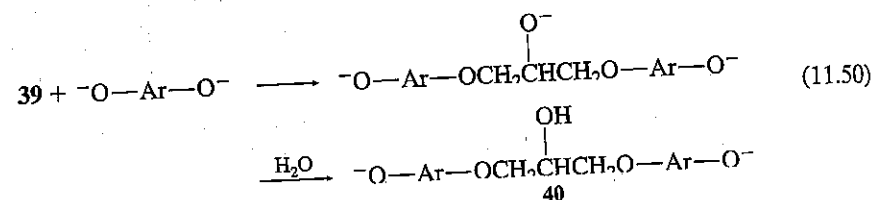
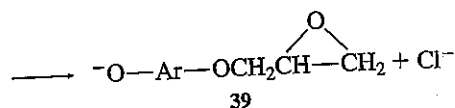
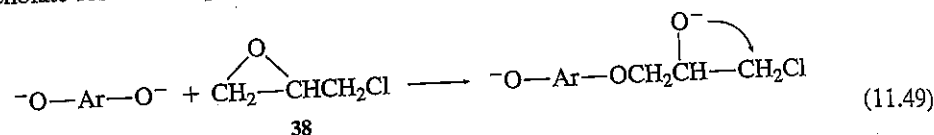


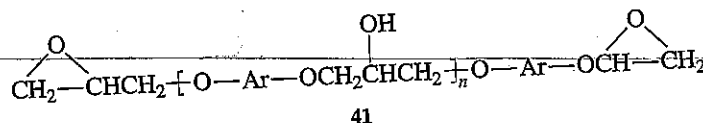
## 11.3.4 Epoxy Resins

Epoxy resins are a special type of polyether. They are synthesized first as oligomers with epoxide end groups that are capable of undergoing further polymerization to form structurally complex network polymers. The fact that a number of books have been devoted to epoxy resins<sup>47-52</sup> attests to their importance. They are widely used as adhesives and structural polymers, especially in composites.

The oligomers are prepared by the step-reaction polymerization of a diphenol, most commonly bisphenol A, and an epoxide-containing compound in the presence of base. Epichlorohydrin (38) is the most widely used comonomer. In its reactions with phenols, 38 reacts in the manner of a diepoxide. The reaction sequence involves the attack by phenolate anion at the less hindered carbon of the epoxide ring, followed by intramolecular displacement of chloride to regenerate an epoxide (39) (11.49). Further reaction (11.50) of 39 with diphenolate results in a product (40) having a pendant hydroxy group.

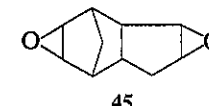
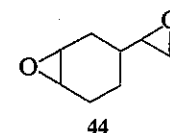
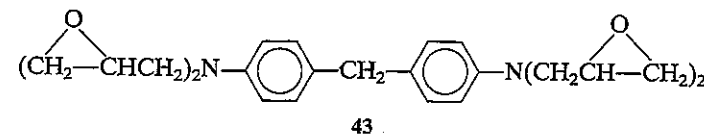
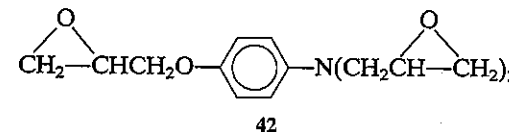


Reaction with excess 38 leads eventually to an epoxide-terminated oligomer (41). The end groups are commonly referred to as *glycidyl ether* groups. The molecular weight of the oligomer is varied by suitable adjustment of the epichlorohydrin excess, and may vary from a viscous liquid to a solid ( $n = 2-25$ ) depending on the degree of polymerization. Optimum properties depend on the application.

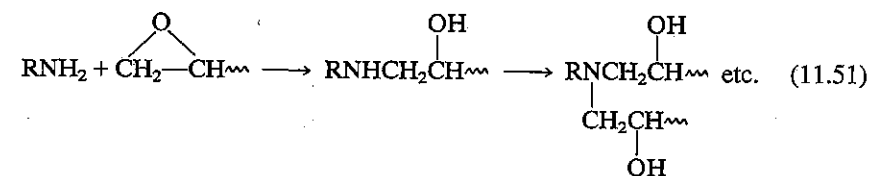


Besides bisphenol A, diphenols such as hydroquinone and resorcinol (1,4- and 1,3-dihydroxybenzene, respectively) have also been used in epoxy formulations, as have certain phenol-formaldehyde condensation products, including novolacs (discussed in Chapter 14).

