

8.6 Industrially Relevant Crosslinking Systems

As described in ► Sect. 8.3.4, polymers that are built up gradually can be cross-linked by using monomers with an average functionality of $\bar{f} > 2$, allowing them to be converted into insoluble three-dimensional networks. In this section, systems in which the cross-linking is carried out in two stages by reaction of a prepolymer (first stage) with a cross-linking agent (second stage) are discussed.

8.6.1 Phenolic Resins

Condensation of phenol with formaldehyde can yield low molar mass, soluble, often still liquid intermediate materials (prepolymers). By further reactions (e.g., by heating), these can be converted into networks that are insoluble and do not melt. These materials are among the oldest industrially used polymers. The condensation of phenol with formaldehyde in aqueous solution is pH-dependent. The prepolymers obtained in an alkaline medium are called *resols* (cross-linked products are called resins or *resites*) (■ Fig. 8.48). The prepolymers prepared in acidic solution are called *Novolac* (■ Fig. 8.49).

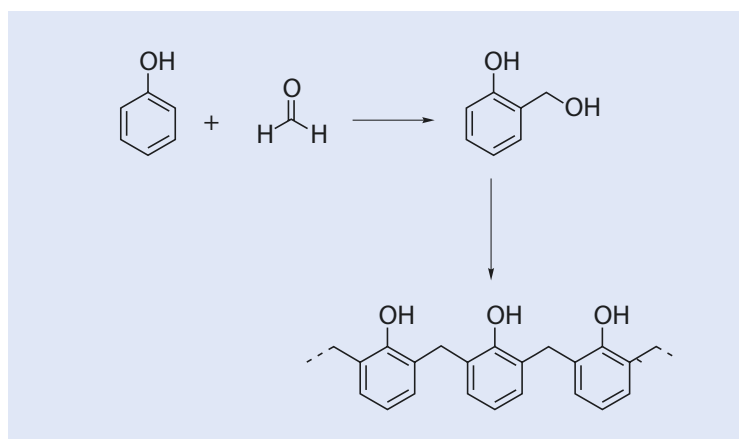
In an acidic environment, an excess of phenol is necessary, otherwise the polymerization cannot be controlled and no stable and storable intermediates are obtained. Novolac is usually solid at room temperature.

Cross-linking of resols is accomplished by heating. At 130 °C methylol phenols simply dehydrate (■ Fig. 8.50).

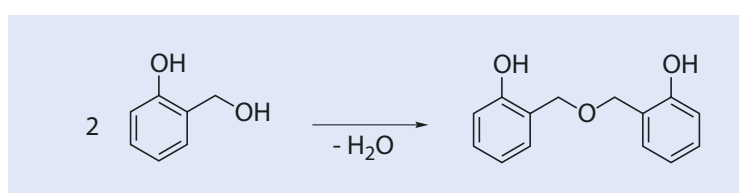
By contrast, at 150 °C, methyl groups are predominantly formed as formaldehyde and water are eliminated, (■ Fig. 8.51).

The crosslinking of Novolac is achieved by adding crosslinking agents, such as hexamethylene tetramine. This hydrolyzes to dimethylol amine and reacts with Novolac as shown in ■ Fig. 8.52.

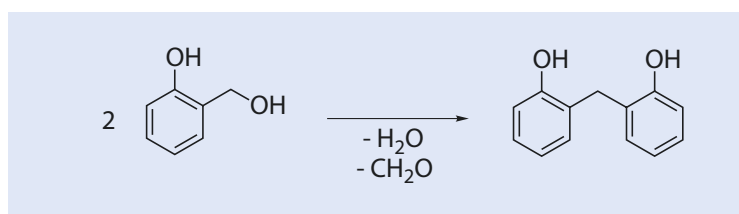
■ **Fig. 8.49** Synthesis of Novolac (at $\text{pH} \leq 3$, ratio of phenol:formaldehyde = 1:0.8)



