The polyfunctional character of the reactants results in a high degree of cross-linking in the product, forming a rigid foam.

REFERENCES

1. Dirreen, G. E.; Shakhashiri, B. Z. *J. Chem. Educ.* **1977**, *54*, 431.
2. We have used a product, Super Foam, marketed by Edmund Scientific Co., 101 E. Gloucester Pike, Barrington, New York 08007. Similar products may be available at paint, hardware, or lumber stores.
3. Hocking, M. B.; Canham, G. W. R. *J. Chem. Educ.* **1974**, *51*, A580.
4. Windholz, M., Ed. "The Merck Index," 9th ed.; Merck and Co.: Rahway, New Jersey, 1976; p 1225.

3.3

Phenol-Formaldehyde Polymer

Concentrated hydrochloric acid is added to a mixture of aqueous formaldehyde, glacial acetic acid, and phenol. After approximately one minute the solution turns pink and solidifies into a cake-like material.

MATERIALS

25 ml 12M formaldehyde, HCHO (Formalin, 37%)
55 ml glacial (17M) acetic acid, CH_3COOH
20 g phenol, C_6H_5OH
55 ml concentrated (12M) hydrochloric acid, HCl
gloves, plastic or rubber
250-ml beaker
100-ml graduated cylinder
stirring rod

PROCEDURE

Perform this demonstration in a hood and wear gloves.

In a 250-ml beaker, mix 25 ml of aqueous formaldehyde, 55 ml of glacial acetic acid, and 20 g of phenol [*1*]. Quickly add 55 ml of concentrated hydrochloric acid while stirring. After about a minute, the solution will turn pink and solidify. The polymerization is exothermic. If not stirred, the resulting polymer is friable, but continuous stirring during polymerization results in a solid mass more resistant to crumbling.

HAZARDS

All compounds used in this demonstration should be handled in a hood. Plastic or rubber gloves should be worn.

Formaldehyde vapors are extremely irritating to mucous membranes. Skin contact can cause dermatitis. Extended exposure to high concentrations of vapor can cause chronic effects such as laryngitis, bronchitis, conjunctivitis, or skin problems. Preliminary data "have indicated the development of nasal cancers in rats exposed to 15 ppm formaldehyde for 18 months" [*2*]. Mixing of formaldehyde with hydrogen chloride "could result in the generation of bis(chloromethyl)ether, a potent human carcinogen" [*3*].

Phenol is toxic and causes burns. It can be absorbed rapidly through the skin. Prolonged inhalation of phenol vapor can have chronic effects.

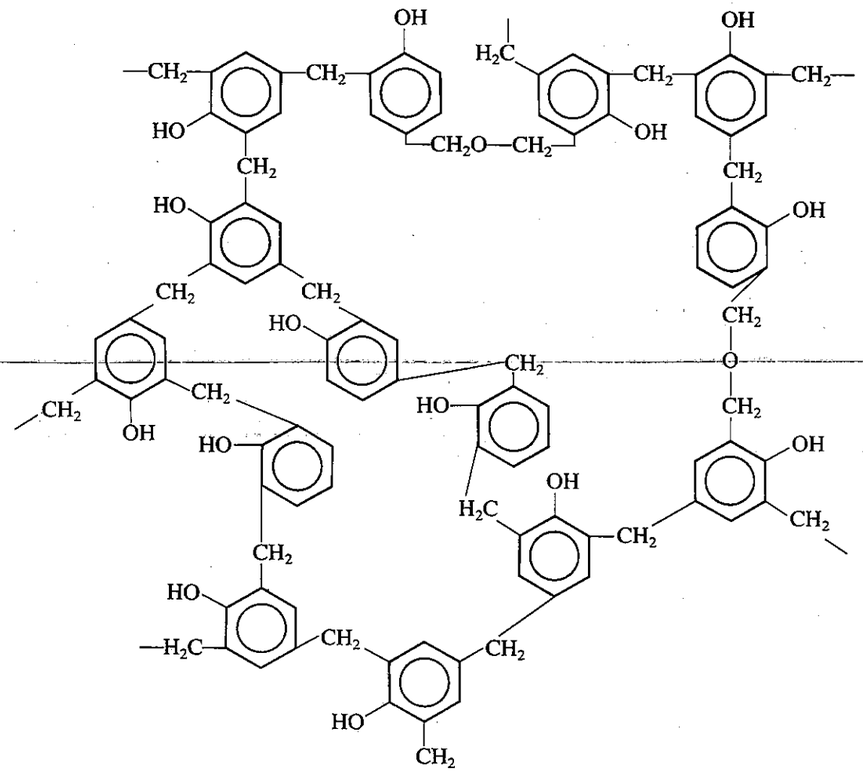
Both glacial acetic acid and concentrated hydrochloric acid can produce skin burns, eye irritation, and irritation of the respiratory tract.

