

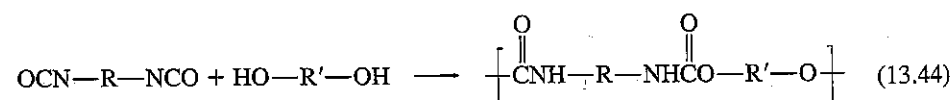
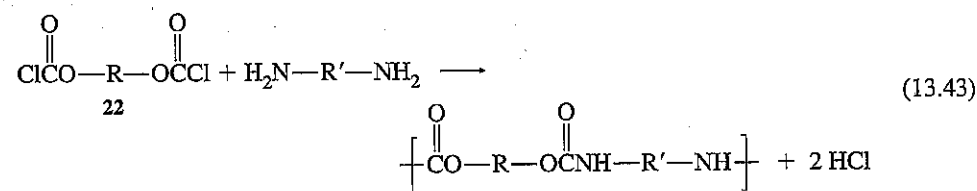
TABLE 13.5. Miscellaneous Methods of Synthesizing Polyureas

Reaction	Number
$\text{H}_2\text{N}-\text{R}-\text{NH}_2 + \text{PhOCOPh} \longrightarrow \left[\text{NH}-\text{R}-\text{NHC}(\text{O})\text{Ph} \right] + 2 \text{PhOH} \quad (13.40)$	(13.40)
$\text{H}_2\text{N}-\text{R}-\text{NH}_2 + \text{ClCN} \begin{array}{c} \text{O} \\ \parallel \\ \text{N} \end{array} \begin{array}{c} \text{O} \\ \parallel \\ \text{N} \end{array} \text{CCl} \longrightarrow \left[\text{NH}-\text{R}-\text{NHCN} \begin{array}{c} \text{O} \\ \parallel \\ \text{N} \end{array} \begin{array}{c} \text{O} \\ \parallel \\ \text{N} \end{array} \text{CN} \right] + 2 \text{HCl} \quad (13.41)$	(13.41)
$\text{H}_2\text{N}-\text{R}-\text{NH}_2 + \text{CO}_2 \xrightarrow[\text{pyridine}]{\text{O}=\text{PH}(\text{OPh})_2} \left[\text{NH}-\text{R}-\text{NHC}(\text{O})\text{Ph} \right] + \text{H}_2\text{O} \quad (13.42)$	(13.42)

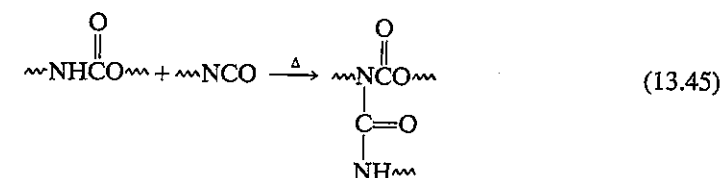
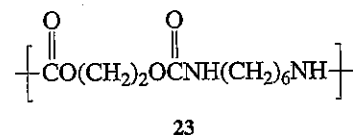
13.5 Polyurethanes

Like polyureas, polyurethanes are carbonic acid derivatives. An older term for them is *poly-carbamate*, from carbamic acid (RNHCO_2H). Polyurethanes are used in a wide variety of products, including fibers (particularly the elastic variety), elastomers, foams, coatings, and adhesives. A number of books have been written on the subject.⁴⁵⁻⁴⁸

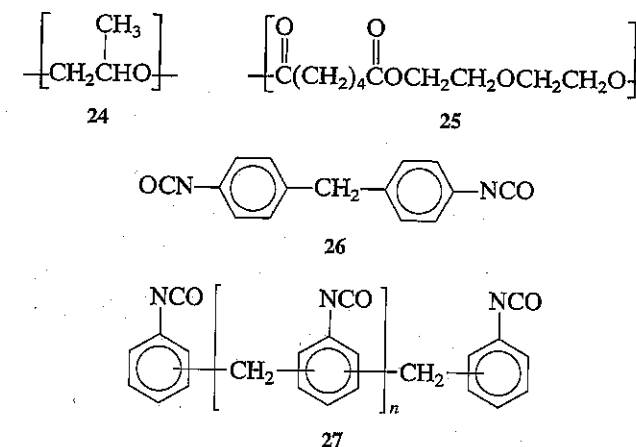
There are two principal methods of forming polyurethanes: the reaction of bischloroformates (22) (made from dihydroxy compounds with excess phosgene) with diamines (13.43), and, more important from the industrial perspective, the reaction of diisocyanates with dihydroxy compounds (13.44), which has the advantage of no byproducts. Bischloroformates