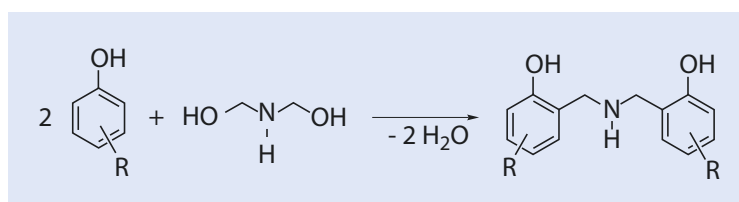
■ **Fig. 8.50** Elementary step in the cross-linking of a resol by dehydration ($T = 130\text{ }^\circ\text{C}$)



■ **Fig. 8.51** Elementary step in the cross-linking of a resol by elimination of water and formaldehyde ($T = 150\text{ }^\circ\text{C}$)



■ **Fig. 8.52** The cross-linking of Novolac with dimethylol amine



Phenolic resins are used mainly as molding compounds with fillers. The hardened (cross-linked) resins are tough construction materials with good resistance to stress cracking. Webs of paper or tissues impregnated with phenolic resins can be processed into laminates.

8.6.2 Urea Resins

The reaction products of formaldehyde with urea (carbamide) are called urea resins. This reaction, which is a Mannich reaction, is pH-dependent.

In a neutral to slightly alkaline environment, well-defined products are created (■ Fig. 8.53).

■ **Fig. 8.53** Conversion of urea with formaldehyde to urea resin precursors in a neutral to slightly alkaline environment

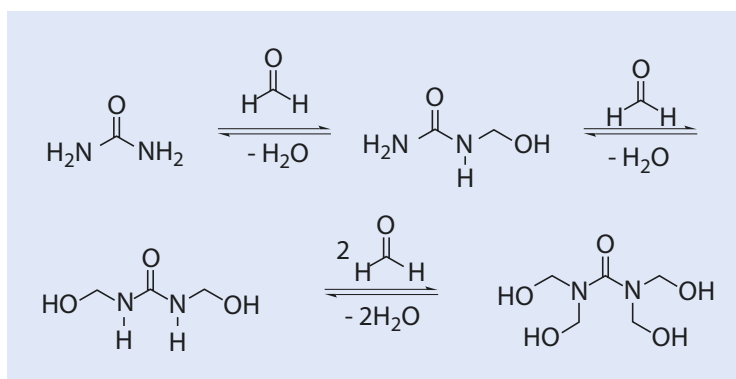
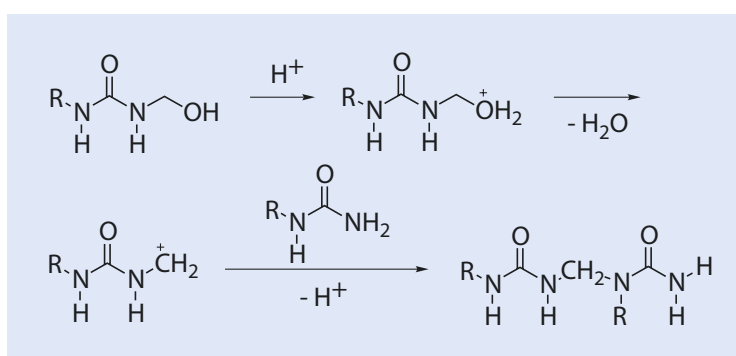
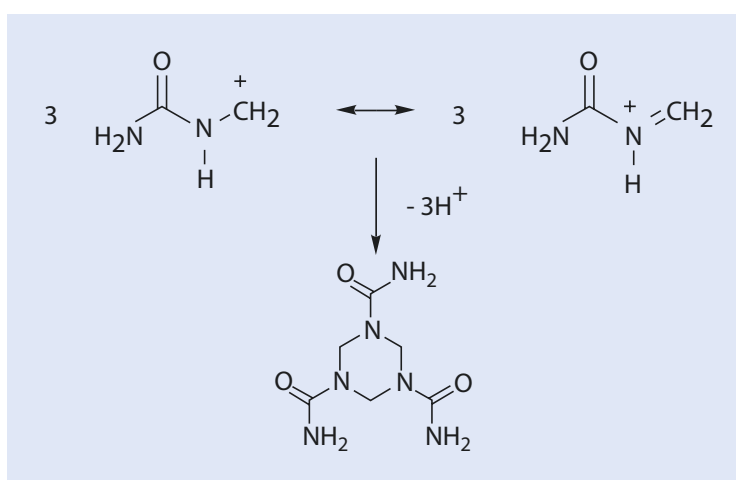


