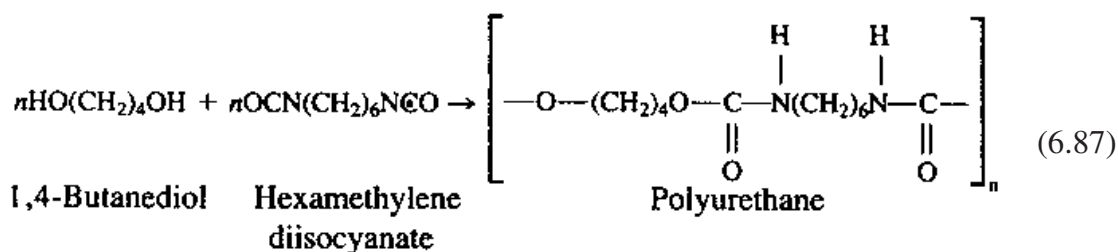


6.10 POLYURETHANES AND POLYUREAS

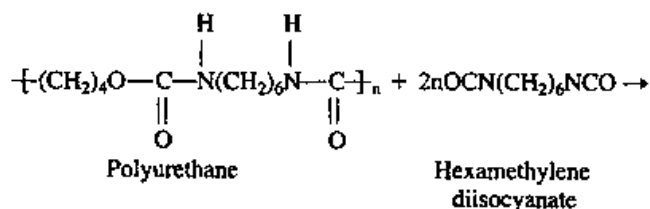
Urethanes, or carbamates, are well-known organic compounds that were formerly used for the characterization of alcohols. Since the fractional conversion (p) of the reaction is relatively high, Bayer was able to prepare numerous useful polyurethanes (PUs) by the reaction of dihydric alcohols and diisocyanates. For example, a crystalline polymeric fiber (Perlon U) may be prepared by the reaction of 1,4-butanediol and hexamethylene diisocyanate as shown in the following equation.



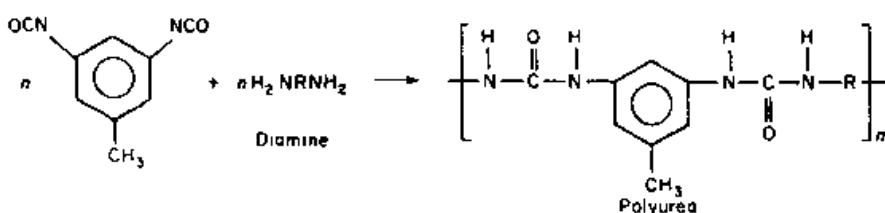
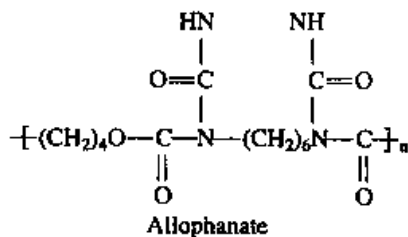
Reactants with an even number of carbon atoms as used in Eq. (6.87) produce higher melting polymers than those with an odd number of carbon atoms. The melting point is decreased as the number of methylene groups is increased, and increased by the incorporation of stiffening groups such as phenylene groups.

Isocyanates react with water to produce unstable carbamic acids, which decompose to form diamines and carbon dioxide, which acts as a blowing agent. Hence, polymeric foams are produced when traces of moisture are present in the reactants. Since many of these forms are formed in situ and isocyanates are toxic, it is preferable to use isocyanate-terminated prepolymers. The latter are prepared from flexible or rigid hydroxyl-terminated polyesters or polyethers.

Crosslinked PU coatings, elastomers, or foams may be produced by using an excess of the diisocyanate, which reacts with the urethane hydrogen to produce an allophanate, or by incorporating polyols such as glycerol or pentaerythritol in the reactant mixture. The diamines produced by the decomposition of carbamic acids react with diisocyanates to produce polyureas. Equations for the formation of an allophanate and a polyurea are shown below.



(6.88)



(6.89)

Many polyurethanes are produced from diisocyanates and macroglycols, also called polyols. The most widely used diisocyanates are tolylene diisocyanate (TDI), methylene isocyanate (MDI), and polymeric isocyanate (PMDI). Mixtures of these can be obtained from the acid-catalyzed condensation of aniline and formaldehyde. MDI and PMDI are coproducts with the MDI separated using distillation.

Aniline, in turn, is produced from the nitration of benzene followed by hydrogenation of the resulting nitrobenzene. The 2,4- and 2,6-toluene diisocyanates (TDIs) are produced from the analogous nitration of toluene followed by the hydrogenation of the resulting dinitrotoluenes.

The polyols are generally either polyether- or polyester-based. Polyether diols are formed from the ring-opening polymerization of alkylene oxides.

Foams

Flexible foams are formed from reaction of the diisocyanates and polyether triols with the trifunctionality producing a three-dimensional network. The foams are generally formed from the introduction of water into the system, which in turn reacts with unreacted isocyanate groups producing carbon dioxide gas giving an open-celled structure used in bedding, furniture, automotive seating, and carpet backing.

More rigid foams are generally formed from the reaction between PMDI and difunctional polyether diols. The multifunctionality is controlled by the use of PMDIs with differing numbers of unreacted isocyanate groups and use of polyols with a functionality greater than 2. The increased crosslinking results in a more rigid product. These materials are used in refrigeration, building and construction, insulation, and storage.

Elastomers

Polyurethane elastomers are segmented block copolymers containing so-called hard (less flexible) and soft segments. The hard segments consist of a stiffer, more rigid polyurethane

portion derived from reaction of the diisocyanate with a short-chained glycol such as ethylene glycol. The soft or flexible portion is derived from the polyester diols with degrees of polymerization generally above 15. The hard segments often aggregate in domains held together by hydrogen bonding mainly between the urethane segments. These polyurethanes can be either thermoset or thermoplastic depending on whether or not crosslinking is introduced.

Reaction injection molding (RIM) is an increasingly important technology that emphasizes the production of thermoset polyurethanes. Here liquid monomers are mixed together under high pressure prior to injection into the mold. Polymerization occurs within the mold.

Polyurethane elastomers are used in the automotive industry. Most automotive dash panels are RIM-produced. Polyurethane elastomeric materials exhibit good abrasion resistance, chemical resistance, and good tear strength with a wide variation of flexibility available. These polyurethanes are also used in fabrics and sporting goods.

Such polymers are also referred to as segmented polyurethanes and are described in greater detail in Chapter 9.

Coatings

Polyurethanes are also widely used as coating materials sold as finished polymers, two-part systems, and prepolymer systems. Water-based systems are now available allowing easy home use. Aromatic diisocyanate-derived coatings generally offer poor external light stability while aliphatic-derived systems offer good light stability.