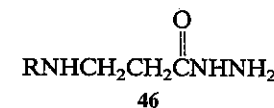
While the glycidyl ethers represent the most common type of epoxy prepolymer, other epoxide structures are used commercially, among them multifunctional glycidyl amines such as 42 and 43, cycloaliphatic compounds such as vinylcyclohexene dioxide (44) and dicyclopentadiene dioxide (45), epoxidized diene polymers, and epoxidized oils.



Further polymerization of prepolymer to form crosslinked polymer (curing) can be accomplished several ways, although amines and carboxylic acid anhydrides are most commonly used. Amines react by nucleophilic addition to the epoxide ring (11.51). Diamines and polyamines are also used as curing agents and, in some applications, the epoxy resin is blended with other polymers such as melamine- or urea-formaldehyde resins, which cause crosslinking by essentially the same reaction to give network copolymer. Reaction with amines is exothermic and is known to be catalyzed by proton donors.

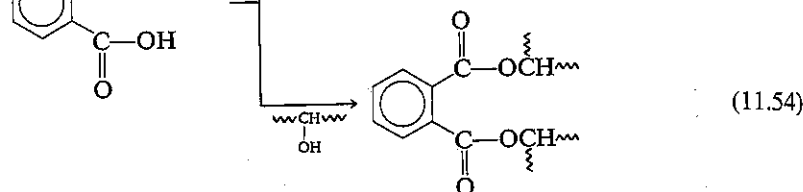
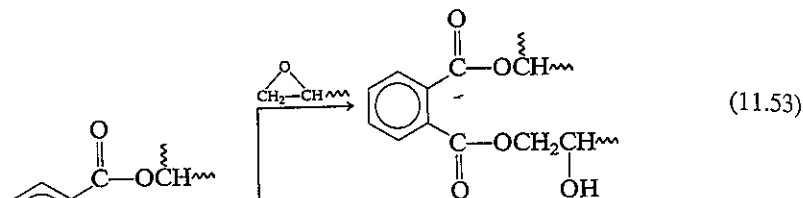
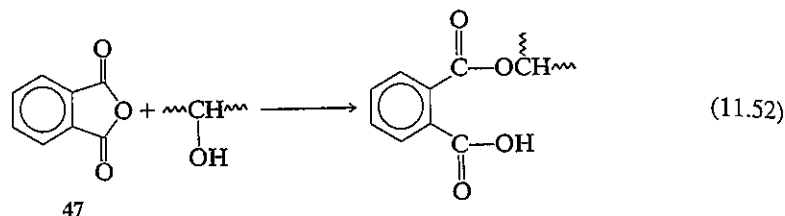


Partially cured epoxy resins that are stable in storage but cure further on heating can be prepared<sup>53</sup> by adding hydrazides of structure 46. Resins of this type are called *B-stage* resins (A-stage refers to uncured resins, B-stage to partially cured, and C-stage to fully cured.)

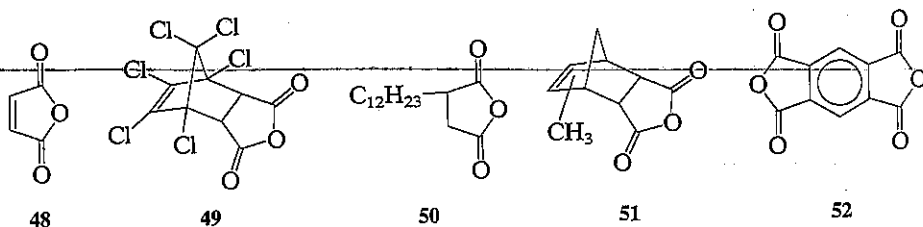


Anhydrides—for example, phthalic anhydride (47)—react with pendant hydroxyl groups to give ester acids (11.52). The acid group then reacts with epoxide groups (11.53) or other hydroxyls (11.54) to form more ester groups. Ether groups also form by the acid-catalyzed

reaction between hydroxyl and epoxide groups. Obviously crosslinking of epoxy resins is a very complex process, and it is impossible to give a definitive structure for the final product.

