

POLYURETHANES

The polymers known as polyurethanes include materials that incorporate the carbamate group, -NHCOO- , as well as other functional groups, such as ester, ether, amide, and urea. The name polyurethane is derived from ethyl carbamate, known as urethane. Polyurethanes are usually produced by the reaction of a polyfunctional isocyanate with a macroglycol, a so-called polyol, or other reactants containing two or more groups reactive with isocyanates. Often a combination of a macroglycol and a short-chain glycol extender is used to produce segmented block copolymers. The macroglycols are based on polyethers, polyesters, or a combination of both. In recent years diamines have also been used as comonomers in order to achieve higher reaction rates in molding and spray applications. In addition to the linear thermoplastic polyurethanes, obtained from difunctional monomers, branched or cross-linked thermoset polymers are made with higher functional monomers. Linear polymers have good impact strength, good physical properties, and excellent processibility, but limited thermal stability (owing to their thermoplasticity). Thermoset polymers, on the other hand, have higher thermal stability but sometimes lower impact strength (rigid foams). The higher functionality is obtained with higher functional isocyanates (polymeric isocyanates), or with higher functional polyols. Cross-linking is also achieved by secondary reactions. For example, urea groups are generated in the formation of water-blown flexible foams. An isocyanato group reacts with water to form a carbamic acid, which dissociates into an amine and carbon dioxide, with the latter acting as a blowing agent. The amine reacts with another isocyanate to form a urea linkage. Further reaction of the urea group with the isocyanate leads to cross-linking via a biuret group. Water-blown flexible foams contain urethane, urea, and some biuret groups in their network structure. Urea-modified segmented polyurethanes are manufactured from diisocyanates, macroglycols, and diamine extenders. Polyurethane network polymers are also formed by trimerization of part of the isocyanate groups. This approach is used in the formation of rigid polyurethane-modified isocyanurate (PUIR) foams.

The addition polymerization of diisocyanates with macroglycols to produce urethane polymers was pioneered in 1937 by O. Bayer (1). The rapid formation of high molecular weight urethane polymers from liquid monomers, which occurs

even at ambient temperature, is a unique feature of the polyaddition process, yielding products that range from cross-linked networks to linear fibers and elastomers. The enormous versatility of the polyaddition process allowed the manufacture of a myriad of products for a wide variety of applications.

The early German polyurethane products were based on tolyene diisocyanate (TDI) and polyester polyols. In addition, a linear fiber, Perlon U, was produced from the aliphatic 1,6-hexamethylene diisocyanate (HDI) and 1,4-butanediol. Commercial production of flexible polyurethane foam in the United States began in 1953. In Germany a toluene diisocyanate consisting of an isomeric mixture of 65% 2,4-isomer and 35% 2,6-isomer was used in the manufacture of flexible foam, whereas in the United States the less expensive 80:20 isomer mixture was used. In 1956, DuPont introduced poly(tetramethylene glycol) (PTMG), the first commercial polyether polyol; the less expensive polyalkylene glycols appeared by 1957. The availability of the lower cost polyether polyols based on both ethylene and propylene oxides provided the foam manufacturers with a broad choice of suitable raw materials, which in turn afforded flexible foams with a wide range of physical properties. Polyether polyols provide foams with better hydrolytic stability whereas polyester polyols give superior tensile and tear strength. The development of new and superior catalysts, such as Dabco (triethylenediamine) and organotin compounds, has led to the so-called one-shot process in 1958, which eliminated the need for an intermediate prepolymer step. Prior to this development, part of the polyol was treated with excess isocyanate to give an isocyanate-terminated prepolymer. Further reaction with water produced a flexible foam.

The late 1950s saw the emergence of cast elastomers, which led to the development of reaction injection molding (RIM) at Bayer AG in Leverkusen, Germany, in 1964. Also, thermoplastic polyurethane (TPU) elastomers and Spandex fibers were introduced during this time. In addition, urethane-based synthetic leather was introduced by DuPont under the trade name Corfam in 1963.

The late 1950s also witnessed the emergence of a new polymeric isocyanate (PMDI) based on the condensation of aniline with formaldehyde. This product was introduced by the Carwin Co. (later Upjohn and Dow) in 1960 under the trade name PAPI. Similar products were introduced by Bayer and ICI in Europe in the early 1960s. The superior heat resistance of rigid foams derived from PMDI prompted its exclusive use in rigid polyurethane foams. The large-scale production of PMDI made the coproduct 4,4'-methylenebis(phenyl isocyanate) (MDI) readily available, which has since been used almost exclusively in polyurethane elastomer applications. Liquid derivatives of MDI are used in RIM applications, and work has been done since the 1990s to reinforce polyurethane elastomers with glass, graphite, boron, and aramid fibers, or mica flakes, to increase stiffness and reduce thermal expansion. The higher modulus thermoset elastomers produced by reinforced reaction injection molding (RRIM) are also used in the automotive industry. In 1969 Bayer pioneered an all-plastic car having RIM-molded bumpers and fascia; in 1983 the first plastic-body commercial automobile (Pontiac Fiero) was produced in the United States.

The polymerization step can be conducted in a mold, in an extruder (TPU production), or continuously on a conveyor (block foam production). Also, spraying

of the monomers onto the surface of a substrate produces polyurethane coatings. The resulting polymers can be thermoplastic, which allows reprocessing by injection molding, extrusion, blow molding, and other remelting processes, or they are thermoset polymers as used in the RIM process in the molding of automotive bumpers, or in the manufacture of cellular polyurethanes.

Polyurethanes are a primary component of the global polymer market. They amount to about 6% of the total world plastic use. The world consumption of polyurethanes in 2000 was about 8 million tons, with a global growth averaging around 3–4% a year. The Western Hemisphere uses about 3 million metric tons per annum, Western Europe approximately 2.6 million metric tons per annum, the remainder being used in Asia and Africa.

Today's global polyurethane industry has been reshaped by several mergers of the 1980s and 1990s. Some of the familiar players, such as ICI, Upjohn, Olin, Rhone Poulenc, Union Carbide, and Arco, sold their polyurethane businesses; Bayer, the principal global isocyanate producer, strengthened its position in polyether polyols by acquiring the Arco polyol business in 1999. Also Dow, the other leading producer of polyether polyols, acquired Union Carbide in 1999, which further strengthened its position in polyols. The primary polyurethane players of the new millennium are Bayer, BASF, Dow, and Huntsman, the latter through the purchase of the global ICI business. Lyondell, which acquired the TDI businesses from Olin and Rhone Poulenc, sold the Arco polyol business to Bayer in 1999, thereby indicating their intent to eventually exit polyurethanes. Over the years the primary polyurethane chemical producers underwent forward integration by buying primary polyurethane system houses, ie their principal customers. Recent examples include the acquisition of Essex, a leading producer of automotive windshield adhesives and sealants, and of Flexible Products and General Latex, which are polyurethane foam system houses, by Dow; and BASF acquired IPI International, a producer of insulation foam systems.

In Asia and South America, the primary global chemical producers formed joint ventures with primary local companies, some of which established small volume manufacturing sites. In contrast, Dow/Mitsubishi built an isocyanate distillation plant in Yokaichi, Japan, to separate PMDI/MDI feedstock. Dow has another distillation plant in Delfzijl, Holland, which has been increased by 60% in 2000. In this plant feedstock from Dows Estarreja, Portugal, plant is separated into PMDI and MDI. Although distillation plants are less costly, the other primary producers seem to be involved in building global-size facilities in Asia. For example, BASF plans to build a new 140-kt/a TDI plant in Yosu, South Korea by 2003. A present MDI plant at this site will be simultaneously expanded to 160 kt/a. Also, several major facilities are planned for mainland China. A recent project by Bayer, the building of a major TDI plant in Taiwan, was cancelled because of local opposition to the plant. Enichem in Italy, which acquired its isocyanate technology from ICI, is a regional producer of isocyanates and polyols.

The major producers of polyurethane chemicals also manufacture TPU elastomers. DuPont was also at one time involved in polyurethanes, but it sold its TDI technology to Dow and exited the synthetic leather business. However, DuPont is still the principal force in the production of polyurethane fibers (Lycra). Through the acquisition of Uniroyal and Witco, the Crompton & Knowles Corp. became a

principal force in polyurethane elastomers, which are now sold under the trade name CK Witco. Manufacturing and marketing arrangements include a rigid foam system marketing deal between Huntsman and Shell, and a manufacturing joint venture of BASF and Shell. The latter is named Basell CV, which opened a new styrene monomer/propylene oxide plant at Moerdijk in the Netherlands with a capacity of 250 kt/a of propylene oxide. Another plant in Singapore is scheduled to open in 2002. Some of the new polyols are used to supply Huntsman, which is the only primary polyurethane company without a polyol manufacturing capability.

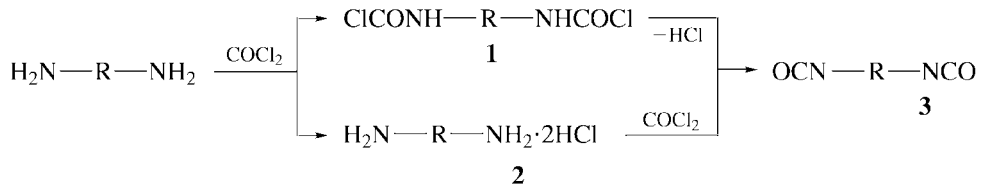
One of the current trends in polyurethanes is the gradual replacement of TDI by the less volatile PMDI or MDI in many applications. The production of PMDI/MDI is a coproduct process, which is economically viable because the market requires amounts of both isocyanates in the amounts presently produced. All primary producers remove some of the higher priced MDI (up to 50%) by vacuum distillation. A process for the manufacture of only MDI does not exist.

Elimination of chlorinated fluorocarbon (CFC) blowing agents and the reduction of emission of volatile organic compounds (VOCs) have been ongoing. The latter leads to a rapid increase in the use of water-based polyurethane dispersions in coating applications. Flexible foam producers have eliminated auxiliary blowing agents, and the rigid foam producers use water-blown formulations in combination with hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs), or hydrocarbons. Adhesives and sealants are reformulated from solvent-based products to 100% solid-and water-based systems.

Isocyanates

The synthesis, reactions, and manufacture of isocyanates were reviewed in 1997 (2), and the chemistry and technology of isocyanates is the subject of a recent book (3).

The standard method of synthesis of isocyanates is the phosgenation of amines or amine salts. The phosgenation of amines to isocyanates was pioneered by Hentschel in 1884 (4). Using this method, a solution of the diamines in chlorobenzene is added to excess phosgene in the same solvent below 20°C. The resultant slurry consisting of the dicarbamoyl chloride (**1**) and the diamine dihydrochloride (**2**) is treated with excess phosgene at temperatures up to 130°C. Upon heating above 65°C the dicarbamoyl chloride dissociates to generate diisocyanate (**3**). The conversion of **2** is very slow, and the use of polar solvents or higher pressures increases the rate of reaction.



In the laboratory a slurry of the diamine salts, obtained by treating a solution of the diamines with hydrogen chloride or carbon dioxide, is treated above 100°C until a clear solution is obtained. Instead of the toxic phosgene gas, the liquid trichloromethyl chloroformate (diphosgene) (5) or the solid bistrichloromethyl carbonate (triphosgene) (6) can be used in the laboratory. The phosgene oligomers have to be used with caution because the toxic monomer can be generated readily and all reactions have to be performed under a fume hood.

In the continuous manufacture of diisocyanates, the by-products (hydrogen chloride and excess phosgene) are vented and separated. The recovered phosgene is recycled and part of the hydrogen chloride is used in the aniline/formaldehyde condensation. The solvents used in the phosgenation of the diamines are aromatic hydrocarbons, especially chlorobenzene and *o*-dichlorobenzene. Occasionally, more polar solvents, such as ethyl acetate, dioxane, nitrobenzene, or dimethylsulfone, are used. Excess phosgene can also be used as solvent if the reaction is conducted under high pressure. Dimethylformamide (DMF) and phenyltetramethylguanidine catalyze the phosgenation reaction (7).

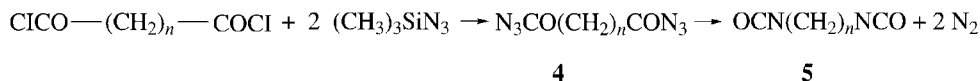
Aliphatic diamines are also phosgenated in a two-phase reaction using methylene chloride and aqueous sodium hydroxide. The diamine and phosgene are dissolved in methylene chloride and the form **2** is instantaneously neutralized with sodium hydroxide. The generated diisocyanate remains in the solvent phase, and excess phosgene is also neutralized with sodium hydroxide, which enhances the safety of phosgene handling. The highly exothermic reaction requires efficient cooling. A disadvantage of this process is the use of a slight excess of phosgene, which cannot be recovered.

Instead of phosgene and its oligomers, oligomeric *t*-butylcarbonates are also used to convert diamines into diisocyanates. For example, sterically hindered aromatic diamines react with di-*t*-butyldicarbonate in the presence of dimethylaminopyridine in acetonitrile at room temperature to give sterically hindered aromatic diisocyanates. In this manner 3,6-3',6'-tetramethyl MDI is obtained in 93% yield (8). Also, aliphatic diamines react with di-*t*-butyltricarboxylate at room temperature to give a high yield of the corresponding diisocyanates (9).

Since the early 1970s, attempts have been made by the principal global producers of isocyanates to avoid the use of the toxic phosgene in the manufacture of isocyanates. Attempts to produce TDI and PMDI by nonphosgene processes have failed. However, two aliphatic diisocyanates, CHDI and TMXDI, are manufactured using nonphosgene processes. Hüls and BASF have also announced plans to use nonphosgene processes for the manufacture of IPDI in their new plants which are under construction. In the new, nonphosgene chemistry, isocyanic acid, generated by thermolysis of urea, reacts with diamines to give a bis-urea derivative. Subsequent reaction with diethylamine affords tri-substituted urea derivatives, which are thermolyzed in an inert solvent in the presence of an acidic catalyst to give the diisocyanate (10). Gaseous ammonia is the only by-product in this process. Also, reaction of aliphatic diamines with carbon dioxide, in the presence of triethylamine, affords biscarbamate salts, which can be dehydrated with phosphoryl chloride to give the diisocyanate (11).

Another laboratory method of synthesis of diisocyanates is the thermolysis of bisacylazides (**4**) (Curtius reaction). For example, dicarboxylic acid chlorides react

with trimethylsilyl azide to give (4), which is thermolyzed in an inert solvent to give the diisocyanates (5), $n = 3-10$ (12).



The preparation of aliphatic diisocyanates, using bisacylazides, has to be conducted with caution because an explosion occurred in the preparation of ethylene diisocyanate by using this method (13). Ethylene diisocyanate is readily obtained by dehydrochlorination of a heterocyclic allophanoyl chloride derivative obtained in the phosgenation of ethyleneurea (14).

The commodity aromatic isocyanates TDI and PMDI/MDI are most widely used in the manufacture of urethane polymers. Toluene diisocyanate, TDI, is a distilled 80:20 mixture of 2,4- and 2,6-isomers. However, pure 2,4-TDI and a 65:35 mixture of the 2,4- and 2,6-isomers are also commercially available. Pure 2,4-TDI, mp 19.5–21°C, is obtained on cooling of 80:20 TDI. The manufacture of TDI involves nitration of toluene, hydrogenation to the diamines, and phosgenation. Separation of the undesired ortho derivatives, such as 2,3- and 3,4-dinitrotoluene, is necessary because their presence interferes with the polymerization of TDI (15).

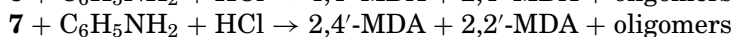
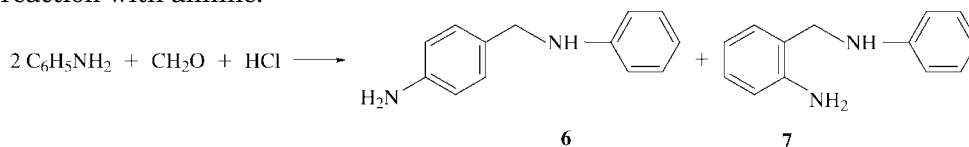
The other commodity isocyanate, PMDI/MDI, is based on benzene. Mononitration of benzene, catalytic reduction to aniline, followed by condensation of aniline with formaldehyde produces oligomeric amines, which are phosgenated to give mixtures of PMDI and MDI. MDI is separated from PMDI by continuous thin-film vacuum distillation.