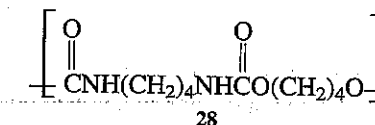
are less reactive than ordinary acid chlorides; nevertheless they react with diamines at low temperatures under interfacial conditions.^{8,49} Polyurethane 23 prepared this way, for example, melts at about 180°C, compared with 295°C for nylon-46. Reaction (13.44) is actually more complex because the urethane groups, once formed, can react further with free isocyanate (13.45) to form *allophanate* groups, which leads to chain branching and crosslinking.



Industrial polyurethane production is based primarily on low-molecular-weight aliphatic hydroxy-terminated polyethers such as poly(propylene glycol) (24), or polyesters such as poly(diethylene glycol adipate) (25). Low-molecular-weight diols such as 1,4-butanediol and 1,6-hexanediol are also used as chain extenders. The most important isocyanates are a mixture of 2,4-toluenediisocyanate (17) and its 2,6 isomer (principally the former), methylene-4,4'-diphenyldiisocyanate (26) (MDI), and "polymeric isocyanate" (27), which is derived from the reaction product of aniline with formaldehyde. Aliphatic diisocyanates such as 1,6-hexanediisocyanate and the hydrogenation product of MDI are used primarily in light-stable coatings.

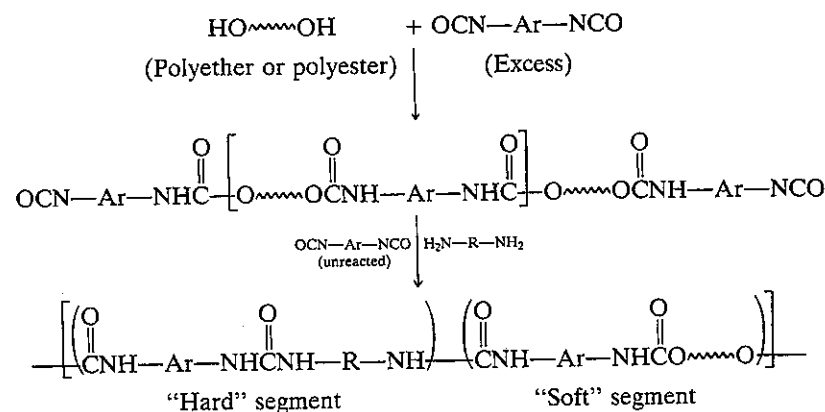


Polyurethane 28 was one of the early fibers produced in Germany as an alternative to the patent-protected nylon fibers. Made from 1,6-hexanediisocyanate and 1,4-butanediol (13.45), it was marketed by Bayer under the trade name Perlon U. Today the most important polyurethane fibers consist of elastomeric AB block copolymers containing alternating "soft" and "hard" segments.^{50,51} (Du Pont's Spandex is an example.) Typically, an



aromatic diisocyanate is reacted in excess with a hydroxy-terminated polyether or polyester having an average molecular weight of 2000 to 3000 to yield an isocyanate-terminated polymer that is, in turn, reacted with a diamine chain extender. The sequence of steps is shown in Scheme 13.1. Note that chain extension occurs via urea rather than urethane linkages.

Elastomeric fibers exhibit morphological characteristics similar to those of thermoplastic elastomers. The hard segments associate into crystalline microdomains while the pre-

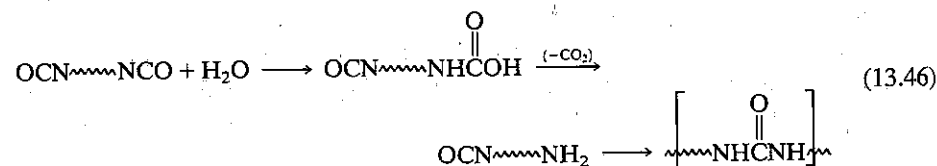


SCHEME 13.1. Synthesis of an elastomeric polyurethane for fiber applications.

