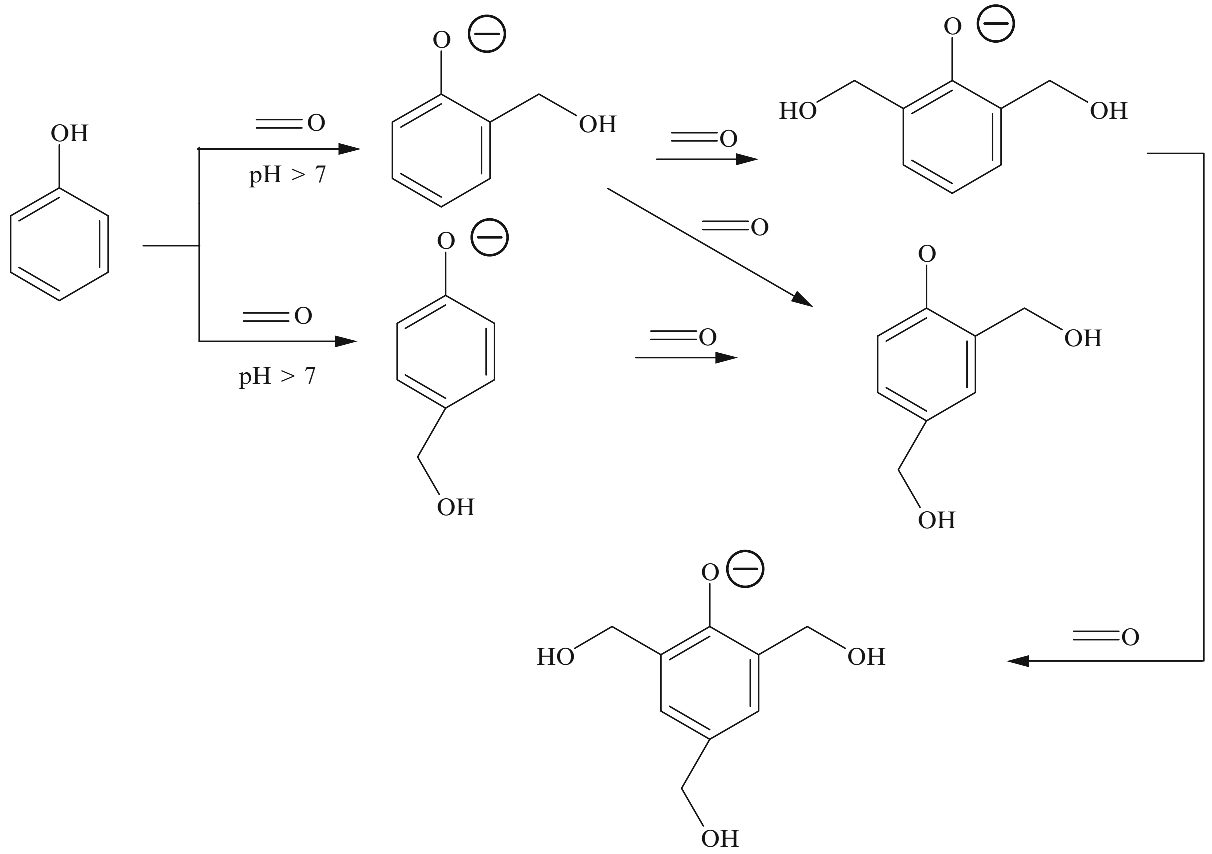
These thermosetting resins form in reactions of phenols with formaldehyde in water in the presence of catalytic amounts of bases. Under these conditions, phenol exists as a resonance-stabilized anion:



The addition of the phenol anion to formaldehyde is a typical nucleophilic reaction:



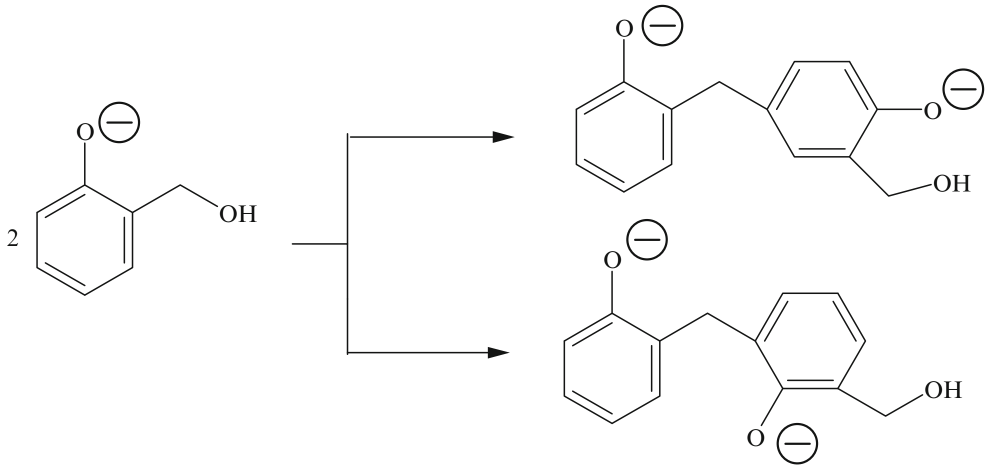
Both *ortho* and *para* methylolphenols form in the above reaction. Phenol is very reactive and monosubstituted phenols are hard to isolate from the reaction mixture, because di- and trisubstitution occurs rapidly. No substitutions were ever shown to take place in the *meta* position. The overall reaction is as follows:



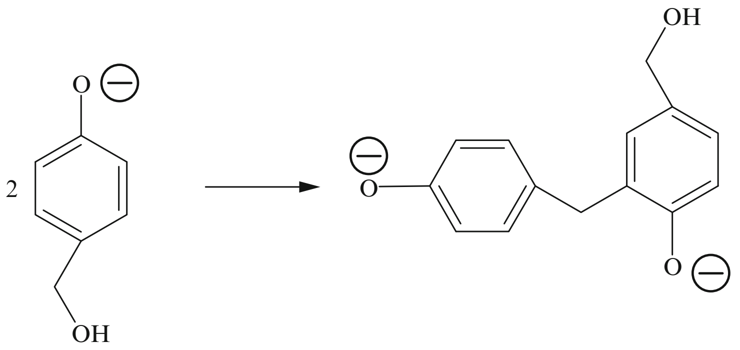
When an aqueous reaction of phenol and formaldehyde, catalyzed by sodium hydroxide, is carried out at 30°C for 5 h, the products are [147]:

2,4,6-trimethylolphenol	37%
2,4-dimethylolphenol	24%
2,6-dimethylolphenol	7%
p-methylolphenol	17%
o-methylolphenol	12%

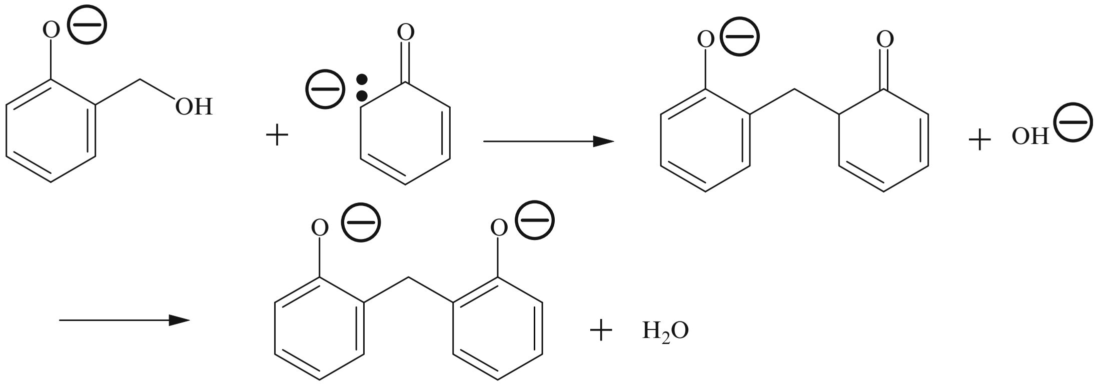
The remaining 3% is unreacted phenol. As the reaction continues, methylolphenols condense with each other to form methylene bridges:



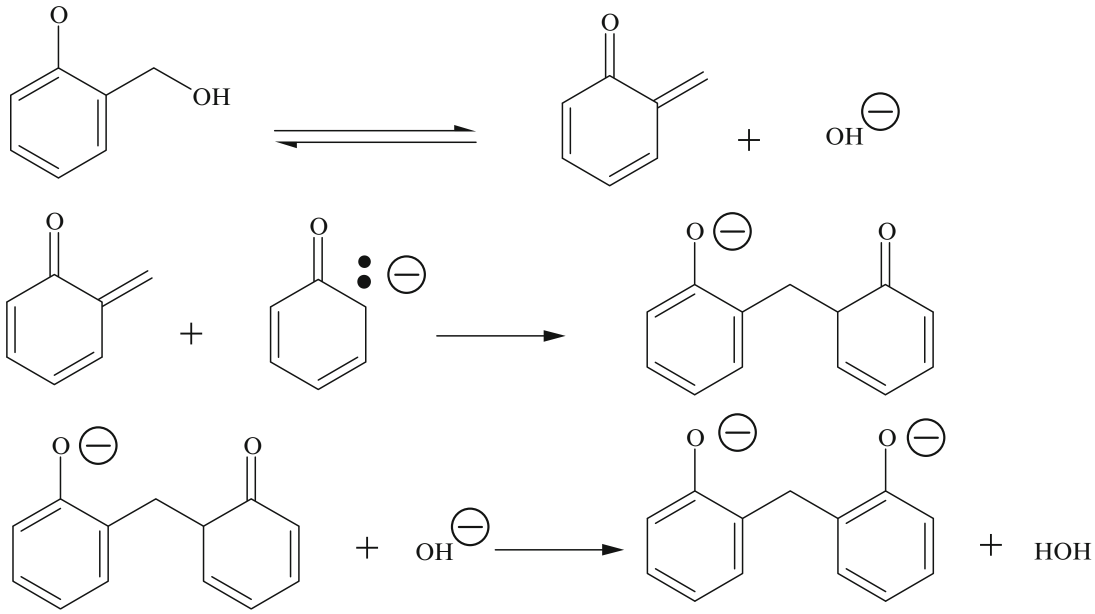
The *para* substituted methylolphenols, of course, react in the same manner:



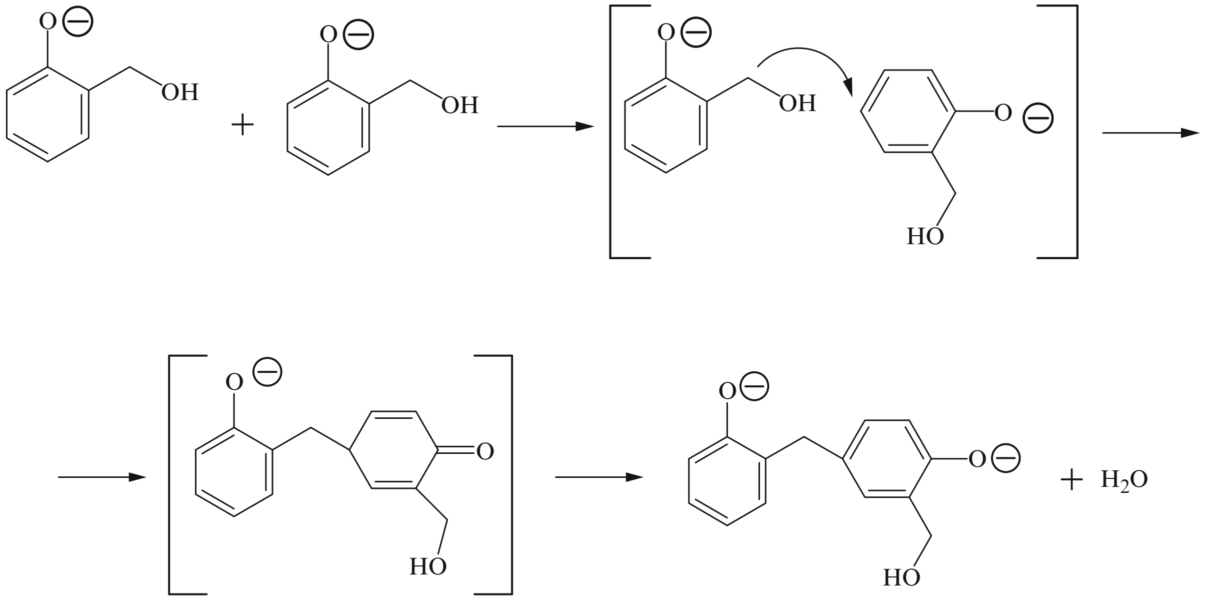
Formation of methylene bridges take place by one of two mechanisms. One is a direct S_N2 displacement:



The other one is addition of methylolated phenols to molecules of quinone methides that form at typical reaction conditions, particularly when the temperatures are elevated [144–146]:

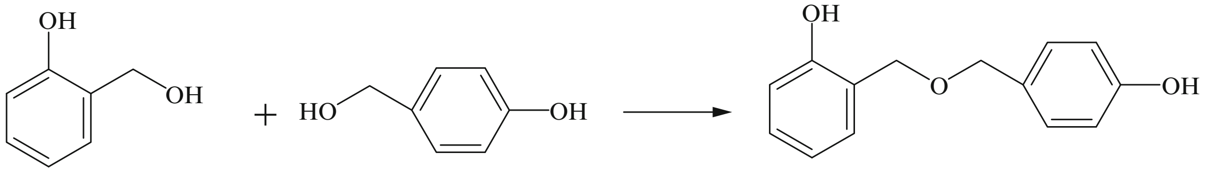


Two methylol-substituted phenols react with each other by the same mechanism:

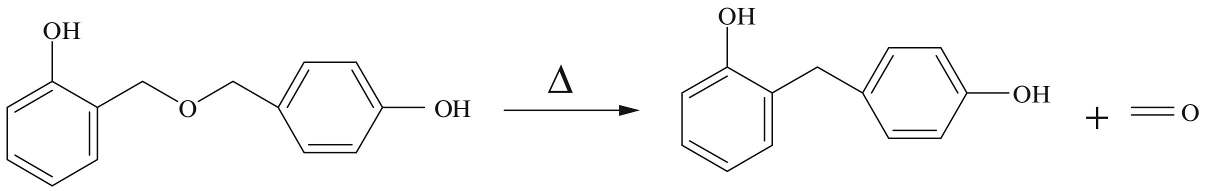


The same can be shown for *para* substituted methylolphenols. As the reaction continues, it leads to formation of trinuclear and tetra nuclear phenolic resins.

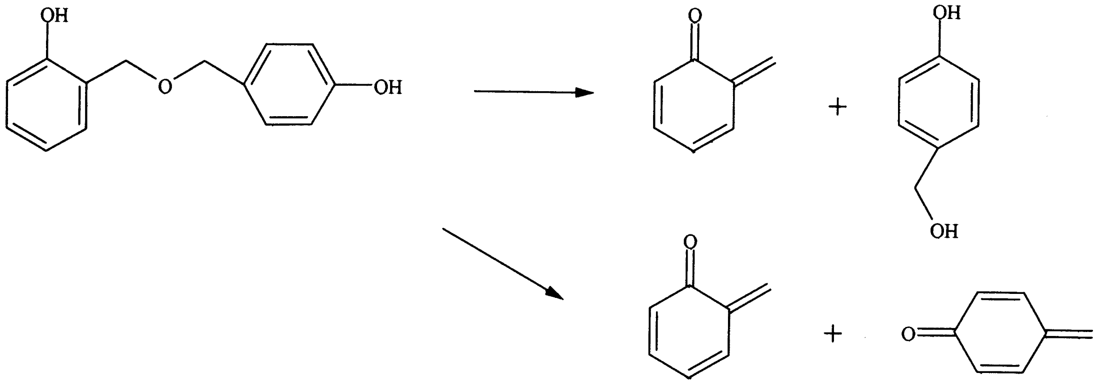
A typical liquid resole is quite low in molecular weight. It may contain no more than two or three benzene rings. Carried a little further, the condensation yields a solid resole. The pH is usually adjusted to neutral before the resoles are heated further for cross-linking. Under neutral or slightly acidic conditions, the methylol groups tend to form dibenzyl ethers:



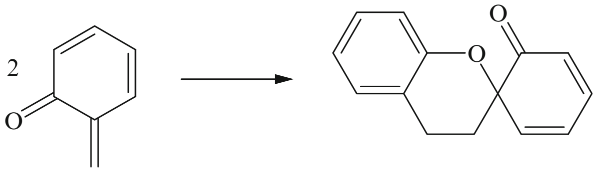
These dibenzyl ethers are unstable at higher temperatures, such as 150°C, and decompose to yield methylene bridges and formaldehyde [147]:



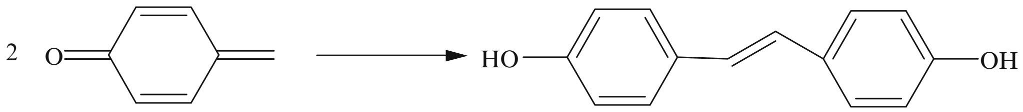
The structure of a typical resole contains both dimethylene ether and methylene bridges as well as methylol groups. Fusible and soluble resols are called A-stage resins. Further reactions cause these resins to pass through a rubbery stage where they can still be swollen by solvents. This is called B-stage. The finally cross-linked material is called C-stage resin. The cross-linking process involves complex and competing reactions. Each may be influenced by reaction conditions. When cross-linking of resoles take place at neutral or slightly acidic conditions, both methylene and ether linkages form. Upon heating, the ethers in turn split out formaldehyde, as shown above. The dibenzyl ethers [144–146, 148] also break down at elevated temperatures and form quinone methides:



The quinone methides can undergo a variety of reactions including cycloadditions with other methides to form chroman groups:

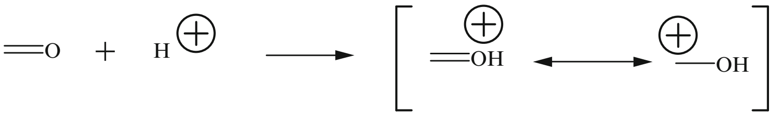


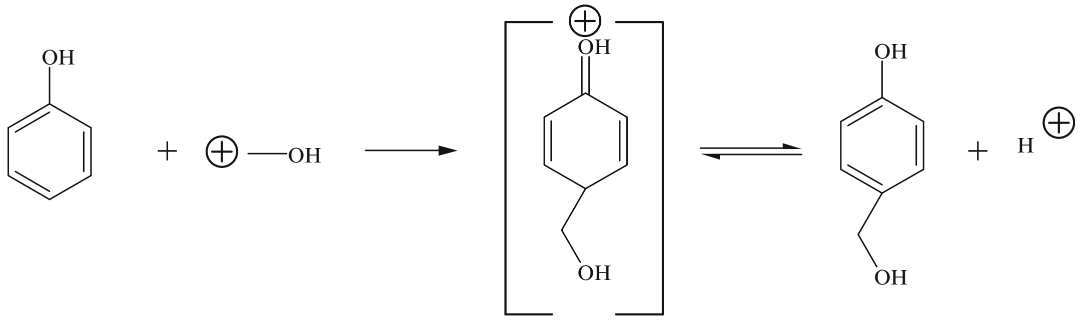
The *para* quinone methides can couple:

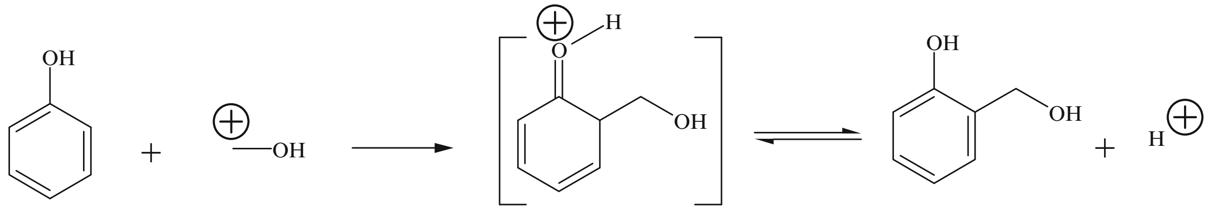


7.12.2 Novolacs

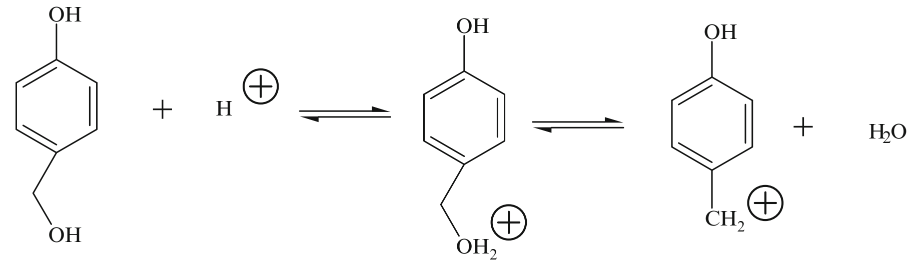
The phenolic resins that form in acid-catalyzed condensations of phenols with formaldehyde are different from resols. At pH below seven protonation of the carbonyl group of formaldehyde takes place first and is followed by electrophilic aromatic substitution at the *ortho* and *para* positions of the phenol. The initial steps of the reactions also take place in water. Here, however, a molar excess of phenol (1.25:1) must be used, because reactions on equimolar basis under acidic conditions form cross-linked resins. At a ratio of eight moles of formaldehyde to ten moles of phenol, novolacs of approximate molecular weight of 850 form [148]. When the ratio of formaldehyde to phenol is 9:10, a molecular weight of approximately 1,000 is reached. This appears to be near the limit, beyond which cross-linking results. The reaction is as follows:

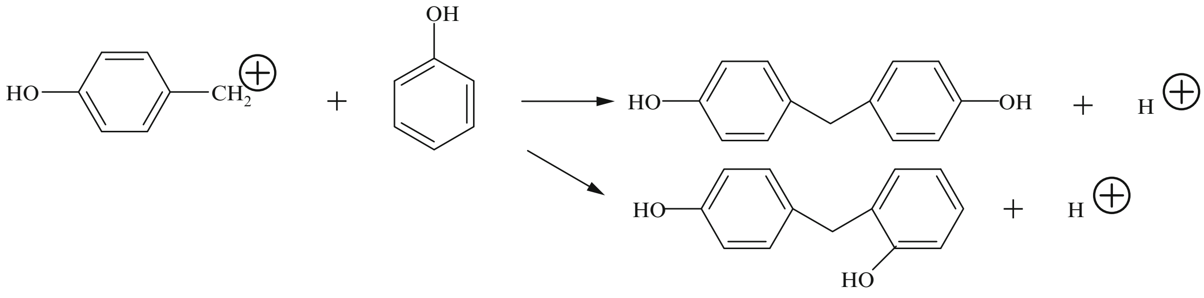






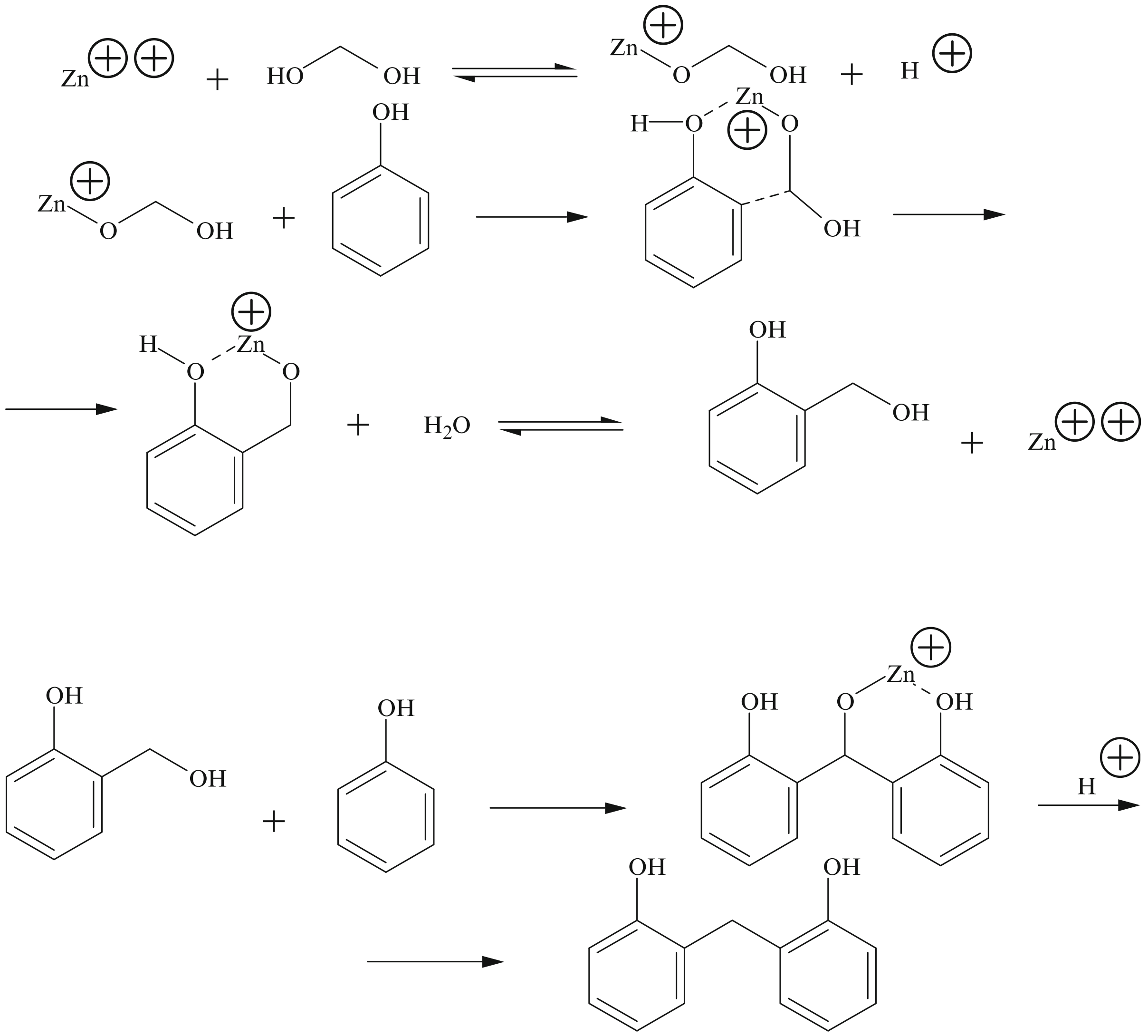
Because the reaction is taking place at pH below 7, the above shown *p*- and *o*-methylolphenols are transitory and are present in small concentrations only. Hydrogen ions convert them to benzylic carbocations that react rapidly with free phenol. This can be illustrated as follows:



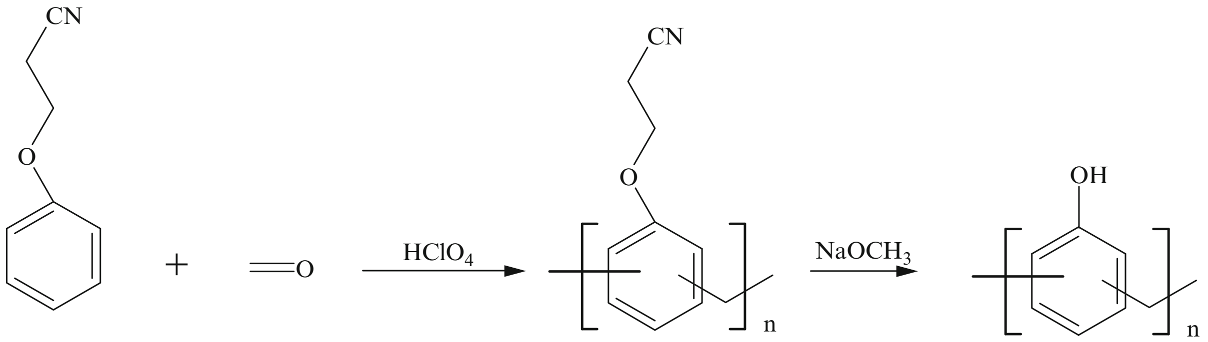


The *ortho* substituted methylolphenols react in the same manner.