PMDIs are crude products that vary in exact composition. The main constituents are 40–60% MDI; the remainder is the other isomers of MDI, triisocyanates, and higher molecular weight oligomers. Important product variables are functionality and acidity. Rigid polyurethane foams are mainly manufactured from PMDI. The so-called pure MDI is a low melting solid that is used for high performance polyurethane elastomers and spandex fibers.

Liquid MDI (Isonate 143-L) is produced by converting some of the isocyanate groups in MDI to carbodiimide groups, which react with the excess isocyanate present to form a small amount of the trifunctional four-membered ring cycloadduct (16). The presence of the cycloadduct lowers the melting point of MDI to give a liquid product. In most applications the trifunctional cycloadduct will dissociate into difunctional monomers; therefore, this type of liquid MDI can be used in the manufacture of linear polyurethanes. Liquid MDI products are also made by reaction of the diisocyanate with small amounts of glycols. These products are called prepolymers. MDI products enriched in 2,4-MDI are also available. The latter are used in the manufacture of flexible MDI foams.

The manufacture of the oligomeric amine precursors for PMDI/MDI is conducted by continuously adding formaldehyde to aniline in the presence of less than the stoichiometric amount of hydrochloric acid at room temperature in agitated reactors. The reaction mixture is gradually heated to 100°C over a period of several hours. The reaction can also be conducted under pressure at higher temperatures in order to increase the rate of reaction. However, the oligomeric amines produced in this manner contain higher amounts of 2,2'- and 2,4'-methylenedianiline

(MDA). The acid-catalyzed aniline/formaldehyde reaction proceeds in two steps. At room temperature aniline reacts with formaldehyde to form N-substituted carbonium ions which attack aniline in the para- and ortho-position to give a mixture of *p*-aminobenzylamine (PABA), (**6**), *o*-aminobenzylamine (OABA), (**7**), and oligomeric benzylamines. Subsequent heating affects dissociation of the benzylamines to give C-bonded carbonium ions, which form another C–C bond in their reaction with aniline.



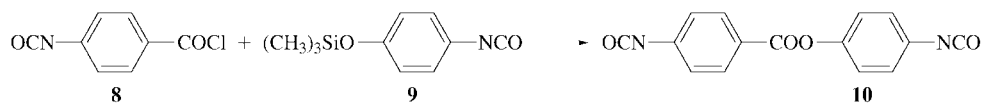
The variables affecting the product distribution are aniline concentration, hydrochloric acid concentration, and temperature. The higher the excess of aniline, the higher is the diamine concentration. Higher hydrochloric acid concentration and lower initial temperature favor the formation of 4,4'-MDA. Attempts were made over the years to replace the aqueous hydrochloric acid catalyst with slower reacting solid acidic clay catalysts, but the obtained product distribution was different, and therefore this approach was never used.

The commercial manufacture of TDI and PMDI/MDI is the continuous phosgenation under pressure of the amine precursors in an inert solvent at elevated temperatures. The by-products, hydrogen chloride and excess phosgene, are continuously vented and separated. The recovered phosgene is recycled and the hydrogen chloride is used in the aniline/formaldehyde condensation, or it is sold or reoxidized to chlorine to be reused in the manufacture of phosgene. In case of the manufacture of PMDI, some of the diisocyanate (MDI) is separated by continuous vacuum distillation using a wiped film evaporator. In this operation the residual PMDI, which still contains MDI, is only subjected to a short heat treatment. The advantage of the simultaneous manufacture of both isocyanates is a quantitative yield because the by-products of the phosgenation reaction are contained in the residual PMDI.

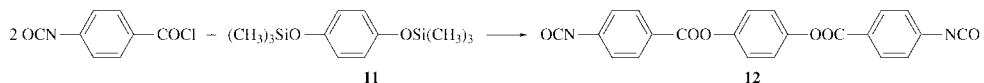
The current prices of the commodity aromatic isocyanates (DM/kg) are TDI: 3.6; PMDI: 2.8; MDI: 4.3. The light-stable aliphatic isocyanates are somewhat more expensive.

Several higher-priced aromatic diisocyanates, such as *p*-phenylene diisocyanate (PPDI), 1,5-naphthalene diisocyanate (NDI), and bitolyene diisocyanate (TODI), are also available. These symmetrical high melting diisocyanates give high melting hard segments in polyurethane elastomers.

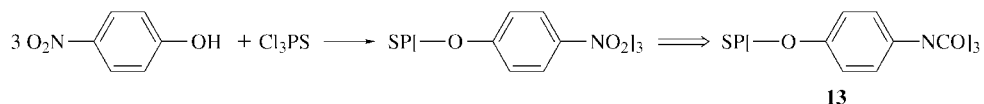
Aromatic diisocyanates are also obtained in the coupling of suitable monoisocyanates. For example, reaction of 4-isocyanatobenzoyl chloride (**8**) with a trimethylsiloxy-substituted isocyanate (**9**) affords diisocyanato benzoates (**10**) (17).



Triad diisocyanates (**12**) are obtained in the reaction of two equivalents of 4-isocyanatobenzoyl chloride with the silylated hydroquinone derivative (**11**) (18).

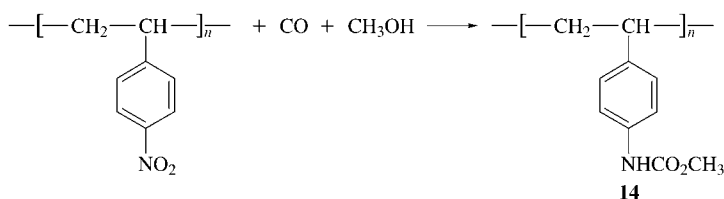


The aromatic triisocyanate (**13**) is obtained in the reaction of 4-nitrophenol and thiophosphoryl chloride, followed by reduction and phosgenation. (19). This triisocyanate is sold under the trade name Desmodur RF (Bayer) as a glue for rubber adhesive solutions.



Aromatic triisocyanates as cross-linkers are more readily obtained by trimerizing 2,4-TDI. In this reaction the more reactive isocyanate group in the 4-position undergoes trimerization to produce a triisocyanate (20).

Also, aromatic polyisocyanates are obtained in the copolymerization of styrene with cinnamoyl azide (21). Blocked polyisocyanates (**14**) are obtained from *p*-nitrostyrene and carbon monoxide in methanol, using a ruthenium catalyst (22).



Polyurethanes obtained from aromatic diisocyanates undergo slow oxidation in the presence of air and light causing discoloration, which is unacceptable in some applications. In contrast, polyurethanes obtained from aliphatic diisocyanates are color stable, although it is necessary to add antioxidants and uv-stabilizers to the formulations to maintain the physical properties of the polymers with time.

The elusive parent diisocyanate, $\text{O}=\text{C}=\text{N}-\text{N}=\text{C}=\text{O}$, is only stable at -75°C , and therefore it is not suitable as a monomer for polyurethanes (23). The least costly aliphatic diisocyanate is hexamethylene diisocyanate (HDI), which is obtained by phosgenating the nylon intermediate hexamethylenediamine (HDA). Because of its low boiling point, HDI is mostly used in the form of its derivatives, such as biurets, allophanates, dimers, or trimers (24). Isophorone diisocyanate (IPDI) and its derivatives are also used in the formulation of rigid coatings, while hydrogenated MDI (HMDI) and cyclohexane diisocyanate (CHDI) are used in the formulation of flexible coatings and polyurethane elastomers.

HDA is commercially produced from adipic acid or butadiene. The catalytic hydrogenation of adiponitrile to HDA is common in both routes. The phosgena-

Table 1. Phosgenation Processes for Aliphatic Diisocyanates

Method	Rate of reaction	Diamine concentrations	Yields
Diamine salts ^{a,b}	Very slow	Lowest	Highest
Diamines	Faster	Higher	High
Two-phase ^c	Very fast	High	Lower

^aHydrochlorides or carbamates from diamines and carbon dioxide.

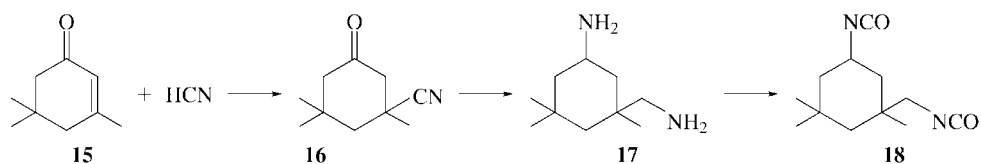
^bThis reaction can also be conducted using excess phosgene as solvent.

^cUsing water, sodium hydroxide, and methylene chloride.

tion of the diamine is conducted continuously in chlorobenzene. In Table 1 the advantages and disadvantages of several phosgenation processes for aliphatic diisocyanates are shown.

In a recent patent a nonphosgene synthesis of HDI is described (25). Reaction of HDA with urea and ethanol, in the presence of $\text{Co}(\text{OAc})_2$ at 170–175°C, affords the biscarbamate, which is thermolyzed in a thin-film evaporator at 260–270°C.

The other significant aliphatic diisocyanate, IPDI, is based on isophorone chemistry. Trimerization of acetone gives isophorone (**15**), which on reaction with HCN affords the β -cyanoketone (**16**). Reductive amination of (**16**) to the diamine (**17**), followed by phosgenation, gives IPDI (**18**).



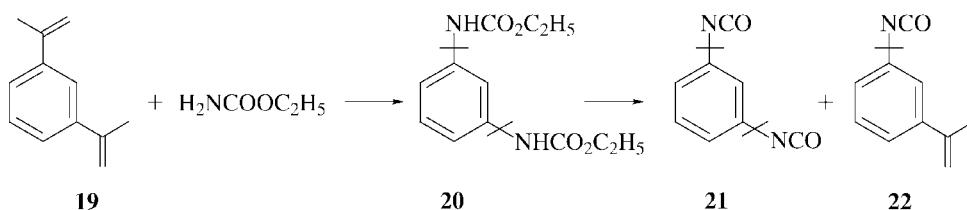
An example of a nonphosgene route to IPDI is the reaction of **17** with urea and *n*-butanol in the presence of dibutyl carbonate at 210–220°C. Thermolysis of the biscarbamate at 270–280°C at 30 mbar affords **18** (26). IPDI is a mixture of 72% *cis* isomers and 28% *trans* isomers (27).

HMDI was originally produced by DuPont as a coproduct in the manufacture of Quiana fiber. After terminating Quiana production DuPont sold the product to Bayer. Today, a crude mixture of the diamines obtained in the acid-catalyzed aniline/formaldehyde reaction is supplied by Bayer to Air Products, which is performing the ring hydrogenation. The phosgenation of the ring hydrogenated diamines is performed by Bayer. Commercial HMDI is a mixture of three stereo isomers (*trans*–*trans*, mp 65°C; *cis*–*trans*, mp 36°C; and *cis*–*cis*, mp 61°C). The direct formation of a blocked HMDI is conducted by ring hydrogenation of caprolactam blocked MDI (28).

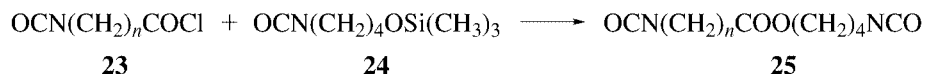
Semicommercial aliphatic diisocyanates include *trans*-cyclohexane-1,4-diisocyanate (CHDI) and *m*-tetramethylxylene diisocyanate (TMXDI). A coproduct in the production of TMXDI is *m*-isopropenyl- α,α -dimethylbenzyl isocyanate (TMI), which can be copolymerized with other olefins to give aliphatic polyisocyanates. These aliphatic diisocyanates are manufactured using nonphosgene routes. Akzo has developed the CHDI process based on scrap polyester fiber. Ring hydrogenation of dimethyl terephthalate (DMT), transesterification with diethylene glycol, followed by reaction with ammonia provides a diamide, which

is N-chlorinated. Hofmann rearrangement in the presence of diethylamine produces the blocked diisocyanate, which is subsequently deblocked on heating in the presence of hydrogen chloride (29). Cyclohexyl diisocyanate (CHDA) can also be obtained by catalytic hydrogenation of *p*-phenylenediamine. Most likely, this approach has economic advantages over the multistep process based on fiber scrap.

The manufacture of TMXDI, developed by American Cyanamid, is based on the reaction of *m*-isopropylidenebenzene (19) with ethyl carbamate to give the blocked diisocyanate (20). Thermolysis affords a mixture of TMXDI (21) and the monoisocyanate (TMI) (22) (30).



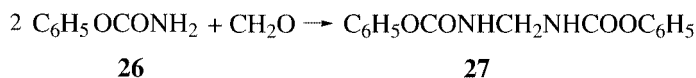
The coupling of ω -isocyanatocarboxylic acid chlorides (23) with silylated aliphatic hydroxy-isocyanates (24) is another method of synthesis of aliphatic diisocyanates (25), containing ester groups in their structure (31).



In Table 2 the physical properties and the manufacturers of the commercial isocyanates are listed.

Blocked and Modified Isocyanates

Masked or blocked diisocyanates are used in coating applications. The blocked diisocyanates are storage-stable, nonvolatile, and easy to use in powder coatings. Blocked isocyanates are produced by reaction of the diisocyanate with blocking agents such as caprolactam, 3,5-dimethylpyrazole, phenols, oximes, acetoacetates, or malonates. Upon heating at 120–160°C, the blocked isocyanates dissociate and the generated free isocyanate reacts with hydroxyl groups available in the formulation to give high molecular weight polyurethanes. In the case of acetoacetates and malonates, the free isocyanates are not regenerated, but the adducts undergo transesterification reactions with the present polyol upon heating (32). A phenol-blocked methylene diisocyanate (27) is obtained in the reaction of phenyl carbamate (26) with formaldehyde (33).

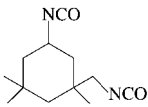
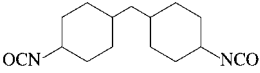


The blocking of isocyanato groups with phenol is used in the formation of hyperbranched polyurethanes from a benzylalcohol derivative, having two

Table 2. Properties of Commercial Isocyanates

Name	Structure	CAS Reg. No.	Boiling point °C _{kPa^a}	Melting point °C	Producer
PPDI		[104-49-4]	110–112 _{1,6}	94–96	Akzo
TDI		[1321-38-6]	121 _{1,33}	14 ^b	BASF, Bayer, Dow, Lyondell, Enichem, Mitsui
MDI		[101-68-8]	171 _{0,13}	39.5	BASF, Bayer, Dow, Enichem
PMDI		[9016-87-9]			
NDI		[3173-72-6]	244 _{0,017}	130–132	Bayer, Mitsui
TODI		[91-97-4]	160–170 _{0,066}	71–72	Nippon-Soda
XDI		[3634-83-1]	159–162 _{1,6}		Takeda
TMXDI		[58067-42-8]	150 _{0,4}		American Cyanamid
HDI	OCN(CH ₂) ₆ NCO	[822-06-0]	130 _{1,73}		Bayer, Lyondell, Mitsui, Hüls
TMDI		[83748-30-5]	149 _{1,33}		
		[15646-96-5]			
CHDI		[2556-36-7]	122–124 _{1,6}		Akzo
HXDI		[38661-72-2]	98 _{0,053}		Takeda

Table 2. (Continued)

Name	Structure	CAS Reg. No.	Boiling point °C _{kPa} ^a	Melting point °C	Producer
IPDI		[4098-71-9]	153 _{1.33}		BASF, Bayer, Hüls, Lyondell
HMDI ^c		[5124-30-1]	179 _{0.12}	trans-trans 65 cis-trans 36 cis-cis 61	Bayer

^aTo convert kPa to mm Hg, multiply by 7.5.