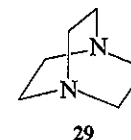
dominant soft segments, which constitute the continuous phase, remain amorphous and randomly coiled. Upon stretching, the soft segments become elongated and crystalline, but when the tension is removed they rapidly revert to the amorphous state.

A variety of conventional elastomers and thermoplastic elastomers are also marketed. The high reactivity of the isocyanate group makes polyurethanes ideally suited to RIM technology.⁵² Large-scale objects such as automobile bumpers are made this way.

Polyurethane foams⁵³ are made from isocyanate-terminated prepolymers having a molecular weight of about 3000 prepared according to reaction (13.44) using excess diisocyanate. Water is added, which causes an increase in molecular weight by formation of urea groups with simultaneous loss of carbon dioxide (13.46). As the evolved gas causes the polymer to foam, the polymerization reaction increases the viscosity and sets the foam before it collapses. A low-boiling liquid such as dichloromethane, which is boiled by the reaction exotherm, is usually added to augment the foaming action of the carbon dioxide.

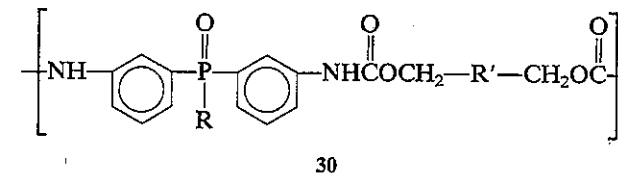


Flexible foams are usually prepared from dihydroxy polyesters or polyethers, rigid foams from polyhydroxy prepolymers. Rigid foams are sometimes prepared without water by reacting a hydroxyl-terminated prepolymer with diisocyanate in the presence of a blowing agent. In this case, molecular weight buildup is via urethane linkages. Such foams are particularly effective insulators because the blowing agents, trapped in the foam cells, have very low thermal conductivity. Metal salts such as stannous 2-ethylhexanoate and tertiary amines, particularly diazabicyclo[2.2.2]octane (29) (commonly called DABCO), are normally used to catalyze urethane formation. DABCO is a more effective catalyst than most other tertiary amines, possibly because the rigid cyclic system minimizes steric interference.

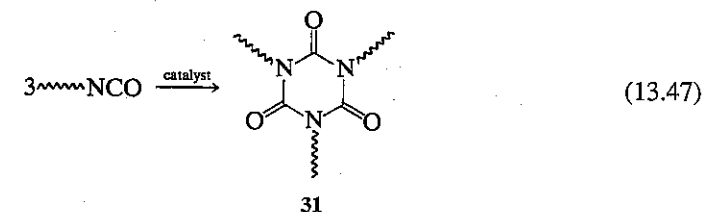


The reaction of diisocyanates with carboxyl-terminated polyesters (reaction 13.33), as discussed earlier, is also used to make flexible foams, in this case by amide formation. It is not uncommon to see such reactions included under urethane foams even though no urethane chemistry is involved. In other words, all foam manufacture that uses diisocyanates tends to be grouped under polyurethanes.

Flexible foams are used as insulators, including textile laminates for cold-weather clothing; automobile crash panels; upholstery; bedding; carpet underlays; synthetic sponges; and other miscellaneous uses. Rigid foams are most commonly used in insulated construction panels, for packaging delicate items, for lightweight furniture, and for marine flotation equipment. The use of these materials in construction has prompted attempts at preparing nonflammable polyurethanes. Phosphorus-containing polyurethanes of type 30, for example, are self-extinguishing.⁵⁴



A different strategy for reducing flammability of foams is to convert terminal and pendant isocyanate groups to *polyisocyanurates*.⁵⁵ The trimerization reaction (13.47) is facilitated by alkali metal alkoxide, phenoxide, and carboxylate catalysts. The isocyanurate moiety (31) serves the dual purpose of reducing flammability and increasing thermal stability.



For "one-pot" coatings formulations, polyurethanes typically prepared with polyesters containing polyfunctional alcohols are treated with excess diisocyanate. Upon exposure to atmospheric moisture, the isocyanate-terminated polymer cures by forming urea linkages according to reaction (13.46). Reaction of the urea groups with unreacted isocyanate leads to further crosslinking via *biuret* groups (13.48). In other one-pot coatings, the isocyanate groups are reacted with a "blocking group" such as phenol, which dissociates on heating to regenerate the isocyanate groups.