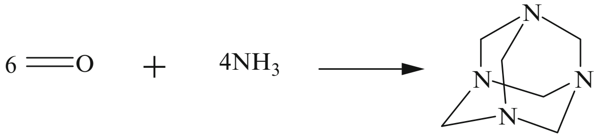
Further metholylation of dihydroxy diphenyl methanes takes place until all the formaldehyde is used up. Methylol groups react with each other quickly and form methylene bridges. The *para* position is more reactive than *ortho* [144–146] at pH below 3. The opposite is true, however, at pH 5–6, where the *ortho* position is more reactive. Typical novolacs formed in these reactions are not very high in molecular weight and contain no more than six to ten benzene rings. If divalent metal salts, like zinc acetate in acetic acid, are used to catalyze the reaction, then the *ortho* positions become considerably more reactive [150]. As a result, *ortho*-methylene bridges predominate in the products:



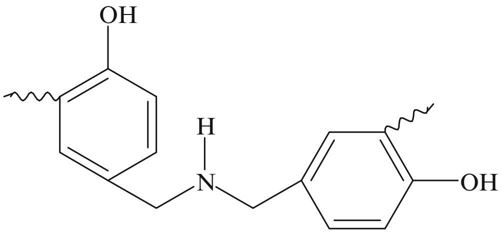
It is possible to form high molecular weight novolacs by carrying out the reactions of alkyl phenyl ethers with formaldehyde in acetic acid in the presence of perchloric acid [149]:



Novolacs are cross-linked by additions of more formaldehyde to the soluble, thermoplastic materials. The additional formaldehyde can be in the form of paraform, an oligomer of formaldehyde that decomposes to formaldehyde upon heating. It can also come from hexamethylenetetramine, a condensation product of formaldehyde with ammonia:



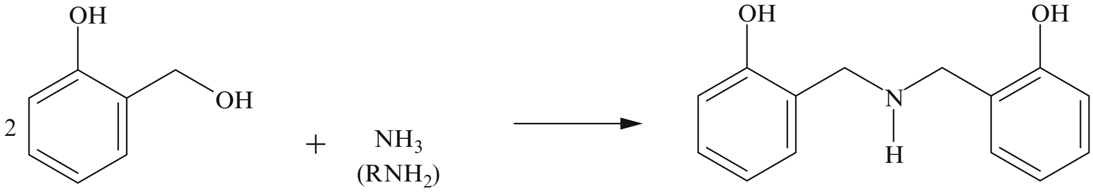
Hexamethylenetetramine decomposes to formaldehyde and ammonia upon heating. Some of the ammonia is picked up by the novolacs with the result that there are some benzylamine bridges in the product:



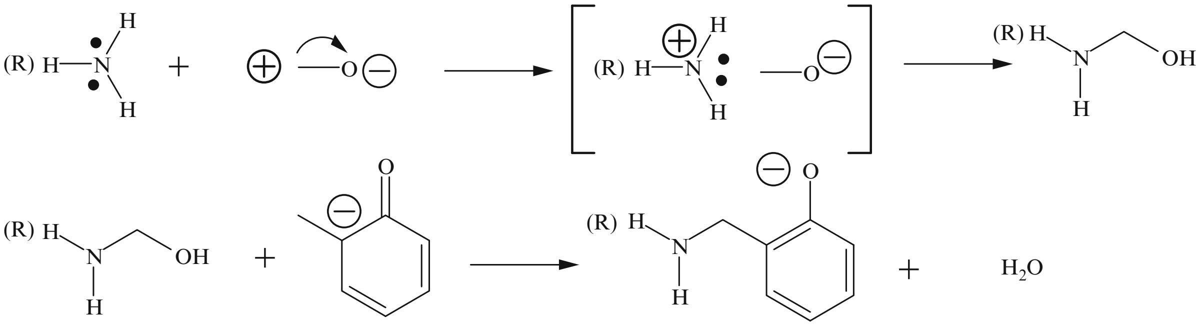
The mechanism of this reaction is discussed in the next section.

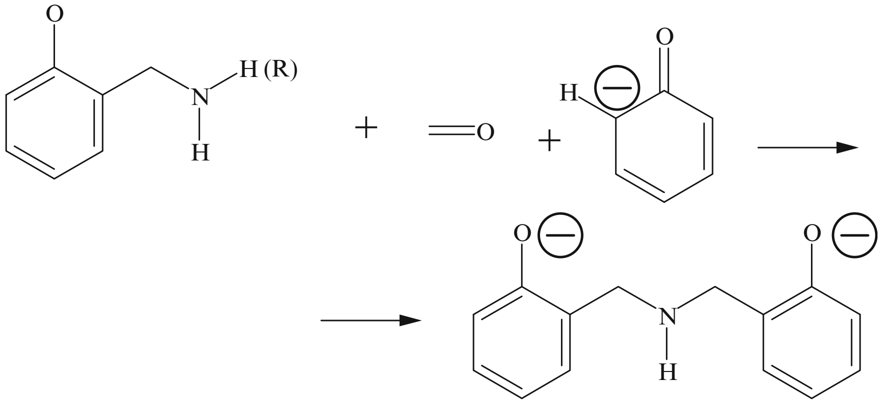
7.12.3 *Ammonia-Catalyzed Phenolic Resins*

These resins differ from the other resols, because there are some benzylamine bridges present in their structure. The reactions result in early losses of water and allow higher molecular weight buildups before the resins gel. Nitrogen-containing resols are darker in color than regular resols. The di benzylamine bridges form as follows [145]:



The overall mechanism can be shown as a special case of a Mannich reaction:





In amine or ammonia-catalyzed reactions [145], the additions and the condensations occur almost simultaneously with each other. Methylol groups are still present in the finished resins to the extent of 15–30 groups per 100 phenol residues. The structures are branched and the degree of branching depends upon the amine used.