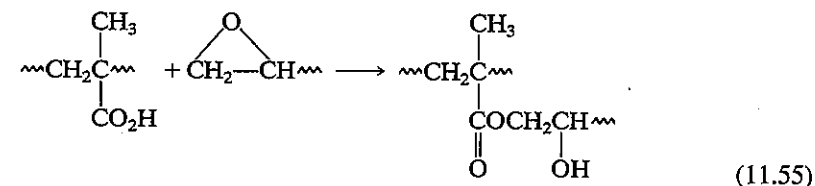


Curing with anhydrides is usually catalyzed by amine. Some of the more common anhydrides in commercial use include phthalic (47), maleic (48), and chlorendic (49); the liquid anhydrides, dodecenylsuccinic anhydride (50) and nadic methyl anhydride\* (51); and pyromellitic dianhydride (52). Liquid Diels-Alder adducts derived from maleic anhydride and terpenes have also been reported.<sup>54</sup> It appears that Diels-Alder adducts improve the high-temperature stability of epoxy resins because the retrograde Diels-Alder reaction generates alkenes in the polymeric network, which crosslink further and cause more char formation.<sup>55</sup> The advantages of a dianhydride such as 52 are that the cure rate is higher and the final product is more densely crosslinked. Whichever curing agent is used, there is a preponderance of free hydroxy groups in the cured polymer, which gives rise to the superior adhesive properties of epoxies.



\*Nadic methyl anhydride is the common name for methylbicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride, the Diels-Alder adduct of the mixed methyl-substituted cyclopentadienes with maleic anhydride.

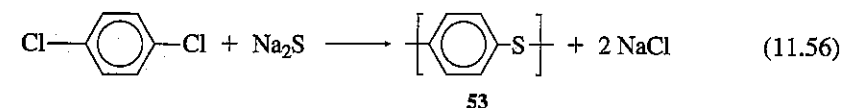
Because of the reactive end groups, epoxy resins are easily grafted onto other polymers. Thermosetting acrylic polymers have been prepared, for example, by reaction of an epoxy resin with an acrylic to form a graft copolymer (11.55) capable of being crosslinked. For certain coatings applications, epoxies are also reacted in analogous fashion with drying oil fatty acids to take advantage of the free radical crosslinking propensity of the fatty acid. (Drying oil polymerization is discussed in the next chapter.)



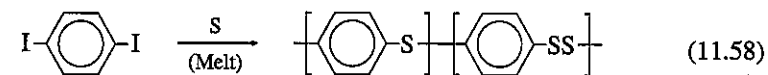
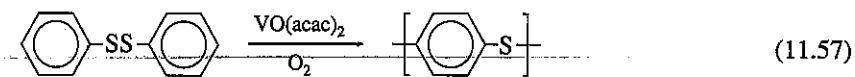
## 11.4 Polysulfides, Poly(alkylene polysulfide)s, and Polysulfones

### 11.4.1 Polysulfides

Polysulfides, or poly(alkylene sulfide)s as they are sometimes called, are the sulfur analogs of polyethers. The polysulfide that has achieved the greatest commercial success is poly(*p*-phenylene sulfide) (PPS) (53).<sup>56</sup> An engineering plastic, PPS is manufactured by Phillips Petroleum (trade name Ryton) by the reaction of *p*-dichlorobenzene with sodium sulfide (11.56) in a polar solvent at about 250°C. The polymer is highly crystalline with a  $T_m$  of about 290°C, and it can be made electrically conducting by the addition of dopant (*cf.* Chapter 4). When first made, PPS has a relatively low molecular weight, but heating in air causes chain extension and some crosslinking. The heat-cured polymer is used as an engineering plastic for applications requiring good chemical and heat resistance, while the low-molecular-weight PPS is used as a coating.