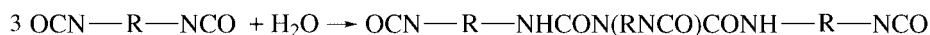
^bMixture of 80% 2,4-isomer [584-84-9] and 20% 2,6-isomer [91-08-7].

^cMixture of stereoisomers.

NHCOOC₆H₅ groups in the 3,5-position (34). Intramolecular dimers derived from long-chain aliphatic diisocyanates (35) and macrocyclic ureas (36) are also used as masked aliphatic diisocyanates.

Blocked aliphatic isocyanates or their derivatives are used for one-component coating systems. Masked polyols are also used for this application. For example, polyols capped with vinyl or isopropenyl ethers produce polyacetals, which do not react with isocyanates. Hydrolysis of the acetals with moist air regenerates the hydroxyl groups, which undergo polyurethane reaction with isocyanate-terminated prepolymers (37). In addition, substituted oxazolines are used as masked cross-linkers (38). Ketimine cross-linkers are also utilized in the formulation of one-component coating systems (39). Hydrolysis of ketimines produces diamines, which undergo a very fast reaction with isocyanate-terminated prepolymers. Blocked isocyanates are also used in the cross-linking of acrylic resins for automotive coatings. Incorporation of masked diisocyanates into epoxy resins lowers the moisture absorption in the derived coatings (40).

Other modified commercial diisocyanates include diisocyanate prepolymers, biurets, and isocyanurates (trimers). Asymmetric trimers (iminooxadiazine diones) are also obtained from aliphatic diisocyanates, using fluoride-based catalysts. The modifications of the commercial isocyanates are necessary to lower their melting points, or to lower their vapor pressure. The prepolymers used in the manufacture of polyurethanes are mainly urethane modified diisocyanates, formed in the reaction of the diisocyanate with a small amount of a macrodiol. Hydroxy-terminated prepolymers can also be prepared, but they are of no commercial significance. To raise the vapor pressure of aliphatic diisocyanates they are converted into allophanates, biurets, or triisocyanurates (trimers). HDI is mainly used as the biuret, (28), which is formed in the reaction of 3 mol of HDI with 1 mol of water, or other active hydrogen containing compounds, such as hydrated inorganic salts, tertiary alcohols, formic acid, pivalic acid, hydrogen sulfide, monoamines, or diamines.



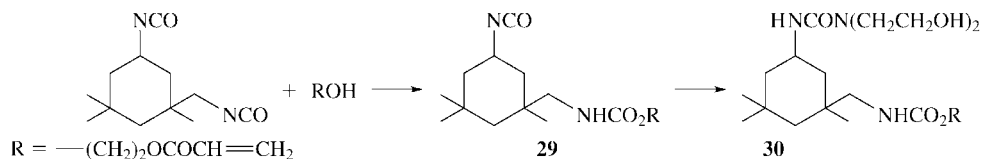
28

High temperature (>270°C) reaction of HDA with excess HDI is a commercial process to produce the HDI biuret (41). The excess HDI is removed by thin-film vacuum distillation. For the conversion of HDI into a triisocyanurate

derivative (trimer), using benzyltrimethyl ammonium hydroxide as the catalyst, it is advantageous to remove carbon dioxide from the diisocyanate by sparging with nitrogen (42). When tributylphosphine is used as the catalyst a mixture of dimers and trimers (3:2) is obtained (43). Sometimes prepolymers are used as coreactants in the trimerization of HDI (44). Also, mixtures of HDI and IPDI are used to generate the mixed trimers (45). On standing, HDI biurets slowly generate monomeric HDI; therefore, it is advantageous to use allophanates as the diisocyanate derivatives because allophanates do not dissociate on standing. Glycols, polyols, or monoalcohols are used to initiate allophanate formation.

The derivatization of IPDI is easier to accomplish because of the different reactivities of the two isocyanate groups in the molecule. For example, preferential dimerization of the primary isocyanate group is observed in the trialkylphosphine-catalyzed reaction (46). Trimerization of IPDI in the presence of quaternary ammonium salts affords mainly the isocyanurate trimer (47). Attempted biuret formation from IPDI and $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ gives a mixture of ureas and biurets (48). A biuret derivative is also obtained from IPDI and HDA (49).

The use of catalysts plays a role in determining which isocyanate group in IPDI is more reactive. For example, in the reaction of IPDI with *n*-butanol at 50°C the secondary isocyanate group is 1.6 times more reactive than the primary isocyanate group in both stereoisomers. Using dibutyltin dilaurate as the catalyst, the reactivity of the secondary NCO group is about 12 times higher than the primary NCO group. However, using a tertiary amine catalyst (DABCO) the primary NCO group is 1.2 times more reactive than the secondary NCO group (50). The selective reactivities of the isocyanate groups in IPDI can be utilized to generate a diol containing an acrylic double bond for cross-linking (51). Reaction of the initially formed carbamate (29) with diethanolamine affords the diol (30).



The selective reaction of the *p*-isocyanato group in 2,4-TDI is used to produce the TDI dimer, which is a higher melting solid diisocyanate. In Table 3 some modified commercial diisocyanates are listed.

Polyols

Polyether Polyols. The polyether polyols used in the manufacture of polyurethanes are hydroxy-terminated macromolecules, with molecular weights ranging from 250 to 8000. Lyondell/Bayer has provided pilot plant diols/triols having molecular weights of 10,000 to 15,000 for lubricant and surfactant applications. The hydroxy functionality can range from 2 to 8. The economically attractive polyether polyols based on alkylene oxides are listed in Table 4.

Other speciality initiators derived from natural products are also manufactured. Examples include formose, lactose, α -methyl glucoside, and

Table 3. Modified Commercial Diisocyanates

Modification	Description	Unreacted isocyanate, % ^a	Viscosity at 25°C, MPa ^b	NCO ^c	Application and trade names
Urethane	MDI and low mol. weight weight polyether diol	60	800	22	PU RIM elastomers
	TDI and low mol. weight triol ^d	<0.5	2,000	12.5	Lupranate MP 102 (BASF) Mondur PF (Bayer) Isonate 181 (Dow) Coatings
	MDI and polyester Polyol	13	2,000 ^d	6.5	Mondur CB (Bayer) Elastomers Baytec (Bayer)
Allophanate	TDI and low mol. weight diol	70	20	4.0	Flexible PU foam Mondur HR (Bayer)
Biuret	HDI ^e	<0.7	10,000	22	Coatings Desmodur N (Bayer)
Dimer	TDI	<0.7	Solid	13 (48) ^f	Desmodur TT (Bayer)
Trimer	IPDI ^g	<0.7	2,000	12	Coatings (Huels)
Carbodiimide	MDI, partial reaction	70	40	29	Elastomers Lupranate MM 103 (BASF) Mondur CD (Bayer) Isonate 143-L (Dow)

^aBased on total mixture.

^bTo convert MPa to psi, multiply by 145.

^cWt% NCO (equivalent weight = 42).

^dRemoval of excess isocyanate under vacuum.

^ePartial reaction followed by removal of excess isocyanate.

^fIn parentheses: amount of isocyanate available after thermolysis of the dimer.

^g30% solvent modification.

Table 4. Commercial Polyether Polyols

Product	Nominal functionality	Initiator	Cyclic ether ^a
Poly(ethylene glycol) (PEG)	2	Water or EG ^b	EO
Poly(propylene glycol) (PPG)	2	Water or PG	PO
PPG/PEG ^c	2	Water or PG	PO/EO
Poly(tetramethylene glycol) (PTMG)	2	Water	THF
Glycerol adduct	3	Glycerol	PO
Trimethylolpropane adduct	3	TMP	PO
Pentaerythritol adduct	4	Pentaerythritol	PO
Ethylenediamine adduct	4	Ethylenediamine	PO
Phenolic resin adduct	4	Phenolic resin	PO
Diethylenetriamine adduct	5	DETA	PO
Sorbitol adduct	6	Sorbitol	PO
Sucrose adduct	6	Sucrose	PO

^aEO: ethylene oxide, PO: propylene oxide, THF: tetrahydrofuran.

^bEG: ethylene glycol, PG: propylene glycol.

^cRandom or block copolymers.

soybean-derived polyols. Propoxylation of dairy waste also affords polyether polyols. DuPont has developed a fermentation process to convert glucose into 1,3-propanediol, a useful polyurethane extender.

The alkylene oxide polymerization is usually initiated by alkaline hydroxides, especially potassium hydroxide. In the base-catalyzed polymerization of propylene oxide (PO), some rearrangement occurs to give allyl alcohol. Further reaction of allyl alcohol with PO produces a monofunctional alcohol. Therefore, polyether polyols derived from PO are not truly difunctional. By using zinc hexacyano cobaltate as catalyst, a more difunctional polyol is obtained (52). Olin has introduced the difunctional polyether polyol under the trade name Poly-L. This product is now available from Arch Chemicals. Similar polyols free of monol contamination are available from Arco/Lyondell/Bayer and Asahi.

Ethylene oxide is manufactured by direct oxidation of ethylene, in contrast PO is only obtained in coproduct processes. The classical process, chlorination of propylene, is still used by Dow, one of the world's largest producer of polyether polyols. In contrast, all other producers use the Halcon process, based on the simultaneous production of PO and styrene monomer or *t*-butyl alcohol. In view of the demise of MTBE (methyl-*t*-butyl ether based on *t*-butyl alcohol) as a fuel additive, the styrene coproduct process (POSM) will remain as the economically viable route to PO. A recent example is the new (SMPO) plant of Basell at Moerdijk in the Netherlands. The largest producer of PO, the former Arco (now Lyondell), has sold its global polyol business to Bayer in 1999. Lyondell will also provide Bayer a long-term, low cost supply of PO. Recently, Dow announced that it also will use the POSM route to PO in a new facility.

The backbone of the polyether polyols are either PO homopolymers or random or block copolymers with ethylene oxide. Important characteristics of the polyol are their hydroxy functionality, hydroxy equivalent weight, and their

reactivity and compatibility with the other components used in the polyurethane formulation. Blending of polyols of different functionality, molecular weight, and reactivity can be used to tailor a polyol for a specific application. Since primary hydroxy groups are more reactive than secondary hydroxy groups, it is advantageous to produce block copolymers with terminal primary hydroxyl groups by using ethylene oxide last in a block copolymer. Capping with ϵ -caprolactone also produces primary hydroxyl groups. Trichlorobutylene oxide-derived polyols are used as fire retardants. The hydrophobicity of polyether polyols can be modified by homo- or copolymerization with 1,2-butylene oxide or styrene oxide. The higher molecular weight polyether polyols are soluble in organic solvents. Poly(PO) is soluble in water up to a molecular weight of 760, and copolymerization with ethylene oxide expands the range of water solubility. Random copolymers are obtained by polymerizing mixtures of PO and ethylene oxide. The viscosity of polyether polyols increases with hydroxyl equivalent weight.

With amine initiators the so-called self-catalyzed polyols are obtained, which are used in the formulation of rigid spray foam systems. The rigidity or stiffness of a foam is increased by aromatic initiators, such as Mannich bases derived from phenol, phenolic resins, toluenediamine, or methylenedianiline (MDA). BASF/Dow have formed a venture into Mannich polyols for spray foam applications.

In the manufacture of highly resilient flexible foams and some thermoset RIM elastomers, graft or polymer polyols are used. Graft polyols are dispersions of free-radical-polymerized mixtures of acrylonitrile and styrene partially grafted to a polyol. Polymer polyols are available from BASF, Dow, and Union Carbide. *In situ* polyaddition reaction of isocyanates with amines in a polyol substrate produces polyharnstoff dispersion (PHD) polyols, which are marketed by Bayer (53). In addition, blending of polyether polyols with diethanolamine, followed by reaction with TDI, also affords a urethane/urea dispersion (54). The polymer or PHD-type polyols increase the load bearing properties and stiffness of flexible foams. Interreactive dispersion polyols are also used in RIM applications where elastomers of high modulus, low thermal coefficient of expansion, and improved paintability are needed.

Polyester Polyols. Initially polyester polyols were the preferred raw materials for polyurethanes, but today the less expensive polyether polyols dominate the polyurethane market. An exception are the inexpensive aromatic polyester polyols, which have been introduced for rigid foam applications. These are obtained from residues of terephthalic acid production or by transesterification of DMT or poly(ethylene terephthalate) (PET) scrap with glycols. TBI of France is the first European company to manufacture aromatic polyester polyols directly from PET scrap bottles at Isoire with a capacity of 10 kt/a. Phthalates and terephthalates are also used.

Polyester polyols are based on saturated aliphatic or aromatic carboxylic acids and diols or mixtures of diols. The carboxylic acid of choice is adipic acid because of its favorable cost/performance ratio. For elastomers, linear polyester polyols of molecular weight of ca 2000 are preferred. Branched polyester polyols, formulated from higher functional glycols, are used for foam and coating applications. Polyester polyol-derived polyurethanes have a lower hydrolytic stability

compared to polyurethanes made from polyether polyols, but they have better oxidative and thermal stabilities.

In addition, polyester polyols are made by the reaction of caprolactone with diols. Poly(caprolactone diols) are used in the manufacture of TPU elastomers with improved hydrolytic stability (55). The hydrolytic stability of the poly(caprolactone diol)-derived TPUs is comparable to TPUs based on the more expensive long-chain diol adipates (56). Polyether/polyester polyol hybrids are synthesized from low molecular weight polyester diols, which are extended with PO.

The most important chain extenders are ethylene glycol, diethylene glycol, propylene glycol, 1,4-butanediol, cyclohexanedimethanol, and hydroquinone dihydroxyethyl ether. Recently, 1,3-propanediol (57) and 1,2,4-butanetriol (58) have become available as new polyurethane raw materials. Since ethylene glycol-extended polyurethanes are prone to thermal degradation, ethylene glycol is only used as a RIM extender in thermoset polyurethanes.

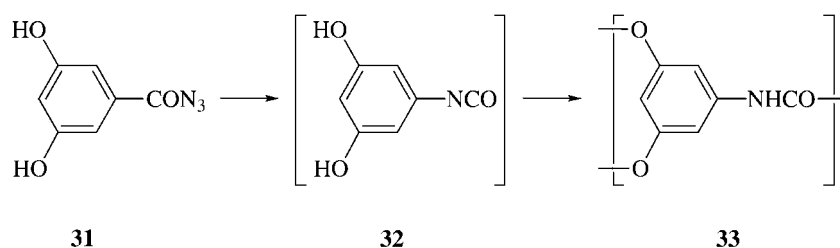
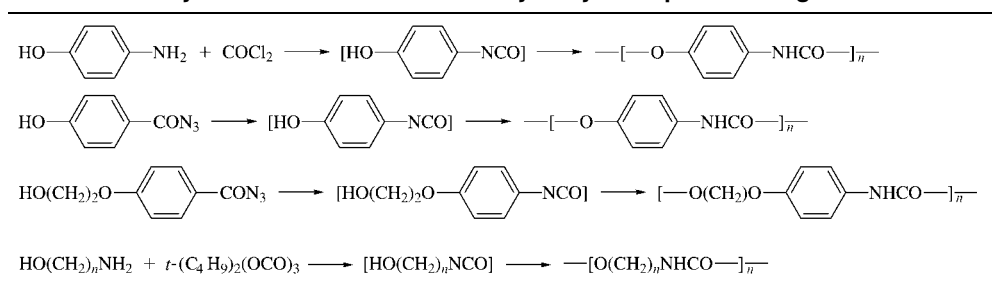
Linear Polyurethanes and Poly(urethane ureas)

The chemistry and technology of polyurethanes is described in Reference 59. Numerous co-workers at Bayer have contributed to this book. Another important compilation of polyurethane technology can be found in Reference 60. This book is comprised of articles from Dow scientists. Also, a summary of polyurethane chemistry and technology is found in the somewhat older book compiled by ICI researchers (61).