Fig. 8.54 Individual steps of the acid-catalyzed cross-linking of urea resin precursors



■ **Fig. 8.55** Trimerization of urea in an acidic environment



In an acidic environment, cross-linked structures rapidly form (■ Fig. 8.54).

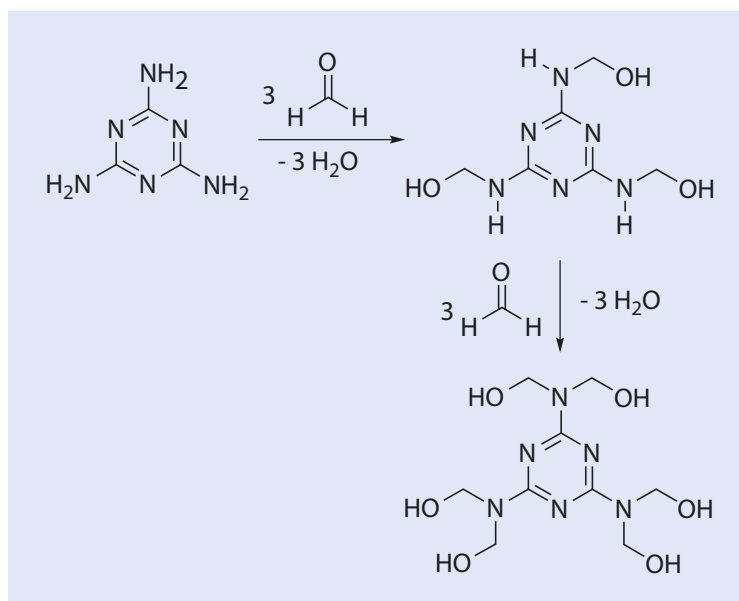
The cross-linking can be continued to incorporate all the -NH_2 groups. In addition, the carbenium ion can trimerize (■ Fig. 8.55).

Thereafter, the NH_2 groups can react further (as described above) and cross-link. The urea resins are similar in their properties and their applications to phenolic resins.

8.6.3 Melamine Resins

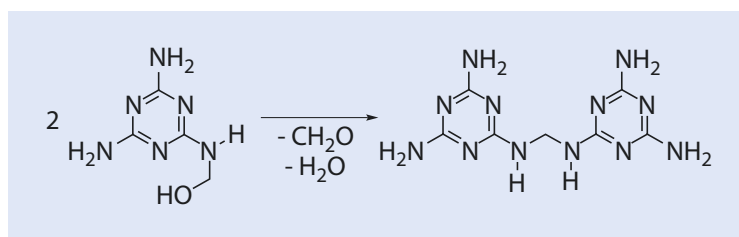
Melamine (1,3,5-triaminotriazine) and formaldehyde react stepwise to yield intermediates which have similar structures to those of urea resins (■ Fig. 8.56).

■ **Fig. 8.56** Formation of melamine resin precursors from melamine and formaldehyde



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■ **Fig. 8.57** Principle step in the cross-linking of melamine resins with elimination of water and formaldehyde



At elevated temperatures (140–160 °C), the molecules bridge and form a network (■ Fig. 8.57).

Cross-linked melamine resins have slightly better mechanical and thermal properties than both phenolic and urea resins. They are used especially for the production of light-colored or white components, instead of phenolic and urea resins which have a dark, natural color.