DISPOSAL

The product contains acid and probably unreacted formaldehyde or phenol; before handling, it should be washed thoroughly with dilute aqueous sodium hydroxide solution and then water. The washed polymer should be discarded in a waste container.

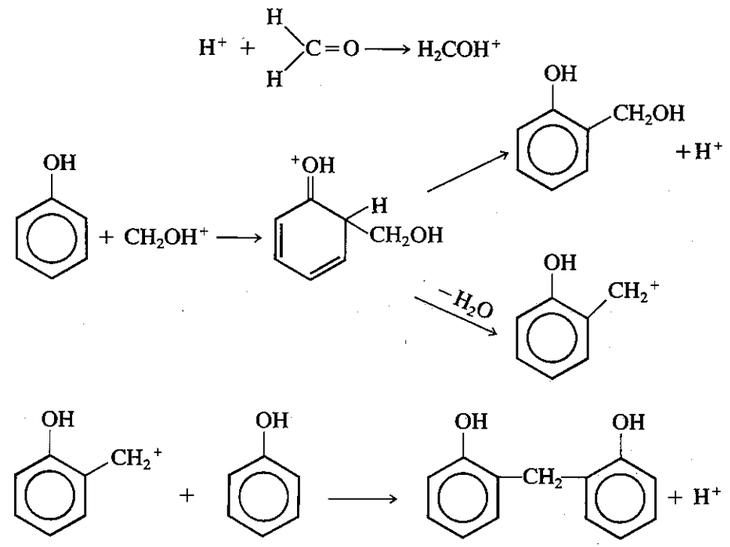
DISCUSSION

In general, phenol-formaldehyde resins are condensation polymers consisting of aromatic rings linked by methylene groups. The product linkages occur primarily in the ortho or para position to the phenolic hydroxyls (see figure). In addition, ether linkages are found under conditions of excess formaldehyde and neutral pH.



Representative methylene and ether linkages in a phenol-formaldehyde polymer [*4*].

In this demonstration, prepared with a molar excess of formaldehyde and under acidic conditions, the product resin is formed by reactions that lead mostly to methylene bridges. The reaction sequence can be illustrated as follows [*4*]:



All possible bridges do not form, because all phenolic rings do not lie in the same plane. These gaps in the resin weaken the polymer. The presence of occluded reaction materials and by-products, such as water, causes further weakening.

REFERENCES

1. Wilson, A. S.; Peterson, V. R. *J. Chem. Educ.* **1978**, *55*, 652.
2. "Prudent Practices for Handling Hazardous Chemicals in Laboratories." *Natl. Res. Counc.* **1981**; Committee on Hazardous Substances in the Laboratory; p 131.
3. "Prudent Practices for Handling Hazardous Chemicals in Laboratories." *Natl. Res. Counc.* **1981**; Committee on Hazardous Substances in the Laboratory; p 30.
4. Ravve, A. "Organic Chemistry of Macromolecules"; Marcel Dekker: New York, 1967; Ch. 17.

3.4

Resorcinol-Formaldehyde Polymer

When several drops of potassium hydroxide or hydrochloric acid solution are added to a hot yellow solution containing resorcinol and formaldehyde, an exothermic reaction produces a brittle red solid.

MATERIALS FOR PROCEDURE A

6 g resorcinol (1,3-dihydroxybenzene), $C_6H_4(OH)_2$

10 ml distilled water

8 ml 12M formaldehyde, HCHO (Formalin, 37%)

1 ml 3M potassium hydroxide, KOH (To prepare 10 ml of solution, dissolve 1.7 g of KOH in water and dilute to 10 ml.)

gloves, plastic or rubber

150-ml beaker

10-ml graduated cylinder

hot plate

dropper

MATERIALS FOR PROCEDURE B

6 g resorcinol (1,3-dihydroxybenzene), $C_6H_4(OH)_2$

10 ml distilled water

8 ml 12M formaldehyde, HCHO (Formalin, 37%)

2 ml concentrated (12M) hydrochloric acid, HCl

gloves, plastic or rubber

150-ml beaker

10-ml graduated cylinder

dropper

PROCEDURE A

Perform this demonstration in a hood and wear gloves.

Place 6 g of resorcinol, 10 ml of distilled water, and 8 ml of formaldehyde solution in a beaker [*1*]. Heat the mixture to boiling and remove from the heat source. Immediately add 5–10 drops of 3M potassium hydroxide. Caution: spattering may occur. Within a few seconds an exothermic reaction produces a red, glassy polymer.

Gas evolution may cause the polymer surface to bubble and become porous. The polymer will darken as it cures and become very brittle. Wash the polymer thoroughly with water before handling.

PROCEDURE B

Perform this demonstration in a hood and wear gloves.

Place 6 g of resorcinol, 10 ml of distilled water, and 8 ml of formaldehyde solution in a beaker. Slowly add, by drops, 2 ml of concentrated hydrochloric acid solution. The resulting polymer is pink.