Polyurethanes are generally obtained by reacting a difunctional hydroxy compound with a diisocyanate to yield A_2B_2 polymers. AB-type polyurethanes are obtained by cationic ring-opening polymerization of cyclic carbamates (62). Polymerization of monomers containing a hydroxyl and an isocyanate group in the monomer also affords AB polymers. The latter are usually generated *in situ* because of the incompatibility of both groups. An exception are substituted isocyanatophenols obtained in the phosgenation of aminophenols. While 4-isocyanatophenol undergoes homopolymerization after removal of the solvent, alkyl substituents adjacent to the functional groups increase the stability of isocyanatophenols (63). The reactive functional groups can also be generated from suitable precursors. For example, 4-hydroxybenzoyl azide, upon thermolysis, produces the AB homopolymer (64). From 4-(2-hydroxyethoxy)benzoyl azide the corresponding aliphatic/aromatic AB polyurethanes are obtained, the coproduct being gaseous nitrogen (65). An aliphatic AB monomer can be generated from aminoalcohols and di-*t*-butyltricarboxylate. In the presence of $Zr(acac)_4$ the monomer undergoes homopolymerization. In this manner aliphatic polyurethanes $[-(CH_2)_x-NHCO-]_n$, $X = 4-12$ are obtained (66). These reactions are summarized in Table 5. Desilylation of silylated hydroxyester isocyanates with HF in pyridine also affords the corresponding AB homopolymer (67).

The generation of isocyanates from azide precursors is also utilized in the formation of hyperbranched polyurethanes **33** by thermolysis of 3,5-dihydroxybenzoyl azide (**31**) (68). The ABB-type monomer (**32**), generated *in situ*, undergoes polymerization to form a network polymer.

Table 5. AB Polyurethanes Generated from Hydroxyl Group Containing Monomers



The majority of commercial polyurethanes are A_2B_2 polymers. The useful physical properties of polyurethanes are derived from their molecular structure and determined by the choice of building blocks as well as the supramolecular structures caused by atomic interaction between chains. The ability to crystallize, the flexibility of the chains, and spacing of polar groups are of considerable importance, especially in linear thermoplastic materials. In rigid cross-linked systems, such as polyurethane foams, other factors such as density determine the final properties.

The unique properties of linear TPUs are attributed to their long-chain structure. TPU elastomers are segmented block copolymers, comprising of hard- and soft-segment blocks. The soft-segment blocks are formed from long-chain polyester or polyether polyols and MDI; the hard segments are formed from short-chain diols, mainly 1,4-butanediol, and MDI. Under ambient conditions the higher-melting hard segments are incompatible with the soft segments, and microphase separation occurs. The hard segments aggregate into crystalline domains, in which hydrogen bonding of the $-\text{NH}-$ groups of the urethane chain bond to neighboring carbonyl groups occurs. Upon melting, the crystalline domains are disrupted and the polymer can be processed. In Table 6 the melt temperature of hard segments formed from MDI and glycols are shown. The 1,4-butanediol extended MDI-based polyurethane has the highest melting hard segment (69).

The symmetrical MDI is more suitable for the preparation of segmented polyurethane elastomers having excellent physical properties. Segmented polyurethanes are also obtained from 2,6-TDI, but an economically attractive separation process for the TDI isomers has yet to be developed.

The melt viscosity of a TPU depends on the weight-average molecular weight and is influenced by chain length and branching. TPUs are viscoelastic

Table 6. T_m of Model Hard Segments Derived from MDI and Glycols

Linear glycol	Hard segment T_m , °C
1,2-	199.7
1,3-	203.8
1,4-	208
1,5-	172.2
1,6	168
1,7-	164
1,8-	176
1,10-	174

Table 7. Macrodiols for TPU (mol wt 2000)

Polyol	T_g , °C	T_m , °C
Poly(propylene glycol)	-73	-
Poly(tetramethylene glycol)	-100	32
Poly(1,4-butanediol adipate)	-71	56
Poly(ethanediol 1,4-butanediol adipate)	-60	17 (37)
Poly(caprolacton) diol	-72	59
Poly(1,6-hexanediol carbonate)	-62	49

materials which behave like a glassy, brittle solid, an elastic rubber, or a viscous liquid, depending on temperature and time scale of measurement. With increasing temperature, the material becomes rubbery because of the onset of molecular motion. At higher temperatures a free-flowing liquid forms. The melt temperature of a polyurethane is important for processibility. Melting should occur well below the decomposition temperature. Below the glass-transition temperature (T_g), the molecular motion is frozen, and the material is only able to undergo small-scale elastic deformations. For amorphous polyurethane elastomers, the T_g of the soft segment is ca -50 to -60°C , whereas for the amorphous hard segment, T_g is in the 20 – 100°C range. The T_g and T_m of the more common macrodiols used in the manufacture of TPU are listed in Table 7.

Polyester and polyether diols are used together with MDI to manufacture TPU elastomers. The polyester diols are obtained from adipic acid and diols such as ethylene glycol, 1,4-butanediol, or 1,6-hexanediol. The preferred molecular weights are 1000 – 2000 , and low acid numbers are essential to ensure optimal hydrolytic stability. Also, caprolactone-derived diols and polycarbonate diols are used. Polyether diols are mainly poly(tetramethylene glycol) (PTMG), but polyalkylene oxide-derived diols are also used. TPUs contain wax to aid in mold release and diatomaceous silica for added slip and as antiblocking agents in films. Antioxidants (hindered phenols or hindered amines) and uv-stabilizers (benzotriazoles) are also added to improve the environmental resistance.

The bulk polymerization of the polyurethane monomers is conducted by mixing the liquid monomers and catalysts at room temperature (one-step method),

or by prereacting the diisocyanates with part of the polyol to form a prepolymer, which is subsequently reacted with the remaining polyol to form the final polymer (two-step method). Part of the heat of reaction of the polymerization process is not generated if prepolymers are used. Prepolymers are often made at a ratio of NCO/OH of 2:1 in order to minimize free diisocyanate; prepolymers with a ratio of NCO/OH larger than 2:1 are called quasi prepolymers and these contain free diisocyanate. HDI or TDI prepolymers free of the diisocyanate are often made by removing the volatile diisocyanate by continuous vacuum distillation. Preformulated systems containing an isocyanate A side and a polyol B side, the latter also containing catalysts, surfactants, and blowing agents, are available from system houses. Carbodiimide-modified MDI offers advantages in polyester-based systems because of improved hydrolytic stability (70).

Solution polymerization of the monomers is also conducted in some applications. The solvents used have to be inert to isocyanates. Highly polar solvents (DMF, etc), which are excellent solvents for polyurethanes, have to be used with caution (71). Polyurethanes are also obtained by interfacial polymerization of isocyanatocarboxylic chlorides and glycols to give polyester urethanes (72).

In view of the morphological differences of MDI- and TDI-derived polyurethanes, the former are more suitable for the preparation of segmented polyurethane elastomers, while the latter are mainly used in the construction of flexible polyurethane foams. Segmented TPUs with excellent physical properties are also obtained from 2,6-TDI (73).

For economic reasons the bulk one-step polyaddition method is predominantly used to produce polyurethanes. For example, TPUs are produced by reaction extrusion. In this process the liquid monomers are mixed in a twin screw extruder, and the finished polymer is continuously extruded and pelletized. In the formulation of extrusion-grade TPUs a slight excess of the macrodiol is used. Reaction extrusion is also used in the manufacture of polyurethane engineering thermoplastics produced from MDI and higher boiling glycols, such as 1,6-hexanediol and cyclohexanedimethanol (74). These polymers were introduced by Upjohn/Dow under the trade name Isoplast. Blends of engineering plastics (ABS, acetal, nylon, polyesters, and polycarbonates) with TPUs are also finding uses in some polymer applications (75). The blends or alloys are readily produced by dry-blending and reextrusion.

Segmented elastomeric polyurethane fibers (Spandex fibers) based on MDI have also been developed. DuPont introduced Lycra in 1962. The generic name Spandex fibers designates elastomeric fibers, in which the fiber-forming substance is a long-chain polymer consisting of >85% of polyurethane. Extenders used in Spandex fibers include hydrazine and ethylenediamine. DuPont uses a dry-spinning process in which the polymer solution in DMF is extruded through a spinnerette into a column of circulating hot air. Other producers that use the dry-spinning process include Bayer (Dorlastan) and Asahi Chemical Industry (Asahi Kasei Spandex). Wet-spinning processes are also used, in which isocyanate-terminated prepolymers are extruded into a nonaqueous diamine bath. Globe manufacturing is producing Glospan, using this process. Nishin Spinning Co. uses a melt extrusion process to produce Mobilon.

Poly(urethane ureas) are obtained in many aromatic isocyanate applications. For example, water-blown flexible polyurethane foam incorporates urea

linkages in its network structure. The reaction of the isocyanate with water provides an amine function, which reacts with more isocyanate to afford the urea segments. Poly(urethane ureas) are also used in elastomer applications, where diamines are used as chain extenders. Examples include cast elastomers made from TDI prepolymers and MOCA (3,3'-dichloro-4,4'-diaminodiphenylmethane) and RIM elastomers, using diethyltoluenediamine (DETDA) as a chain extender. This chemistry is also used in the formulation of spray elastomers. Aromatic amine-terminated polyols, obtained by hydrolysis of prepolymers based on 2,4-TDI and PPG or polyester polyols, are used with solid high melting aromatic diisocyanates to give one-component systems that cure without moisture. Amine-terminated polyols are also used in RIM and spray applications.

Because of the versatility of the polyurethane system it is possible to introduce comonomers which can affect the physical properties of the derived polymers. For example, photo cross-linkable polyurethanes are formulated using 2,5-dimethoxy-2,4'-diisocyanato stilbene as a monomer (76). Comonomers, having an azoaromatic chromophore, are used in optical bleaching applications (77), or in the formation of photorefractive polymers (78). The latter random polymers have second-order nonlinear optical (NLO) properties. Linear polymers are also obtained from HDI/PTMG and diacetylenic diols. These polymers can be cross-linked through the acetylenic linkages producing a network polymer with properties similar to poly(diacetylenes) (79).

Thermodegradable polyurethanes are produced from MDI, polycaprolactone diol, and 2,2-azobis(2-cyanopropanol). The polymers degrade at about 120°C, and the initial weight loss corresponds to the amount of azo groups in the polymer (80). When the polymerization of MDI and 1,4-butanediol is conducted in 60-crown-20 (60C20) or 36-crown-12 (36C12), respectively, polyrotaxenes are obtained consisting of polyurethane chains enclosed in the crown ethers (81).

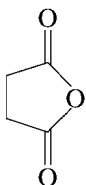
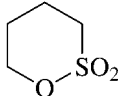

Polyurethane Ionomers

The versatility of the polyurethane system is further exemplified by the formulation of ionic polymers (see IONOMERS). Polyurethane ionomers are segmented polymers in which ionic groups are separated by long-chain apolar segments (82). In the presence of water the ionic centers are hydrated. This effect enables ionomers to form stable dispersions in water, and solventless polyurethane coatings are formulated in this manner. The use of *N*-alkyldiethanolamines or dimethylol propionic acid as extenders allows incorporation of ionic groups into the polymer backbone. Also, reaction of -NH- group containing polyurethane chains with sodium hydride, followed by reaction with 1,3-propane sultone, affords ionomers. When the ionic centers are located in the hard segment, they align to form a domain morphology. Anionic dispersions have greater stability than cationic dispersions, but cationic polymers show better adhesion to glass.

Examples of the grafting of ionic groups to the urethane or urea backbone in linear polymers are shown in Table 8.

Ionic polymers are also formulated from TDI and MDI (86). Poly(urethane urea) and polyurea ionomers are obtained from divalent metal salts of *p*-aminobenzoic acid, MDA, dialkylene glycol, and 2,4-TDI (87). In the case of

Table 8. Grafting of Ionic Groups to Linear Polymers

Functional group	Acid precursor	Base	Pendant group	Reference
—NH—		KOH	$\text{—NCOCH}_2\text{CH}_2\text{COOK}$	83
—NH—		KOH	$\text{—N(CH}_2)_3\text{SO}_3\text{K}$	84
—NHCONH—		Et ₃ N	$\text{—NHCON(CH}_2)_3\text{SO}_3^- (\text{C}_2\text{H}_5)_3\text{NH}^+$	83
—NHCONH—			$\text{—NHCONCH}_2\text{CH}_2\text{COOH}$	83
—NHCONH—	CH ₂ O, NaHSO ₃		$\text{—NHCONCH}_2\text{SO}_3\text{Na}$	85

polyureas, the glycol extender is omitted. If TDI is used in coating applications, it is usually converted to a derivative to lower the vapor pressure. A typical TDI prepolymer is the adduct of TDI with trimethylolpropane (Desmodur L).

Liquid Crystalline Polyurethanes

Liquid crystalline polyurethanes are formulated from mesogenic diols, such as 4,4'-bis(ω -hydroxyalkoxy)biphenyls and 2,4-TDI. Examples of the mesogenic diols include 4,4'-bis(6-hydroxyhexoxy)biphenyl (88) and 4,4'-bis(2-hydroxyethoxy)biphenyl (89). More rigid diisocyanates, such as 2,5-TDI and PPDI, are also used with mesogenic diols to form liquid crystal polyurethanes (90). Partial replacement of the mesogenic diols by PTMG with different molecular weights shows that the lower molecular weight flexible spacers form a more stable mesophase and exhibit higher crystallinity (91) (see LIQUID CRYSTALLINE POLYMERS, MAIN-CHAIN; LIQUID CRYSTALLINE POLYMERS, SIDE-CHAIN).

Another approach to liquid crystal polyurethanes involves the attachment of cholesterol to the polyurethane chain utilizing the dual reactivity in 2,4-TDI. In the initial reaction of the diisocyanate with cholesterol the 4-carbamate is produced, which on reaction with diethanolamine affords a diol, which is subsequently polymerized with 2,4-TDI (92).

Liquid crystal polyurethanes are also obtained from mesogenic ester diisocyanates (17). Also, a triad diol, bis(*p*-oxymethylphenyl)terephthalate, is used with HDI, HMDI, or TDI to give liquid crystal polyurethanes (93).

Thermoset Polyurethanes

Flexible Polyurethane Foams. The largest market segment in polyurethanes consists of flexible foams. A flexible polyurethane foam results from the reaction of an aromatic diisocyanate with a mixture of a polyol, water, a surfactant, and a catalyst. Sometimes a coblowing agent is added, but this practice is no longer viable because of environmental considerations. The reaction of the diisocyanate with water generates carbon dioxide gas, which is used as the blowing agent. The simultaneously generated urea acts as a chain extender. The number of moles of water in a polyurethane flexible foam formulation is typically 1–5 times the number of equivalent moles of polyol. Most commercial flexible foam is produced from TDI. In the 2,4-isomer the initial reaction occurs at the nonhindered isocyanate group in the 4-position. The unsymmetrically substituted ureas formed in the subsequent reaction with water are more soluble in the developing polymer matrix. Low density flexible foams are not readily produced from MDI or PMDI; enrichment of PMDI with the 2,4'-isomer of MDI affords a steric environment similar to the one in TDI, which allows the production of low density flexible foams that have good physical properties (94). The use of high performance polyols based on a copolymer polyol allows production of high resiliency (HR) slabstock foam from either TDI or MDI (95).

Flexible foams are three-dimensional agglomerations of gas bubbles separated from each other by thin sections of polyurethanes and polyureas. The microstructures observed in TDI- and MDI-based flexible foams are different. In TDI foams monodentate urea segments form after 40% conversion, followed by a bidentate urea phase, which is insoluble in the soft segment. As the foam cures, annealing of the precipitated discontinuous urea phase occurs to optimize alignment through hydrogen bonding (96).

The formation of cellular products also requires surfactants to facilitate the formation of small bubbles necessary for a fine-cell structure. The most effective surfactants are polyoxyalkylene–polysiloxane copolymers. The length and ethylene oxide/PO (EO/PO) ratio of the pendant polyether chains determine the emulsification and stabilizing properties. In view of the complexity of the interaction of surfactant molecules with the growing polymer chains in foam production, it is essential to design optimal surfactants for each application. Flexible polyurethane foams require surfactants that promote improved cell-wall drainage. This allows the cell walls to become more open during the foaming reaction. Also, the shift away from TDI to MDI in molded HR foams adds new demands on foam surfactants (97).