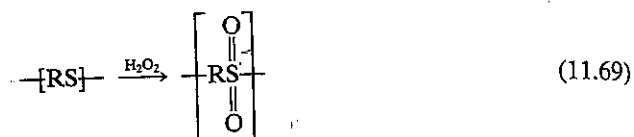
Several other routes to PPS have been reported. Two having possible commercial utility are the oxidative coupling of diphenyl disulfide (or thiophenol) with a vanadium catalyst (11.57, acac = acetylacetonate)<sup>57,58</sup> and the melt condensation of *p*-iodobenzene with sulfur (11.58).<sup>59,60</sup> The latter, which forms product with some disulfide units in the backbone, can be processed to a prepolymer stage, then further polymerization can be effected in the solid state.



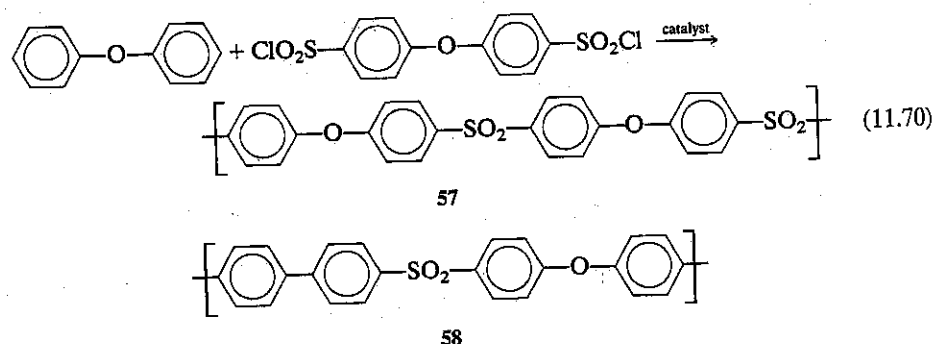
Poly(alkylene polysulfide)s are among the oldest synthetic polymers, having been in commercial use since 1930. They lack the strength of most other synthetic elastomers and tend to have unpleasant odors because of the presence of low-molecular-weight thiols and disulfides. Nevertheless, they are exceptionally resistant to oils and solvents and to weathering, and hence are widely used in gaskets, gasoline hoses, and sealants. Large volumes are now being used as binders for solid rocket propellants.

### 11.4.3 Polysulfones

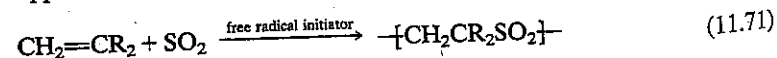
Polysulfones are derivatives of polysulfides and can be prepared from them by oxidation—for example, with hydrogen peroxide (11.69). Introduction of the sulfone group normally results in a much higher polymer melt temperature relative to the polysulfide.



In recent years attention has centered on aromatic polysulfones as thermally stable engineering plastics.<sup>70–73</sup> One method of preparing them by a nucleophilic displacement reaction was described earlier (structure 25). Another commercial route to polysulfones involves a Friedel–Crafts-type reaction using sulfonyl chlorides (11.70). The product in this case (57) is referred to in the plastics industry as a *polyethersulfone*, whereas that described earlier (25) is known simply as *polysulfone* (regardless of the fact that ether formation is the focal point of its synthesis). If diphenyl ether is replaced with biphenyl in reaction (11.70), the product (58) is called a *polyarylsulfone*. Polysulfones 57 and 58 are manufactured by ICI (trade name Victrex) and 3M (Astrel), respectively.



An additional route to polysulfones is the alternating copolymerization of sulfur dioxide<sup>74</sup> with vinyl monomers (11.71). The resultant polymers exhibit relatively low ceiling temperatures (~100°C when R = H, ~0°C when R = CH<sub>3</sub>). Depolymerization occurs on heating or on exposure to ionizing radiation. As a consequence, such polysulfones are useful in electron beam resist applications.



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