7.12.4 Typical Commercial Preparations

The resols are usually prepared in typical reaction kettles, using 1.5–2.0 moles of formaldehyde per mole of the phenol. The reactions are rapid and the condensations to resoles might be accomplished in 1 h. Formaldehyde is often added in the form of formalin. The quantity of the added caustic or ammonia might comprise one percent of the phenol in the reaction mixture. These reactions are carried out at water reflux for a specified time. The pH is then lowered to neutral and the water is distilled off, usually at reduced pressure. The progress of the condensation is followed by measuring the melting point, the gel time (time required for the material to become thermoset at a specified temperature), solubility, or free phenol content.

Better quality novolacs and resoles are prepared in stainless steel resin kettles. For novolacs, a typical recipe might call for mole of phenol to 0.8 moles of formaldehyde (usually added as formalin, a 37% solution in water). Acid catalysts, like oxalic, hydrochloric, or others, are added in amounts of 1–2% by weight of the phenol. Oxalic acid is favored over hydrochloric, sulfuric, or phosphoric due to corrosion problems. In addition, vapors of hydrochloric acid tend to react with vapors of formaldehyde and form a carcinogenic compound, 1,1′-dichlorodimethyl ether. The reactions are conducted at the reflux temperature of water for 2–4 h. Maleic acid is sometimes used to form high melting novolacs. In a typical preparations of novolacs, molten phenol, usually kept at 65°C, is introduced into the reaction kettle and heated to 95°C. The catalyst is then added. This is followed by addition of the formaldehyde solution to the kettle with stirring, at a rate that allows a gentle reflux. After addition, heating and stirring are continued until almost all the formaldehyde is used up. At that point, the resins separate from the aqueous phase. Water is distilled off and the temperature is raised in the process to about 160°C. The unreacted phenol is removed by vacuum distillation. The end of the reaction may be determined by the melting point of the product or by its melt viscosity.

Cresols are also often used in preparations of phenolic resins. These may be individual isomers or mixtures of all three. Cresilic acids, mixtures of all three isomers, rich in *m*-cresol and low in *o*-cresol are preferred.

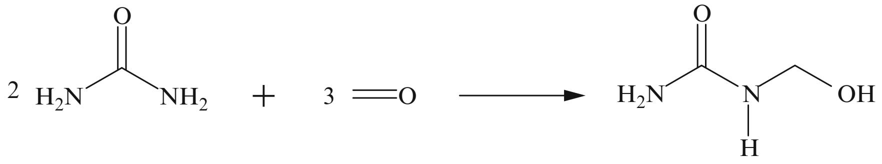
Xylenols (all six isomers) are now also in common use to form alkali-resistant grades of phenolic resins. High 3,5-xylenol mixtures are preferred. Also, resorcinol, which forms very reactive phenolic resins, is used in preparations of cold-setting adhesives. Higher homologues of phenol, like Bisphenol A, are used to prepare special phenol-formaldehyde condensates.

7.13 Amino Polymers

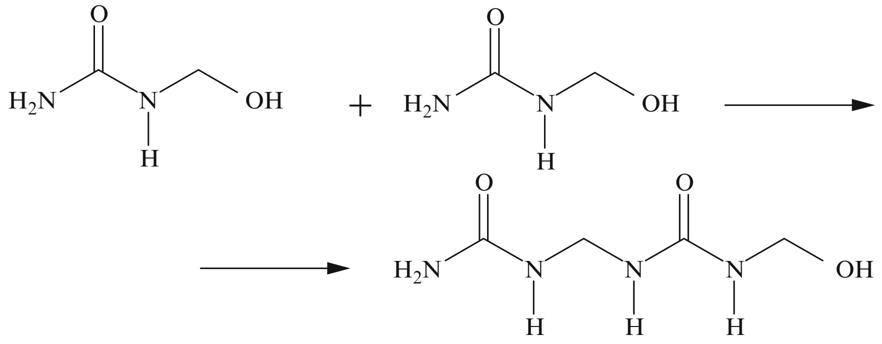
Currently, the bulk of the commercial polymers that would fit into this category are urea-formaldehyde and melamine-formaldehyde resins [151]. Over the years, however, many other materials that might fit into this group were prepared but not adopted for use for various reasons.

7.13.1 *Urea-Formaldehyde Resins*

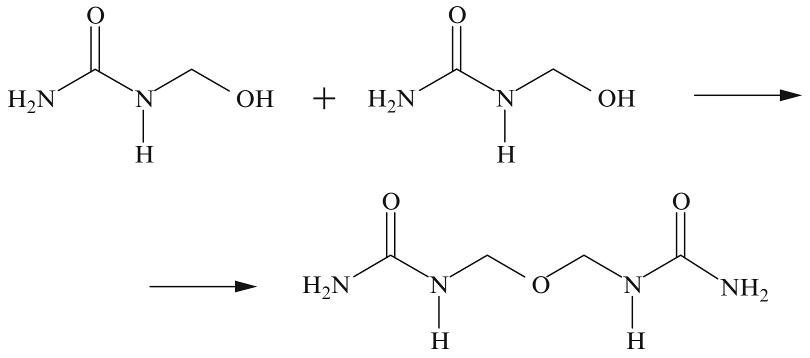
These thermosetting resins find applications in coatings, adhesives, laminating, and molding compositions. The materials are formed in water at a pH above 7 at the start of the reaction, because the methylol derivatives that form condense rapidly at acidic conditions. The initial step, where urea undergoes a nucleophilic addition of formaldehyde, can be shown as follows:



In the past, it was believed by some that further condensations that take place at pH below 7 include formations of cyclic intermediates. This, however, was never demonstrated [151]. NMR spectra of urea-formaldehyde resins show [152] that condensations under acidic conditions proceed via formations of methylene linkages:



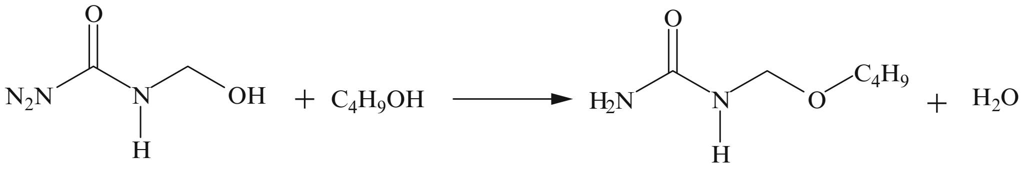
Under alkaline conditions, on the other hand, dimethylene ether groups form instead [152]:



In addition, the more highly condensed water-soluble resins contain hemiformal groups.

Further reactions may not result in formation of polymeric materials [153]. This is especially true when the ratios of formaldehyde to urea are low. Some are of the opinion that linear oligomeric condensates form instead. These urea-formaldehyde condensates separate as colloidal dispersions that are stabilized by association with excess formaldehyde [153]. The cross-linking reaction consists of agglomeration of colloidal particles with an accompanying release of formaldehyde. This opinion is supported by several observations: (1) when one plots the logarithm of solution viscosity against time during the polymerization, the plot exhibits a sharp break. Also, the plot differs from similar ones for phenol-formaldehyde condensation reactions that show continuous increases in viscosity. (2) Scanning electron micrographs of the fully cured resins show surface characteristics that resemble more the surfaces of coagulated and coalesced colloidal particles than those of high molecular weight polymers. (3) X-ray diffraction patterns and laser Raman spectra of the cross-linked resins show that there are crystalline areas in the material and absence of water. Similar patterns are obtained from hydrogen-bonded proteins with close chain packing. On the other hand, FT-IR studies [154] show that methylene and ether cross-links are present in the cured resin. There are also indications of the presence of cyclic ether units. The above information also suggests that the final structure of the urea-formaldehyde resin may be a function of the feed ratio and the pH at which it was formed.

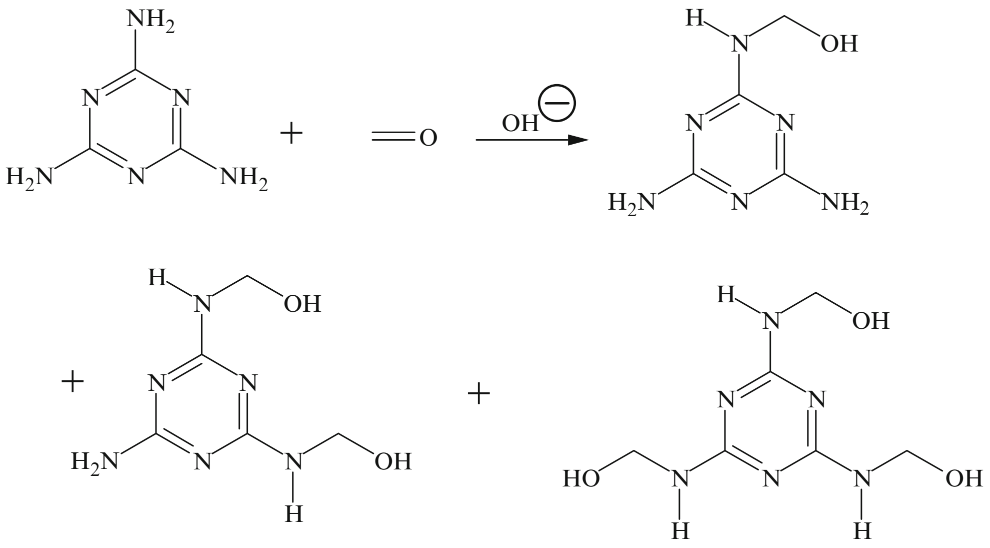
Urea-formaldehyde resins for surface coatings are commonly modified for solubility in organic solvents by reacting them with alcohols to form ether groups. Usually, *n*-butyl alcohol is used. The reaction is carried out under basic conditions, before acidification:



After etherification, the reaction mixture is acidified and the resin is further reacted to acquire the desired degree of condensation. A typical butylated urea-formaldehyde resin contains 0.5–1.0 moles of butyl ether groups per mole of urea.

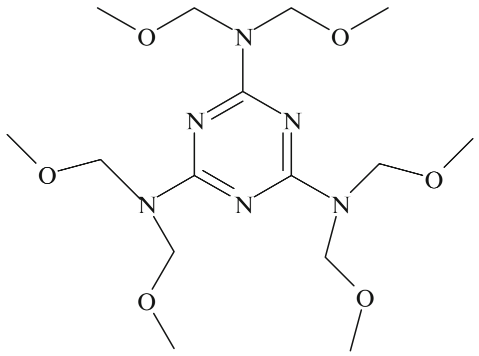
7.13.2 Melamine-Formaldehyde Resins

These resins are quite similar to urea-formaldehyde condensates and, probably, for that reason, find similar applications. Melamine reacts with formaldehyde under slightly alkaline conditions to form mixtures of various methylolmelamines [155]:



Further heating causes condensation into resins. The rate of such resinifications is pH-dependent.

Melamine-formaldehyde resins are also etherified for solvent solubility. Methanol is often used and hexamethyl ether of hexamethylolmelamine as well as higher homologues are available commercially. The hexamethyl ether can be shown as follows:



The ethers cleave upon acidification and network structures form. For methylolated melamines that are not etherified, acidification is not necessary and heating alone is often adequate for network formation. Melamine-formaldehyde resins have the reputation of being harder and more moisture-resistant than the urea-formaldehyde ones.