Flexible slab or bun foam is poured by multicomponent machines at rates of >45 kg/min. One-shot pouring from traversing mixing heads is generally used. A typical formulation for furniture-grade foam having a density of 0.024 g/cm³ includes a polyether triol (mol wt 3000); TDI; water; catalysts, ie, stannous octoate in combination with a tertiary amine; and surfactant. Coblowing agents are often used to lower the density of the foam and to achieve a softer hand. Coblowing agents are methylene chloride, methyl chloroform, acetone, and CFC 11, but the last has been eliminated because of its ozone-depletion potential. Additive systems (98) and new polyols (99) are being developed to achieve softer low density foams. Higher density (0.045 g/cm³) slab or bun foam, also called HR foam, is

similarly produced, using polyether triols having molecular weight of 6000. The use of polymer polyols improves the load-bearing properties.

The uncatalyzed reaction of diisocyanates with macroglycols is of no significance in the formation of polyurethanes. Tailoring of performance characteristics to improve processing and properties of polyurethane products requires the selection of efficient catalysts. In flexible foam manufacturing a combination of tin and tertiary amine catalysts are used in order to balance the gelation reaction (urethane formation) and the blowing reaction (urea formation). The tin catalysts used include dibutyltin dilaurate, dibutylbis(laurylthio)stannate, dibutyltinbis-(isooctylmercapto acetate), and dibutyltinbis(isooctylmaleate). The principal tertiary amines used are Dabco (1,4-diazabicyclo[2.2.2]octane) and higher boiling linear tertiary amines, such as pentamethyldipropylenetriamine and bis(dimethylaminoethyl) ether. Hydroxy groups containing tertiary amines are also used because they become incorporated into the polymer structure, which eliminates odor formation in the foam. Delayed-action or heat-activated catalysts are of particular interest in molded foam applications. These catalysts show low activity at room temperature but become active when the exotherm builds up. In addition to the phenol salt of 1,8-diazabicyclo[5.3.0]undec-7-ene (DBU) the benzoic acid salt of Dabco is also used.

Catalysts for urethane applications are sold by Air Products (Dabco), Abbott (Polycat), Kao Corp. (Kaolizer), Tosoh Corp. (Toyocat), and Union Carbide (Niax). Organic mercury compounds were used in cast elastomers and in RIM systems to extend cream time, ie, the time between mixing of all ingredients and the onset of creamy appearance, but are no longer used today because of toxicity concerns.

For the reaction of TDI with a polyether triol, bismuth or lead compounds can also be used. However, tin catalysts are preferred mainly because of their slight odor and the low amounts required to achieve high reaction rates. Carboxylic acid salts of calcium, cobalt, lead, manganese, zinc, and zirconium are employed as cocatalysts with tertiary amines, tin compounds, and tin-amine combinations.

Flame retardants are incorporated into the formulations in amounts necessary to satisfy existing requirements. Reactive-type diols, such as *N,N*-bis(2-hydroxyethyl)aminomethyl phosphonate (Fyrol 6), are preferred, but nonreactive phosphates (Fyrol CEF, Fyrol PCF) are also used. Often, the necessary results are achieved using mineral fillers such as alumina trihydrate or melamine. Melamine melts away from the flame and forms both a nonflammable gaseous environment and a molten barrier that helps to isolate the combustible polyurethane foam from the flame. Alumina trihydrate releases water of hydration to cool the flame, forming a noncombustible inorganic protective char at the flame front. Flame-resistant upholstery fabric or liners are also used.

There are four main types of flexible slabstock foam: conventional, HR, filled, and high load-bearing foam. Filled slabstock foams contain inorganic fillers to increase the foam density and improve the load-bearing characteristics. High load-bearing formulations incorporate a polymer polyol. Slabstock flexible foam is produced on continuous bun lines. The bun forms while the material moves down a long conveyor. In flat-top bun lines, the liquid chemicals are dispensed from a stationary mixing head to a manifold at the bottom of a trough. More rectangular foams are produced by several newer processes such as Draka, Petzetakis, Hennecke, Planiblock, and Econo Foam. However, the most popular rectangular block

foam process is the Maxfoam process. The high outputs require faster and longer conveyors. An exception is the Vertifoam process in which the reaction mixture is introduced at the bottom of an enclosed expansion chamber. The chamber is lined with paper or polyethylene film, which is drawn upward at a controlled rate. Because the Vertifoam machine is much smaller than the horizontal machines, operational savings can be achieved (100). Two newer slabstock foam manufacturing processes have been developed. The Cannon CarDio process injects liquid carbon dioxide into the foam mix to reduce the density whereas the Bayer/Hennecke NovaFlex process is conducted under reduced pressure to lower the density.

The properties of thermoset flexible polyurethane foams are related to density; load-bearing properties are likewise important. Under normal service temperatures, flexible foams exhibit rubber-like elasticity to deformations of short duration but creep under long-term stress. Maximum tensile strength is obtained at densities of ca 0.024–0.030 g/cm³. The densities are controlled by the amount of water in the formulation and may range from 0.045 to 0.020 g/cm³ by raising the amount of water from 2 to 5%. Auxiliary blowing agents are also used to reduce density and control hardness. The size and uniformity of the cells are controlled by the efficiency of mixing and the nucleation of the foam mix. Flexible foams are anisotropic and the load-bearing properties are best when measured in the direction of foam rise.

A high rate of block foam production (150–220 kg/min) is required in order to obtain large slabs to minimize cutting waste. Bun widths range from ca 1.43 to 2.2 m, and typical bun heights are 0.77–1.25 m. In a flexible foam plant, scrap can amount to as much as 20%. Most of it is used as carpet underlay and in pillows and packaging. The finished foam blocks are stored in a cooling area for at least 12 h before being passed to a storage area or to slitters where the blocks are cut into sheets. In the production plant the fire risk must be minimized. Temperatures of up to 150°C can be reached in the interior of the foam blocks. Blowing of ambient air through the porous foam allows dissipation of the heat generated in the exothermic reaction.

Most flexible foams produced are based on polyether polyols; ca 8–10% (15–20% in Europe) of the total production is based on polyester polyols. Flexible polyether foams have excellent cushioning properties, are flexible over a wide range of temperatures, and can resist fatigue, aging, chemicals, and mold growth. Polyester-based foams are superior in resistance to dry-cleaning and can be flame-bonded to textiles.

In recent years, molded flexible foam products are becoming more popular. The bulk of the molded flexible urethane foam is employed in the transportation industry, where it is highly suitable for the manufacture of seat cushions, back cushions, and bucket-seat padding. TDI prepolymers were used in flexible foam molding in conjunction with polyether polyols. The introduction of organotin catalysts and efficient silicone surfactants facilitates one-shot foam molding, which is the most economical production method.

The need for heat curing has been eliminated by the development of cold-molded or HR foams. These molded HR foams are produced from highly reactive polyols and are cured under ambient conditions. The polyether triols used are of molecular weight 4500–6500 and are high in ethylene oxide (usually >50% primary hydroxyl content). Reactivity is further enhanced by triethanolamine, liquid

aromatic diamines, and aromatic diols. Generally, PMDI, TDI, or blends of PMDI–TDI are used. Load-bearing characteristics are improved by using polymer polyol. HR foams exhibit relatively high SAC (support) factors, ie, load ratio, excellent resiliency (ball rebound > 60%), and improved flammability properties.

Semiflexible molded polyurethane foams are used in other automotive applications such as instrument panels, dashboards, arm rests, head rests, door liners, and vibrational control devices. An important property of semiflexible foam is low resiliency and low elasticity, which results in a slow rate of recovery after deflection. The isocyanate used in the manufacture of semiflexible foams is PMDI, sometimes used in combination with TDI or TDI prepolymers. Both polyester as well as polyether polyols are used in the production of these water-blown foams. Sometimes integral skin molded foams are also produced.

Rigid Polyurethane Foams. Almost all rigid cellular polyurethanes are produced from PMDI. Some formulations, particularly those for refrigerator and freezer insulation, are based on modified TDI (golden TDI) or TDI prepolymers, but these are being replaced by PMDI formulations. The polyaddition reaction is influenced by the structure and functionality of the monomers, including the location of substituents in proximity to the reactive isocyanate group (steric hindrance) and the nature of the hydroxyl group (primary or secondary). Impurities also influence the reactivity of the system; for example, acid impurities in PMDI require partial neutralization or larger amounts of the basic catalysts. The acidity in PMDI can be reduced by heat or epoxy treatment, which is best conducted in the plant. Addition of small amounts of carboxylic acid chlorides lowers the reactivity of PMDI or stabilizes isocyanate-terminated prepolymers.

The polyols used include PO adducts of polyfunctional hydroxy compounds or amines (see Table 4). The amine-derived polyols are used in spray foam formulations where high reaction rates are required. Crude aromatic polyester diols are often used in combination with the multifunctional polyether polyols. Blending of polyols of different functionality, molecular weight, and reactivity is used to tailor a polyol for a specific application. The high functionality of the polyether polyols combined with the higher functionality of PMDI contributes to the rapid network formation required for rigid polyurethane foams.

From the onset of creaming to the end of the rise during the expansion process, the gas must be retained completely in the form of bubbles, which ultimately results in the closed-cell structure. Addition of surfactants facilitates the production of very small uniform bubbles necessary for a fine-cell structure.

Reactive or nonreactive fire retardants, containing halogen and phosphorus, are often added to meet the existing building code requirements. The most commonly used reactive fire retardants are Fyrol 6, chlorendic anhydride-derived diols, and tetrabromophthalate ester diols (PHT 4-Diol). There is a synergistic effect of nitrogen and phosphorus observed in P–N compounds. Phosphonates, such as Fryol 6, are effective in char formation, whereas phosphine oxide-derived fire retardants are reactive in the gas phase. Because the reactive fire retardants are combined with the polyol component, storage stability is important. Nonreactive fire retardants include halogenated phosphate esters, such as tris(chloroisopropyl) phosphate (TMCP) and tris(chloroethyl) phosphate (TCEP), and phosphonates, such as dimethyl methylphosphonate (DMMP). Highly halogenated aromatic compounds, borax, and melamine are also used as fire retardants in rigid foams.

Insulation foams are halocarbon-blown. Chlorofluorocarbons, eg, CFC-11 (bp 23.8°C) and CFC-12 (bp -30°C), were used extensively as blowing agents in the manufacture of rigid insulation foam. Because of the mandatory phaseout of CFCs by Jan. 1, 1996, it had become necessary to develop blowing agents that have a minimal effect on the ozone layer. As a short-term solution, two classes of blowing agents are considered: HCFCs and HFCs. For example, HCFC 141b, CH₃CCl₂F (bp 32°C), is a drop-in replacement for CFC-11, and HFC 134a, CF₃CH₂F (bp -26.5°C), was developed to replace CFC-12. HCFC 142b, CH₃CClF₂ (bp -9.2°C), is the blowing agent used in the 1990s. Addition of water or carbodiimide catalysts to the formulation generates carbon dioxide as a coblowing agent. Longer-range environmental considerations have prompted the use of hydrocarbons such as pentanes and cyclopentane as blowing agents. Pentane-blown foams have already been used in the appliance industry in Europe. Pentane-based formulations are typically used in conjunction with water. Because rigid foams blown with alternative blowing agents have lower values [(m·W)/(m·K)] of about 19.5, as compared to 18.0 for CFC-11-blown foams, they are thus less efficient in their insulation performance. In addition, because rigid polyurethane foams at a density of 0.032 g/cm³ are ca 97% gas, the blowing agents determine the *k*-factor (insulation value).

The catalysts used in the manufacture of rigid polyurethane foams include tin and tertiary amine catalysts. Combinations of catalysts are often used to achieve the necessary balance of reaction rates. This is especially necessary if part of the blowing agent is carbon dioxide, generated in the reaction of the isocyanate with added water. New surfactants are required for the emerging water-coblown formulations, using pentanes as the main blowing agent (101). A typical water-coblown rigid polyurethane formulation is shown in Table 9 (102).

Rigid polyurethane foam is mainly used for insulation. The configuration of the product determines the method of production. Rigid polyurethane foam is produced in slab or bun form on continuous lines, or it is continuously laminated between either asphalt or tar paper, or aluminum, steel, and fiberboard, or gypsum facings. Rigid polyurethane products, for the most part, are self-supporting, which makes them useful as construction insulation panels and as structural elements in construction applications. Polyurethane can also be poured or frothed into suitable cavities, ie, pour-in-place applications, or be sprayed on suitable surfaces. Spray-applied polyurethane foams are produced in densities ranging from 0.021 to 0.048 g/cm³. The lower density foams are used primarily in nonload-bearing applications, eg, cavity walls and residential stud-wall insulation, whereas the

Table 9. Typical Rigid Polyurethane Panel Formulation

Ingredients	Parts
PMDI	135
Polyol	98
Water	1.9
Catalyst	2.0
Surfactant	2.0
HFC 134a	17.0

higher density foams are used in roofing applications. Applicators can buy formulated systems consisting of the isocyanate component, as well as the polyol side containing the catalysts, surfactants, and blowing agent.

During the molding of high density rigid foam parts, the dispensed chemicals have to flow a considerable distance to fill the cavities of the mold. In the filling period, the viscosity of the reacting mixture increases markedly from the initial low value of the liquid mixture to the high value of the polymerized foam. If the viscosity increases rapidly, incomplete filling results. Chemical factors that influence flow properties are differential reactivity in the polyol components and the addition of water to the formulation. Because venting holes allow the escape of air displaced by the rising foam, a moderate degree of overpacking is often advantageous. Newer high pressure RIM machines have simplified the mold-filling procedure, so filling of intricate molds is no longer a problem.

Rigid polyurethane foam is often poured into cavities, providing both thermal insulation and physical strength. Aircraft carrier hulls and refrigerators and freezers are insulated by in-place applied rigid polyurethane foam.

Many of the rigid insulation foams produced in the 1990s are PUIR foams. In the formulation of poly(urethane isocyanurate) foams an excess of PMDI is used. The isocyanate index can range from 105 to 300 and higher. PUIR foams have a better thermal stability than polyurethane foams (103). The cyclotrimerization of the excess isocyanate groups produces heterocyclic triisocyanurate groups, which do not revert to the starting materials but rather decompose at much higher temperatures. In the decomposition of the PUIR foams a char is formed, which protects the foam underneath the char.

The formation of isocyanurates in the presence of polyols occurs via intermediate allophanate formation, ie, the urethane group acts as a cocatalyst in the trimerization reaction. By combining cyclotrimerization with polyurethane formation, processibility is improved, and the friability of the derived foams is reduced. The trimerization reaction proceeds best at 90–100°C. These temperatures can be achieved using a heated conveyor or a RIM machine. The key to the formation of PUIR foams is catalysis. Strong bases, such as potassium acetate, potassium 2-ethylhexoate, and tertiary amine combinations, are the most useful trimerization catalyst. A review on the trimerization of isocyanates is available (104).

Modification of cellular polymers by incorporating amide, imide, oxazolidinone, or carbodiimide groups has been attempted but only the PUIR foams were produced in the 1990s. PUIR foams often do not require added fire retardants to meet most regulatory requirements (105). A typical PUIR foam formulation is shown in Table 10 (106).

The physical properties of rigid urethane foams are usually a function of foam density. A change in strength properties requires a change in density. Rigid polyurethane foams that have densities of $<0.064 \text{ g/cm}^3$, used primarily for thermal insulation, are expanded with HCFCs, HFCs, or hydrocarbons. Often water or a carbodiimide catalyst is added to the formulation to generate carbon dioxide as a cblowing agent. High density foams are often water-cblown. In addition to density, the strength of a rigid foam is influenced by the catalyst, surfactant, polyol, isocyanate, and the type of mixing. By changing the ingredients, foams can be made that have high modulus, low elongation, and some brittleness (friability), or relative flexibility and low modulus.