HAZARDS

All compounds used in this demonstration should be handled in a hood. Plastic or rubber gloves should be worn.

Resorcinol is an irritant to the skin and eyes and can be absorbed through the skin.

Formaldehyde vapors are extremely irritating to mucous membranes. Skin contact can cause dermatitis. Extended exposure to high concentrations of vapor can cause chronic effects such as laryngitis, bronchitis, conjunctivitis, or skin problems. Preliminary data "have indicated the development of nasal cancers in rats exposed to 15 ppm formaldehyde for 18 months" [*2*]. Mixing of formaldehyde with hydrogen chloride "could result in the generation of bis(chloromethyl)ether, a potent human carcinogen" [*3*].

Dust from solid potassium hydroxide is very caustic. Hydrochloric acid vapors are extremely irritating to the skin, eyes, and respiratory system. Potassium hydroxide and hydrochloric acid can both cause severe burns of the skin and eyes.

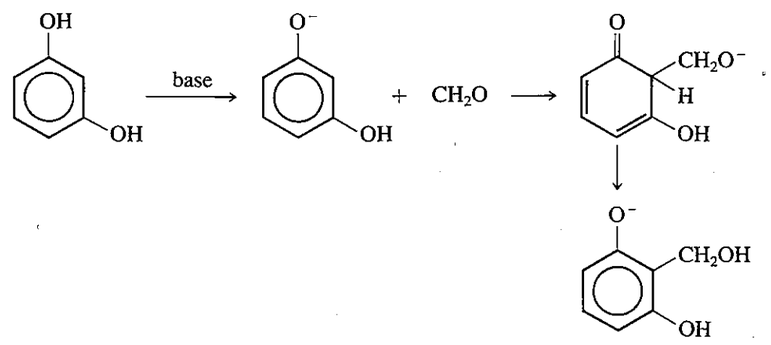
DISPOSAL

The polymer should be washed with water and discarded in a waste container.

DISCUSSION

The reaction of resorcinol (1,3-dihydroxybenzene) with formaldehyde is very similar to the reaction of phenol with formaldehyde (see Demonstration 3.3). Substitution in the meta position by an ortho-para directing group enhances the rate of the reaction. Phloroglucinol (1,3,5-trihydroxybenzene) would react still more rapidly.

Catalysis by a base, as in this demonstration, has been explained by a mechanism in which a phenoxide ion undergoes electrophilic attack by formaldehyde at the ortho or para position [*4*]:



The reaction can also be catalyzed by hydrochloric acid, in which case the polymerization occurs at room temperature and the product is similar in consistency to the phenol-formaldehyde polymer.

REFERENCES

1. Alyea, H. N.; Dutton, F. B., Eds. "Tested Demonstrations in Chemistry," 6th ed.; Journal of Chemical Education: Easton, Pennsylvania, 1965; p 110.
2. "Prudent Practices for Handling Hazardous Chemicals in Laboratories." *Natl. Res. Counc.* **1981**; Committee on Hazardous Substances in the Laboratory; p 131.
3. "Prudent Practices for Handling Hazardous Chemicals in Laboratories." *Natl. Res. Counc.* **1981**; Committee on Hazardous Substances in the Laboratory; p 30.
4. Ravve, A. "Organic Chemistry of Macromolecules"; Marcel Dekker: New York, 1967; Ch. 17.

3.5

Aniline Hydrochloride–Formaldehyde Polymer

Solutions of aniline hydrochloride and formaldehyde are mixed to produce a red gelatin-like polymer.

MATERIALS

15 ml aniline (aminobenzene), $C_6H_5NH_2$

20 ml 6M hydrochloric acid, HCl (To prepare 20 ml of solution, dilute 10 ml of concentrated [12M] HCl to 20 ml with distilled water.)

30 ml 12M formaldehyde, HCHO (Formalin, 37%)

gloves, plastic or rubber

100-ml beaker

50-ml graduated cylinder

250-ml beaker

stirring rod

PROCEDURE

Perform this demonstration in a hood and wear gloves.

Prepare aniline hydrochloride solution in a 100-ml beaker by adding 15 ml of aniline to 20 ml of 6M HCl solution. Either allow the solution to cool to room temperature before use, or prepare the solution in an ice bath and then allow it to warm up to room temperature.

Place 30 ml of formaldehyde solution in a 250-ml beaker. Quickly add the aniline hydrochloride solution with stirring. Within seconds, the mixture turns red and solidifies into a rubbery mass. The polymerization reaction is exothermic, producing a temperature increase to 40–50°C. As a result the surface of the polymer sometimes expands and becomes porous.

HAZARDS

All compounds used in this demonstration should be handled in a hood. Plastic or rubber gloves should be worn.

Aniline is toxic by inhalation, ingestion, or absorption through the skin. Long exposure to the vapor can have chronic effects.