Table 10. Typical PUIR Foam Formulation

Ingredients	Parts
PMDI (250 Index)	208.7
Terate 203 ^a	100
Dabco K-15	5.2
Dabco TMR 30	1.2
Surfactant	2.0
HCFC 141b	35.0

^aCrude aromatic polyester.

Rigid polyurethane foams generally have an elastic region in which stress is nearly proportional to strain. If a foam is compressed beyond the yield point, the cell structure is crushed. Compressive strength values of 10–280 kPa (1–14 psi) can be obtained using rigid polyurethane foams of 0.032-g/cm³ density. In addition, the elastic modulus, shear strength, flexural strength, and tensile strength all increase with density.

Most low density rigid polyurethane foams have a closed-cell content of >90%. Above 0.032 g/cm³, closed-cell content increases rapidly and is generally >99% above 0.192 g/cm³. Bun foam, produced under controlled conditions, has a very fine-cell structure with cell sizes of 150–200 μm.

The availability of PMDI also led to the development of PUIR foams by 1967. The PUIR foams have superior thermal stability and combustibility characteristics, which extend the use temperature of insulation foams well above 150°C. The PUIR foams are used in pipe, vessel, and solar panel insulation; glass-fiber-reinforced PUIR roofing panels having superior dimensional stability have also been developed.

Strong bases, such as potassium acetate, potassium 2-ethylhexoate, or amine–epoxide combinations are the most useful trimerization catalysts. Also, some special tertiary amines, such as 2,4,6-tris(*N,N*-dimethylaminomethyl) phenol (DMT-30), 1,3,5-tris(3-dimethyl-aminopropyl)hexahydro-*s*-triazine, and ammonium salts (Dabco TMR) are good trimerization catalysts.

Semirigid foams are also manufactured. These foams do not fully recover after deformation; they are used in the construction of energy-absorbing automobile bumpers. Integral skin molded foams have an attached densified water skin, which is produced during manufacture. The preferred isocyanate for integral skin foams is carbodiimide-modified liquid MDI, which is used with ethylene oxide-capped polyols or polymer polyols. Thicker skins are obtained by lowering mold temperatures and increasing the percentage of overpack.

Interpenetrating Polymer Networks (IPNs)

Polyurethanes are used extensively in the formation of IPNs because of their inertness and reaction latitudes. They are formed from isocyanate-terminated prepolymers, and chain extension and cross-linking are accomplished using mixtures of diols and triols. The other polymer component involved in the formation of the polyurethane-derived IPNs include *p*-styrene, poly(methyl

methacrylate), polyacrylate, polyacrylamide, poly(vinyl chloride)(PVC), nylon 6, unsaturated polyesters, and epoxy polymers. The urethane prepolymers, chain extenders, and cross-linkers as well as the second monomer and its respective cross-linker can be reacted sequentially or simultaneously in solution or better in bulk. The polyurethane chains in the IPNs have reduced hydrogen bonding because of the presence of the polymer chains formed from the second monomer, which interfere with hydrogen bonding.

Sometimes the formation of polyurethane IPNs is conducted under pressure. For example, a 50:50 polyurethane–polystyrene (PU–PS)IPN is obtained from MDI and PTMG, using 1,4-butanediol and trimethylolpropane as extender and cross-linker. The styrene is cross-linked with divinyl benzene. Increased pressure (up to 20,000 kg/cm²) increases the mixing of the components as well as the degree of cross-linking (107). In a similar manner IPNs derived from HDI and polystyrene are obtained (108). A simultaneous poly(isocyanurate)–nylon 6 IPN is obtained by mixing a HDI biuret/caprolactam initiator with caprolactam monomer and a prepolymer made from HMDI and a diol at 95°C, followed by polymerization at 140°C, to afford the poly(isocyanurate) star-shaped nylon-6 IPN (109). PU–PVC IPNs are obtained from MDI and poly(caprolactone) (PCL) and PVC. It was found by nitroxide spin labeling studies that the polyurethane consists of a crystalline PCL and an amorphous PCL phase, and that PVC acts as a plasticizer between the phases (110). A polyurethane–polyester IPN with a ratio typical for sheet molding compound (SMC) is obtained from Isonate 143-L (liquid MDI) poly(caprolactone triol), an unsaturated polyester resin and styrene monomer (111). The polymerization is conducted at 60°C, using different initiators (*t*-butylperoxy-2-ethylhexanoate and cobalt naphthenate) to control the reaction rates. The polyester has a solvent effect on the polyurethane reaction. Prior to gelation, the reaction resembles a solution polymerization, and after gelation a bulk polymerization. A recent book reviews PU-derived IPNs (112).

Thermoset Polyurethane Elastomers

Thermoset polyurethanes are cross-linked polymers, which are produced by casting or RIM. For cast elastomers, TDI in combination with 3,3'-dichloro-4,4'-diphenylmethanediamine (MOCA) are often used.

RIM is another important polymerization method used in the manufacture of thermoplastic or thermoset polyurethanes. This high pressure reactive casting process is conducted in RIM machines. Differences between the low pressure casting process and the high pressure RIM process are in the speed and efficiency of mixing. The isocyanates used in the formulation of RIM systems are liquid MDI products (carbodiimide-modified MDI or MDI prepolymers) and PMDI for structural (SRIM) applications. Also, glass reinforced versions are known as RRIM. The RIM process used in the automotive industry consists of high pressure impingement mixing of reactive liquid monomers resulting in short molding cycles. The principal advantage of this process results from the fact that molds are filled with liquids, which requires only 50 lb/in.² clamping pressure as compared to the 2–5 tons/in.² needed for injection molding of TPUs. In order to improve the green strength of the resultant polymers diamine extenders, such as diethyl

Table 11. Properties of RIM Systems

Properties	Flexural modulus, MPa ^a		
	0.137–0.517	0.517–1.03	1.37–2.75
Tensile elongation, % break	100–300	50–200	<50
Izod impact, J/m ^b	534–801	267–801	<267
Impact strength	High	Medium high	Low
Material description	Elastomer	Pseudo plastic	Plastic
Automotive application	Fascia	Fender	Hood or deck lid

^aTo convert MPa to psi, multiply by 145.

^bTo convert J/m to ft-lb/in., divide by 53.38.

toluenediamine (DETDA), are incorporated in the newer automotive systems. Also, internal mold release (IMR) agents based on zinc stearate compatibilized with primary amines were introduced in 1985. The IMR systems are used to reduce the need to apply external mold release agents. An IMR system offers reduced cycle times, improved productivities, less frequent mold cleaning, and lower scrap rate. In the RIM technology, aromatic diamine chain extenders, such as DETDA, are used to produce poly(urethane ureas) (113), and replacement of the polyether polyols with amine-terminated polyols produces polyureas (114). Some physical properties of RIM systems are listed in Table 11.

Polyurethane Coatings

Polyurethane coatings are used wherever applications require abrasion resistance, skin flexibility, fast curing, good adhesion, and chemical resistance. The polyaddition process allows formulation of solvent based or solventless liquid two-component systems, water-based dispersions, or powder coatings. Two-component polyurethane coatings are prepared by mixing the A and B components prior to application to the substrate. The TDI-trimethylolpropane adduct, the HDI biuret, and the isocyanurate of HDI or IPDI are often used as the polyisocyanate component. These systems cure at ambient temperature to give coatings with excellent properties. In order to increase the pot life of the coating systems, one-component moisture coatings are developed. These systems are based on PMDI, MDI, TDI, or HDI and a polyfunctional polyether polyol. These prepolymers (NCO content 3–16%) are stable when stored under dry conditions at ambient temperature. Blocked isocyanates are also used in the formulation of one-component systems. Thus, storage stable one-component coatings that are heat curable can be formulated by mixing blocked polyisocyanates with macrodiols. Also, solvent-free polyurethane powder coatings are known. Both thermoplastic and thermoset binder systems can be used in powder coatings. Thermoplastic powders are mainly used in thick coating applications (125–1000 μm). Polyester polyurethane powders use caprolactam-blocked IPDI or TDI adducts as cross-linking agents. Caprolactam does not cause yellowing and diffuses with a minimum of degassing. Powdered polyesters and blocked isocyanate adducts must be solids with melting points above 50°C to prevent agglomeration during storage. Powder coating systems also

contain pigments, fillers, catalysts (stannous octoate, etc), and small amounts of flow-control additives, and they are cured by baking at 180–200°C for 15–30 min.

Solutions (5–25% solids) of fully reacted polyurethanes based on MDI or IPDI are also used in coating applications. These coatings are used mostly as finish coats on flexible substrates. Because of concern over airborne solvents aqueous polyurethane dispersions are used today. These polymers are prepared by incorporating ionic groups into their backbone, and both cationic and anionic groups are utilized in the preparation of the ionomers. The solvent and water resistance of films formed from aqueous dispersions can be improved by cross-linking. Ionomers are also used in the formulation of speciality adhesives.

Polyurethane coatings are mainly based on aliphatic isocyanates and acrylic or polyester polyols because of their outstanding weatherability. For flexible elastomeric coatings, HMDI and IPDI are used with polyester polyols, whereas higher functional derivatives of HDI and IPDI with acrylic polyols are mainly used in the formulation of rigid coatings. Plastic coatings, textile coatings, and artificial leather are based on either aliphatic or aromatic isocyanates. For light-stable textile coatings, combinations of IPDI and IPDA (as chain extender) are used. The poly(urethane urea) coatings are applied either directly to the fabric or using transfer coating techniques. The direct-coating method is applied for rainwear because the microporous coating is permeable to air and water vapor, but not to liquid water. Microporous polyurethane sheets (poromerics) are used for shoe and textile applications. Alcantara is an artificial velour leather used in the fabrication of fashion wear. Polyurethane binder resins are also used to upgrade natural leather.

Waterborne polyurethane coatings are formulated by incorporating ionic groups into the polymer backbone. These ionomers are dispersed in water through neutralization. The experimental 1,12-dodecane diisocyanate is especially well suited for the formation of waterborne polyurethanes because of its hydrophobicity (115). Cationomers are formed from IPDI, *N*-methyldiethanolamine, and poly(tetramethylene adipate diol) (116); anionic dispersions are obtained from IPDI, PTMG, PPG, and dimethylol propionic acid (117). The ionic groups can also be introduced in the polyol segment. For example, reaction of diesterdiol, obtained from maleic anhydride and 1,4-butanediol, with sodium bisulfite produces the ionic building block, which on reaction with HDI gives a polyurethane ionomer (118). The weatherability of aliphatic polyurethane coatings is related to their structures. Polyester polyol-based polyurethanes are more uv-resistant than polyether polyol-based polyurethanes, but the latter offer better hydrolytic stability (see URETHANE COATINGS).

For baking enamels and wire and powder coatings, blocked isocyanates are used. Blocked polyurethane coatings do not cure below a certain threshold baking temperature. Catalysts, such as tertiary amines or organometallic tin compounds, are used to lower the curing temperature.

Uses

Furniture and Bedding. In most geographic regions flexible foam applications represent the largest volume uses of polyurethanes. The bulk of the use

is for furniture, automotive seating, bedding, and packaging applications. With a broad range of available load-bearing capacity and resiliency, these materials offer degrees of comfort and protection not approached by any other single cushioning material. Flexible slabstock foam is used approximately 60% in furnishings, 35% in automotive application (seating, crash pads, head-armrests, trim, sound insulation, vibration dampening, carpet backing, sun visors, instrument panels, and energy management), and 5% in packaging and other applications. Bedding applications are centered on flexible foam mattresses of a variety of sizes and densities. However, polyurethane mattresses are still encountering significant competition from traditional coil-spring mattresses. Polyurethane foam mattresses are commonly found in hospitals, hotels, universities, and other high volume institutional-type applications. Foaming in-place is often used for packaging of delicate instruments and military parts.

Carpet cushioning is another application for both prime foam and rebounded scrap foam. The prime foam is virgin foam used as a separate carpet underlay or attached directly to the back of the carpet. The latter allows rapid continuous application of liquid chemicals using reaction polymerization technologies. Systems based on prepolymers of TDI or MDI are used in combination with conventional polyols and inorganic fillers. The rebounded scrap foam is made by adhesive binding ground flexible foam scrap, and it is used as a separate carpet underlay.

A significant volume of flexible foam is used in speciality applications, some of which continue to use the earliest type flexible polyester polyurethane foam used mainly for textile lamination. Reticulated foams are used in air filters.

Construction. Building and construction markets use rigid polyurethane foam produced as boardstock (either produced continuously, discontinuously, or cut from rigid foam buns). The boardstock is then used as roof or wall insulation for commercial and residential buildings, as well as in refrigerated buildings and metal door cores. Residential sheathing uses an aluminum foil-faced boardstock often produced using continuous lamination technologies. Rigid polyurethane foam can also be spray-applied, a technique that is well suited for retrofitting commercial roofs and industrial tank and pipe insulation.

Other significant applications for rigid polyurethane foam include domestic refrigerators and coolers, insulated trailer trucks, shipping containers, and railway cars. Marine applications utilize the flotation/buoyancy characteristics of rigid foams for recreational boats and aircraft carriers. Semirigid polyurethane foam is also used as foam-in-place packaging foam. Polyurethane products are also used in the construction of masks and other life-like surfaces, puppetry, animatronics, and props and sets, both life-size and miniature, for the movie industry.

Spraying of the foam formulation by special two-stream spray guns onto suitable surfaces is often conducted. On-site applications for spray foam include roofs, tanks, vessels, cavity walls, and pipes. Spray-applied polyurethane foams are produced in densities ranging from 1.3 to 3.0 lb/ft² (21–48 kg/m³). The lower-density foams are used primarily in nonload-bearing applications (cavity walls and residential stud-wall insulation). The higher-density foams are used in roofing applications. The 1:1 volume ratio of the A and B components required for spray foams excludes the poly(isocyanurate) chemistry from this application. In spray foam formulations, PMDI in combination with the more reactive amine polyols

are used, and sometimes diamine extenders are added to increase the reaction rate.

Ships transporting liquid natural gas (LNG) are usually insulated with rigid PUIR foam laminates, which provide temperature stabilities from -180 to 150°C . The main fuel tank of the National Aeronautics and Space Administration (NASA) space shuttles is also insulated with PUIR foam. Rigid polyurethane foam is used in engineered foam-in-place packaging of industrial or scientific equipment and in the molding of furniture, simulated-wood ceiling beams, and a variety of decorative and structural furniture components. Rigid foam is also used for the repair of river barges.

Automotive Applications. The global automotive industry utilizes every variation of polyurethane technology. Examples include automotive seating, RIM bumper and fascia, RRIM for light weight rocker panels, rigid polyurethane insulation foam for the walls of refrigerated trucks and underfloor sound insulation, interior panels, and high performance paints and coatings. In 1999 a total of 1.161 million tons of polyurethanes were used in automotive applications (United States: 596 kt/a, Europe: 365 kt/a, and Asia: 200 kt/a).

Recent trends are the increased use of MDI-based flexible foams because higher density foams with good comfort are obtained. Also, dual hardness foam cushioning can be produced more easily with MDI systems. Hot cure TDI foams are being phased out. In Table 12 the distribution of the systems used in the global automotive seating production are shown.

The growth rate of polyurethane RIM/RRIM parts is slowed to only about 1% because of the need to develop products with easier recycling routes, but RRIM-based composite pickup-truck boxes weighing up to 115 kg are currently produced using two separate RRIM molding processes. This trend may positively influence the future growth rate of polyurethane parts. In 1998 RIM/RRIM consumption in Europe was 8935 kt/a, while in the United States, 39,900 kt/a was consumed. The Asian market amounted to 8205 kt/a.

Automotive shock absorbers based on 1,5-NDI and ethylene glycol adipates (Vulkollan) are used in the global automotive markets (total consumption in 1998 was 10.2 kt/a). Systems based on MDI are also used.

For door panels structural RIM molding is used, and fiber reinforced polyurethane interior materials use long fiber injection technologies or compression molding processes. A trend to eliminate PVC in interior panels

Table 12. Global Automotive Seating Systems

System	%
TDI HR cold cure	20
TDI hot cure	22
MDI HR cold cure	33
TM-20 HR ^a	16
Others ^b	3

^a80:20 Blend of TDI 80 with PMDI.

^bFoams produced with cross-linkers or modified grades of TDI.

presents an opportunity for polyurethanes in skins for door and instrument panels. Also, colored polyurethane skins based on aliphatic isocyanates are backfoamed with conventional MDI-based polyurethane spray foam (Recticel process).

Aqueous two-component polyurethane systems for automotive topcoats are under development. Currently the automotive topcoats are made from solvent-based two-component or blocked one-component systems based on HDI trimer (Desmodur N) or IPDI trimer (Desmodur Z) or both in conjunction with an acrylic polyol. The polyurethane topcoats provide the vehicles with a tough and durable finish with excellent long-lasting glossy appearance ("wet look") One-component aqueous dispersions are already used in electrodeposition primers and pigmented base coats. Soft-feel polyurethane coatings are increasingly used for instrument panels and seat covers.

Polyurethane foams are increasingly used for insulation, sound proofing, and carpet backing in automotive applications. Examples include instrument panels, dashboards, armrests, door liners, sound/vibration dampening mats, bumper cores, and sun visors. These semirigid foams are mainly based on PMDI. Semirigid integral skin foams characterized by a tough elastomeric polyurethane skin formed during manufacture of the low density foam core are also used in interior trim parts. Recently Volkswagon insisted on the elimination of amine emission from polyurethane foams installed in their vehicles. The use of reactive tertiary amine catalysts which become bound to the polyurethane foam would solve this problem.

Automotive windshield and backlight sealants were introduced by Essex (now Dow Chemical) in the 1970s. Excellent tensile strength and toughness combined with good adhesion to primed glass allow automobiles to pass 40 mh rollover tests without the windshield popping out. One component windshield sealants utilize diethylmalonate blocked MDI prepolymers to ensure package stability. In the presence of both tin and mercury or bismuth salts, moisture will cure the sealant under ambient conditions. The U.S. market for automotive sealants in 1997 was 68.5 kt/a.

Antilacerent windshields were also considered by bonding single or multiple layers of polyurethanes to the interior windshield. However, the emergence of the use of air bags in cars has eliminated the need for antilacerent windshields. However, modular window gaskets are produced using the RIM process. The MDI systems based on polyether polyols, glycol, or DETDA extenders require painting in order to achieve good weatherability.

Footwear. Polyurethanes are among the most useful materials for footwear applications. The low weight and high level of comfort of microcellular polyurethane soles and their ease of production, using a reaction molding process led to rapid global adaptation of this technology. Apart from the dominant use of microcellular polyurethane elastomers in the production of shoe soles (street shoes, sport shoes, leisure shoes, and safety shoes), polyurethane flexible or semi-flexible foams with or without an integral skin are commonly used to produce in-soles and ski-boot liners. Polyurethanes also offer processing advantages, such as direct molding of the shoe soles to the shoe uppers.

Two basic types of polyurethanes are available as shoe-soling products: polyester- and polyether-based systems. The polyester systems were first

introduced because of their high quality in applications such as safety shoes, boots, and sport shoes. They are also very suitable for direct soling. Lower-cost polyether systems were introduced in the 1970s. Polyether-based systems are the choice for street shoes because of their excellent hydrolytic stability. Polyether polyurethanes also provide better flex resistance at low temperature because of the lower glass transition temperature of the polyether chain. Usually a highly reactive 4000 molecular weight polyether diol is used in combination with a MDI prepolymer and 1,4-butanediol, and small amounts of triols are added to improve the green strength and demolding time. A controlled amount of water and fluorocarbon blowing agents are used in combination with tertiary amine and tin catalysts.

Millable Polyurethane Gums and Elastomers. Polyurethanes with the rheology of natural rubber, so-called *millable gums*, are made by mixing hydroxy-terminated prepolymers and isocyanate cross-linking agents, such as the 2,4-TDI dimer, and other additives on a rubber mill. The milled compound is shaped, compression molded, and heat cured. Millable polyurethane gums are used in synthetic rubber applications such as shock-damping mounts, roll covers, and parts for military vehicles.

Polyurethane elastomers containing ultra high molecular weight polyethylene (UHMWPE) as fillers show improved abrasion resistance. The UHMWPE is dispersed in the polyol in the formation of the filled polyurethanes. Commercial uses include gears, rollers, bushings, and mining screens.

Polyurethanes are also used in the construction of sport surfaces such as all-weather athletic areas, outdoor game areas, children's playgrounds, tennis courts, and multisport halls. The polyether polyurethane systems, mainly based on PMDI, are applied by a pour-in-place method. Often additional rubber granules are added to the system.

Solid polyurethane industrial tires are produced for off-road machines (fork and lift trucks, wheelchairs), pneumatic tires for tractors, backhoe loaders, soft-cast elastomer tires for heavy vehicles and skateboard and roller skate wheels. Polyurethane tires for passenger cars have not as yet been commercialized. Pneumatic tires for tractors are produced using the RIM process. Soft-cast polyurethane elastomers are also used for puncture-free tires, especially for heavy vehicles, replacing the air in pneumatic tires.

Another important application for solid polyurethane elastomers are sealing gaskets in sewage clay pipes. These gaskets are made by casting liquid elastomer systems directly onto the extremities of the pipe. The solidified elastomer will adhere well to the ceramic surface.

Elastomeric spandex fibers are used in hosiery and sock tops, girdles, brassieres, support hose, and swim wear. The use of spandex fibers in sport clothing is increasing.

Polyurethane Adhesives and Sealants. Polyurethane adhesives are known for excellent adhesion, flexibility, toughness, high cohesive strength, and fast cure rates. Polyurethane adhesives rely on the curing of multifunctional isocyanate-terminated prepolymers with moisture or on the reaction with the substrate, eg, wood and cellulosic fibers. Two-component adhesives consist of an isocyanate prepolymer, which is cured with low equivalent weight diols, polyols, diamines, or polyamines. Such systems can be used neat or as solution. The two

components are kept separately before application. Two-component polyurethane systems are also used as hot-melt adhesives.

Waterborne adhesives are preferred because of restrictions on the use of solvents. Low viscosity prepolymers are emulsified in water, followed by chain extension with water-soluble glycols or diamines. PMDI, which has a shelf life of 5–6 h in water, can be used as a cross-linker. Waterborne polyurethane coatings are used for vacuum forming of PVC sheeting to ABS shells in automotive interior door panels, for the lamination of ABS/PVC film to treated polypropylene foam for use in automotive instrument panels, as metal primers for steering wheels, in flexible packaging lamination, as shoe-sole adhesive, and as tie coats for polyurethane-coated fabrics. PMDI is also used as a binder for reconstituted wood products and as a foundry core binder.

Typical one-component elastomeric adhesive formulations are based on a linear poly(butylene adipate) of molecular weight 2000, MDI and 1,4-butanediol as chain extender. Crystallization of the soft polyol segment below 40°C, which occurs after evaporation of the solvent, causes a gain in bond strength. Upon heating of the film with an infrared lamp, the adhesive can be reactivated for bonding. The adhesive systems are manufactured by dissolving the elastomeric polyurethane in the desired solvent or solvent mixture and adding other polymers, fillers, and stabilizers. The polyurethane adhesive technology is also utilized in the formulation of architectural sealants, which are also supplied as both one- and two-component systems. These systems are often modified with epoxy, acrylic, or other polymers and with stabilizers and fillers. One-component automotive windshield sealants utilize diethyl malonate-blocked MDI prepolymers. In the presence of tin, mercury, or bismuth salts moisture will cure the sealant under ambient conditions.

Polyurethane sealant formulations use TDI or MDI prepolymers made from polyether polyols. The sealants contain 30–50% of the prepolymer; the remainder consists of pigments, fillers, plasticizers, adhesion promoters, and other additives. The curing of the sealant is conducted with atmospheric moisture.

Biomedical Polyurethane Applications. Numerous different type of aromatic and aliphatic polyether urethanes and poly(urethane ureas) as well as siloxane–urethane copolymers have been developed for many biomedical applications. The principal products are segmented TPUs based on PTMEG as the soft segment. Biomer, developed by DuPont in the 1960s, uses a diamine as extender, and solutions of the polymer in dimethyl acetamide (DMAc) became available. Biomer was later sold to Ethicon, who withdrew the product from the market in 1991. Pellethane, a TPU based on PTMEG, MDI, and 1,4-butanediol was introduced by Upjohn in the 1970s. Pellethane was used extensively in pacemaker leads, but Dow Chemical, who purchased the chemical division of Upjohn in 1985, decided not to sell Pellethane for biomedical applications, because of potential liabilities. A TPU based on a polycarbonate macroglycol and MDI was introduced recently by Cardiotech (Chromoflex). Improved biodurability was claimed for these polymers (119). Also, Bayer developed improved series of TPUs (Texin 5590), for biomedical applications based on IPDI, using a diamine extender. These poly(urethane ureas) have a higher modulus to allow easy insertion of catheters.

Male polyurethane condoms in the United States had 5% of the market in 1999. The excellent physical properties of TPU films allow the manufacture of very thin condoms by cutting and welding or by solvent dipping.

Polyurethane gels were also developed by Bayer (Levigel) for biomedical applications. These gels are based on quadrafunctional polyether polyols and aliphatic isocyanate prepolymers. The new gels are used in very soft padding for artificial limbs and in the development of wound dressing products. The gels can be foamed to enhance breathability to oxygen and water vapors to promote healing.

Binder Applications. Reconstituted wood products, such as particle boards, wafer boards, medium density fiberboards, and oriented standboards, increasingly use PMDI as a liquid adhesive to bind the wood products. Wood has many hydroxyl groups containing compounds such as cellulose, hemicellulose, and lignin. Polymeric isocyanate binder resins will react with these hydroxyl groups to form chemical bonds between the wood chips. PMDI is a 100% active liquid binder that is easily atomized and provides excellent bonding efficiencies. Dow has developed Isobind, a special PMDI for this application as well as process technology called Optimax, which is available under a licensing agreement with Carbocoll Systems, Inc. The use of isocyanate binders achieves faster cure rates and lower temperature cure as compared to other binder resins. Isocyanate binders cure at about 100°C, while phenol/formaldehyde resins cure at 150°C or higher. The demands of public regulatory agencies for control of formaldehyde products, used extensively as wood binding resins, have intensified interest in formaldehyde-free isocyanate binders.

The PMDI-derived reconstituted wood products have found applications as siding materials, shelves, cabinets, furniture, and pallets. Extra large panels are finding uses in the mobile home industry, where entire walls are fabricated from a single continuous panel with greater rigidity and strength. Shipping containers of lighter weight and uniform properties can also be made. PMDI can also be used as a binder for agro waste products. For example, three-layer laminates consisting of top and bottom layers of coconut husks and a core layer consisting of wood chips provide attractive building panels. Waste straw and bagasse is also used in the manufacture of solid wood-like boards.

The use of PMDI as a binder for foundry cores, rubber waste products, and solid rocket fuel are also known. Isocyanate-terminated prepolymers, often prepared from TDI or MDI with polyether polyols are also used as binders for composite products that require elastomeric properties. Athletic surfaces are sometimes prepared from ground rubber tire scrap bonded with isocyanate-based prepolymers. Similarly, flexible polyurethane foam scrap is bonded with isocyanate prepolymers to form rebonded foam useful as carpet underlay. Solidification of incineration ashes with PMDI-based binder systems is another waste disposal application. In this manner hazardous waste materials undergo chemical fixation and detoxification.

The thickening of SMC can be accelerated using hydroxy-terminated unsaturated polyesters in conjunction with isocyanate-terminated prepolymers. Polyurethane ionomer-based sizings for glass fibers used in RRIM applications are also known.

Synthetic leather products are also produced using a urethane binder. These poromeric materials are produced from textile-length fiber mats impregnated with DMF solutions of polyurethanes. Permeability to moisture vapor is the key property needed in synthetic leather. In addition to shoe applications, poromerics are

Table 13. Major Polyurethane Applications in the United States/Canada and Europe

Market	United States/Canada (%)	Europe (%)
Construction	26	23
Furniture and Bedding	23	24
Elastomers	9.6	7
Coatings	9	10
Appliances	6	7
Footwear	1.0 ^a	8

^aFootwear is no longer manufactured in the United States and Canada.

used for handbags, luggage, and apparel. Polyurethane films having oxygen and water permeability are applied in bandages and wound dressings and as artificial skin for burn victims.

Economic Aspects

In 1998 a total of 2642 kt/a of polyurethanes were consumed in the United States (91%) and Canada (9%). The European consumption in 1998 was 2169 kt/a, and the Asian Pacific Region consumed 1807 kt/a of polyurethane chemicals. Therefore, the total global polyurethane consumption was of the order of 8000 kt/a in 2000. In Table 13 a comparison of significant American and European applications as percentages of the previously mentioned total amounts are shown. With the exception of footwear, the use by application in both regions is almost identical.

The flexible foam market is the largest global polyurethane consumption. In the United States and Canada a total of 1114 kt/a was used in flexible foam applications in 1998. Flexible slab foam is used predominantly in furniture, carpet underlay, and bedding; molded foam is used extensively in transportation. Carpet underlay is manufactured from either virgin or scrap polyurethane foam, which is combined with a binder adhesive.

Of the 687 kt/a of rigid foam produced in the United States and Canada in 1998, more than 50% was used in the construction industry. About 60% of this total was used in laminated boards and insulation panels; about 30% was poured at construction site. Insulated appliances (132 kt/a) and tank and pipe insulation (79 kt/a) are other important uses of rigid insulation foam. Rigid polyurethane foam is produced from PMDI. Another important application of PMDI is particle board binder resins. A total of 160 kt/a of PMDI was used in this application in the United States and Canada in 1998.

The total elastomer consumption in the United States and Canada in 1998 accounted for 245 kt/a. Automotive RIM applications accounted for 65.3 kt/a, TPU for 53.5 kt/a, and Spandex for 26.5 kt/a. Cast elastomers had the highest consumption (100 kt/a). Coatings consumption in the United States and Canada in 1998 was 237 kt/a, and powder coatings accounted for about 20% of the total. Adhesives (105 kt/a) and sealants (80 kt/a) were other important polyurethane applications.

The polyurethane industry is dominated by the multinational isocyanate producers. The principal isocyanate producers (BASF, Bayer, Dow) also manufacture polyols. Dow is one of the largest global producers of polyether polyols, and

Bayer acquired the other primary polyether polyol producer, when it purchased the polyol business of Arco (now Lyondell) in 1999. Also, in 1999 Dow further strengthened its position in polyols when it acquired Union Carbide. Polyether polyols, mainly used for flexible foam production, account for 65 wt% in a flexible foam formulation, 35% in rigid polyurethane foams, and even less in PUIR foams.

The former Olin and Rhone Poulenc TDI production facilities are still operated by Lyondell, but it is unlikely that Lyondell will continue the isocyanate business without the polyether polyol business it sold to Bayer.

Health and Safety Factors; Environmental Aspects

The primary route of exposure to most isocyanates is through inhalation. Isocyanate vapors and aerosol can irritate the mucous membranes in the respiratory tract (nose, throat, lungs) causing nasal irritation, sore throat, coughing, chest discomfort, shortness of breath, and reduced lung function. Persons with a nonspecific bronchial hyperreactivity can respond to extremely low concentrations with similar symptoms as well as asthma attack. Exposure to higher concentrations may lead to bronchitis, bronchial spasm, and pulmonary edema. These effects are usually reversible. As a result of repeated overexposure or a single large dose, certain individuals may develop isocyanate sensitization (chemical asthma), which may cause a reaction to a later exposure at very low concentrations. These symptoms, which can include chest tightness, wheezing, cough, shortness of breath, or asthmatic attack, could be immediate or delayed up to several hours after exposure. Chronic overexposure to isocyanates has been reported to cause lung damage (including decrease in lung function), which may be permanent. Sensitization can either be temporary or permanent.

Both chlorofluorocarbons and methylene chloride are used as blowing agents. Inhalation of high concentrations of chlorofluorocarbons can be dangerous and may cause anesthesia and unconsciousness. Severe acute exposures have caused cardiac arrhythmias, including ventricular fibrillation. Since chlorofluorocarbon vapors are heavier than air, high concentrations can accumulate in confined or low-lying areas, displacing air or oxygen supply. Although these materials are considered nonflammable, they can be heated to decomposition, generate highly toxic phosgene and carbonyl fluoride. In addition, when confined and subject to high temperatures, chlorofluorocarbons may present an explosion hazard.

Like chlorofluorocarbons, methylene chloride is difficult to ignite, but when heated to decomposition, can produce toxic materials such as hydrogen chloride, carbon dioxide, and carbon monoxide. Upon skin contact methylene chloride can cause irritation, drying, and weakening of the skin. Inhalation can cause central nervous system depression, resulting in impaired judgment and reduced motor ability. Inhalation of high concentrations causes cancer in laboratory animals. It is therefore extremely important to follow the manufacturer's recommendation for the safe use and handling of methylene chloride.

Although the products of combustion vary, virtually all polyurethane foams and materials burn, often generating a variety of toxic, potentially lethal gases

and dense smoke. The type and amount of combustion products vary with product composition, fire conditions, oxygen concentration, and other factors. As in all organic fires, the main toxicant is carbon monoxide. Like other nitrogen-containing polymers oxides of nitrogen and hydrogen cyanide can also be released. Fully cured polyurethanes present no health hazards; they are chemically inert and insoluble in water and are the most organic solvents. However, dust can be generated in fabrication, and inhalation of the dust should be avoided. Polyether-based polyurethanes are not degraded in the human body, and are therefore used in biomedical applications.

Some of the chemicals used in the production of polyurethanes, such as the highly reactive isocyanates and tertiary amine catalysts, must be handled with caution. The other polyurethane ingredients, polyols and surfactants, are relatively inert materials having low toxicity.

Isocyanate Toxicity. Isocyanates in general are toxic chemicals and require great care in handling. Oral ingestion of substantial quantities of isocyanates can be tolerated by the human body, but acute symptoms may develop from the inhalation of much smaller amounts. The inhalation of isocyanates presents a hazard for the people who work with them as well as the people who live in the proximity of an isocyanate plant. Adequate control of exposure is necessary to achieve a safe working environment. The suppliers Material Safety Data Sheets (MSDS) have to be consulted for the most current information on the safe handling of isocyanates.

Respiratory effects are the primary toxicological manifestations of repeated overexposure to diisocyanates (120). Once a person is sensitized to isocyanates, lower concentrations can trigger a response (121). Most of the industrial diisocyanates are also eye and skin irritants. Controlling dermal exposure is good industrial hygiene practice. The 1997 American Conference of Governmental Industrial Hygienists (ACGIH) exposure guideline for TDI is 0.005 ppm as a TWA-TLV (an 8-h time-weighted average concentration); the 1997 TLV for TDI in Japan is 20 ppb.

Overexposure to TDI can cause chemical bronchitis (isocyanate asthma) in sensitized individuals. Transient acute asymptomatic changes in respiratory function and deterioration of lung function following long-term repeated exposure have also been encountered. Allergic sensitization may occur within months or after years of exposure to isocyanates. Animal studies using TDI showed no teratologic response at exposure concentrations up to 0.5 ppm. A chronic gavage study indicated tumor formation in the animals, but the study was found to be of doubtful toxicological relevance because of the method used and the excessively high dose levels. Vapor exposure to MDI is limited by the low vapor pressure, corresponding to a saturated atmosphere of 0.1 mg/m³ at 25°C. An acute aerosol inhalation study on PMDI using rats indicated that the 4-h LC₅₀ is 490 mg/m³. The current ACGIH TLV for MDI is 0.051 mg/m³ (0.005 ppm) as a TWA. The OSHA PEL is 0.02 ppm as a ceiling limit.

The toxicity of aliphatic diisocyanates also warrants monitoring exposure to its vapors. HDI has a moderate potential for acute systemic dermal toxicity; rabbit dermal LD₅₀ is 570 mL/kg. However, HDI is severely irritating to the skin and eyes. Irritation, lacrimation, rhinitis, burning sensation to throat and chest, and coughing have all been reported in humans following acute inhalation

Table 14. Acute Toxicity of Diisocyanates in Rats^a

Isocyanate	LC ₅₀ , mg/kg	1 h LC ₅₀ , mg/m ³	Std. vapor pressure conc., ppm
HDI	710	310 ^b	6.8
IPDI	>2,500	260	0.34
TDI	5,800	58–66	19.6
MDI	>31,600		0.1
NDI	>10,000		0.02 ^c

^aRef. 122.^b4 h.^cVapor pressure at 50°C.

exposure to HDI. HMDI has a low eye and dermal irritation potential, as well as a low potential for acute toxicity. Exposure to HMDI aerosol can cause dermal sensitization of laboratory animals. IPDI can cause skin sensitization reactions as well as eye irritation. The acute toxicity of diisocyanates in rats is shown in Table 14.

There are a multitude of governmental requirements for the manufacture and handling of isocyanates. The U.S. Environmental Protection Agency (EPA) mandates testing and risk management for TDI and MDI under Toxic Substance Control Administration (TSCA). Annual reports on emissions of both isocyanates are required by the EPA under SARA 313.

Thermal degradation of isocyanates occurs on heating above 100–120°C. This reaction is exothermic, and a runaway reaction can occur at temperatures > 175°C. In view of the heat sensitivity of isocyanates, it is necessary to melt MDI with caution and to follow suppliers' recommendation. Disposal of empty containers, isocyanate waste materials, and decontamination of spilled isocyanates are best conducted using water or alcohols containing small amounts of ammonia or detergent. For example, a mixture of 50% ethanol, 2-propanol, or butanol; 45% water; and 5% ammonia can be used to neutralize isocyanate waste and spills. Spills and leaks of isocyanates should be contained immediately, ie, by dyking with an absorbent material, such as saw dust.

The total U.S. airborne emission of volatile TDI is estimated by the International Isocyanate Institute (III) to be <25 t, or less than 0.005% of the annual U.S. production. Published data show that TDI has a 1/3 life of 8 s in air at 25°C and 50% RH, and a 0.5-s to 3-day half-life in water, depending on pH and agitation. Without agitation, isocyanates sink to the bottom of the water and react slowly at the interface. Because of this reactivity, there is no chance of bioaccumulation.

Toxicity of Tertiary Amine Catalysts. The liquid tertiary aliphatic amines used as catalysts in the manufacture of polyurethanes can cause contact dermatitis and severe damage to the eye. Inhalation can produce moderate to severe irritation of the upper respiratory tracts and the lungs. Ventilation, protective clothing, and safety glasses are mandatory when handling these chemicals.

Toxicity of Polyurethanes. These polymers can be considered safe for human use. However, exposure to dust, generated in finishing operations, should be avoided. Ventilation, dust masks, and eye protection are recommended in foam

fabrication operations. Polyurethane or polyisocyanurate dust may present an explosion risk under certain conditions. Airborne concentrations of 25–30 g/m³ are required before an explosion occurs. Inhalation of thermal decomposition products of polyurethanes should be avoided because carbon monoxide and hydrogen cyanide are among the many products present.

Because polyurethanes are combustible, they have to be applied in a safe and responsible manner. At no time should exposed foam be used in building construction. An approved fire-resistive thermal barrier must be applied over foam insulation on interior walls and ceilings. Model U.S. building codes specify that foam plastic used on interior walls and ceilings must have a flame-spread rating, determined by ASTM E84, of <75 and smoke generation of <450. The foam plastic must be covered with a fire-resistive thermal barrier either having a finish rating of not less than 15 min or equivalent to 12.7-mm gypsum board, or having a flame-spread rating of <25, smoke generation of <450 (if covered with approved metal facing), and protection by automatic sprinklers. Under no circumstances should direct flame or excessive heat be allowed to contact polyurethane or polyisocyanurate foam. The ASTM numerical flame-spread rating is not intended to reflect hazards presented under actual fire conditions.

Recycling of Polyurethanes. For polyurethanes a wide variety of recycling procedures are considered. Examples include mechanical recycling (rebounded foam, adhesive pressing, particle bonding, regrind, injection molding, compression molding), chemical recycling (glycolysis, hydrolysis), feedstock recovery (pyrolysis, hydrogenation, gasification), and energy recovery (incineration). Especially, the large amounts of polyurethanes generated by ELV (end-of-life disposal of motor vehicles) is of present concern. An average of 20 kg of polyurethane per car is globally used.

The glycolysis procedure, pioneered by Upjohn in the 1970s (123), produces reusable polyols. In this process cut-up or pulverized polyurethane products are fed continuously or in batches into a heated reactor containing single glycol or mixtures of glycol at 185–210°C. A clear solution of a urethane polyol in the used glycol is obtained. This polyol, in admixture with virgin polyol, can be used for the manufacture of rigid polyurethane foams. Several pilot plants operate in Europe to produce polyols for rigid foam manufacture using variations of this process. In one process mixtures of polyurethane and PET scrap are used. Even rigid foam from insulated underground pipelines are recycled using the glycolysis process. The chemistry of the glycolysis process involves transesterification of the carbamate groups in the polyurethanes with the reactive solvent. In this manner three-dimensional network polymers are converted into soluble linear polyurethane group containing polyols.

In order to reuse such a polyol in flexible foam manufacture a subsequent propoxylation step becomes necessary, and Dow Chemical has developed a “tandem chemolysis” process for flexible polyurethane polyols.

Flexible polyurethane foam generated in production or recovered after use as seating foam or packaging foam can be recycled by shredding and mixing with a polyurethane binder to produce carpet underlay. Annually, ca 70 kt/a of carpet underlay produced in the United States is made from recycled flexible foam. Powdered flexible foam is also used as filler (up to 30%) in the manufacture of flexible foam products.

BIBLIOGRAPHY

“Polyurethanes” in *EPST* 1st ed., Vol. 11, pp. 506–563, by K. A. Pigott, Mobay Chemical Co.; “Polyurethanes” in *EPSE* 2nd ed., Vol. 13, pp. 243–303, by J. K. Backus et al., Mobay Corp., a Bayer USA Co.

1. O. Bayer, *Angew. Chem. A* **59**, 257 (1947).
2. H. Ulrich, *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th ed., Vol. **24**, John Wiley & Sons, Inc., New York, 1997, pp. 695–726.
3. H. Ulrich, *The Chemistry and Technology of Isocyanates*, John Wiley & Sons, Inc., Chichester, 1996.
4. W. Hentschel, *Ber. Dtsch. Chem. Ges.* **17**, 1284 (1884).
5. K. Kurita, T. Matsumura, and Y. Iwakura, *J. Org. Chem.* **41**, 2070 (1976).
6. H. Eckert and B. Forster, *Angew. Chem.* **99**, 922 (1987).
7. U.S. Pat. 3492331 (1970), A. A. R. Sayigh and H. Ulrich (to The Upjohn Co.).
8. H. J. Knölker, T. Braxmeier, and G. Schlechtingen, *Angew. Chem. Int. Ed.* **34**, 2497 (1995).
9. H. W. Peerlings and A. W. Meijer, *Tetrahedron Lett.* **40**, 1021 (1999).
10. Eur. Pat. Appl. EP 408277 (1991), E. T. Shawl, J. G. Zajazek, and H. S. Kessling, Jr.
11. T. E. Waldmann and W. D. McGhee, *J. Chem. Soc., Chem. Comm.* 957 (1994).
12. T. Ohkubo and R. Okada, in *Proceedings Polyurethane World Congress*, Vancouver, Canada, 1993, p. 527.
13. J. A. Maclaren, *Chem. Ind. (London)* 395, (1971).
14. H. Ulrich, J. N. Tilley, and A. A. R. Sayigh, *J. Org. Chem.* **29**, 2401, 3334 (1964).
15. W. J. Schnabel and E. Kober, *J. Org. Chem.* **34**, 1162 (1969).
16. U.S. Pat. 3384653 (1968), W. E. Erner and A. Odinak (to The Upjohn Co.).
17. W. Mormann and M. Brahm, *Macromolecules* **24**, 1096 (1991).
18. W. Mormann and M. Brahm, *Polymer* **34**, 187 (1993).
19. H. Holtschmidt and G. Oertel, *Angew. Chem. Int. Ed.* **1**, 617 (1962).
20. P. I. Kordomenos, A. H. Dervan, and J. Kresta, *J. Coat. Technol.* **54**, 43 (1982).
21. A. Liebersohn and D. H. Kohn, *J. Appl. Polym. Sci.* **23**, 3445 (1979).
22. S. R. Gaonkar and co-workers, *Macromolecules* **23**, 3533 (1990).
23. G. Maier and co-workers, *Angew. Chem. Int. Ed.* **35**, 1696 (1996).
24. H. J. Laas, R. Halpaap, and J. Pedain, *J. Prakt. Chem.* **336**, 185 (1994).
25. Eur. Pat. 566925 (1992) (to BASF).
26. DE 3314790 (1983) (to BASF).
27. M. Rochery, I. Vroman, and T. M. Lam, *Liebigs Ann. Chem.* **37**, 259 (2000).
28. Eur. Pat. 23649 (1981) R. Yamamoto and co-workers (to Mitsui Toatsu).
29. Brit. Pat. 2031907 (1980), H. Zengel and co-workers (to BASF).
30. U.S. Pat. 4439616 (1984), B. Singh, L. W. Chang, and P. S. Forgioni (to American Cyanamid).
31. W. Mormann and G. Leukel, *J. Polym. Sci. A* **27**, 4341 (1989).
32. Z. W. Wicks Jr., *Progr. Org. Coat.* **9**, 3 (1981).
33. Z. Wirpsza, in *Proceedings of UTECH*, The Hague, the Netherlands, 1994.
34. R. Spindler and J. M. J. Frechet, *Macromolecules* **26**, 4809 (1993).
35. R. Richter, B. Tucker, and H. Ulrich, *J. Org. Chem.* **46**, 5226 (1981).
36. H. Ulrich, B. Tucker, and R. Richter, *J. Org. Chem.* **43**, 1544 (1978).
37. U.S. Pat. 3923744 (1975), M. V. Sorensen, R. C. Whiteside, and R. A. Hickner (to The Dow Chemical Company).
38. D. C. Scholl, in *Proceedings of Water Borne and Higher Solids Conference*, New Orleans, La., 1985, p. 120.
39. M. Bock and R. Halpaap, *J. Coat. Tech.* **59**, 755 (1987).
40. S. V. Lonikar and co-workers, *J. Appl. Polym. Sci.* **28**, 759 (1990).

41. Eur. Pat. 277353 (1987), H. Woynar, K. König, and J. Pedain (to Bayer A.G.); *Chem. Abstr.* **109**, 191, 119 (1981).
42. Ger. Offen. 3806276 (1989), J. Pedain, M. Bock, and C. G. Dieris (to Bayer A.G.); *Chem. Abstr.* **112**, 99, 527 (1990).
43. Ger. Offen. 3809261 (1989), J. Pedain, K. König, and W. Dell (to Bayer A.G.); *Chem. Abstr.* **112**, 100, 822 (1990).
44. Eur. Pat. 336205 (1988), J. Pedain and co-workers (to Bayer A.G.); *Chem. Abstr.* **112**, 141, 369 (1990).
45. Eur. Pat. 478990 (1990), H. J. Lass and co-workers (to Bayer A.G.); *Chem. Abstr.* **116**, 237, 531 (1992).
46. Ger. Pat. 1934763 (1971), K. Schmitt, J. Disteldorf, and F. Schmitt (to Huels); *Chem. Abstr.* **75**, 7537 (1971).
47. U.S. Pat. 4469867 (1984), J. Disteldorf and W. Hübel (to Huels).
48. T. Lesiak, A. Balewski, and W. Czerwinski, *Angew. Makromol. Chem.* **93**, 61 (1981).
49. A. Balewski and T. Lesiak, *Angew. Makromol. Chem.* **142**, 79 (1986).
50. K. Hatada and co-workers, *J. Appl. Polym. Sci., Part A-1* **28**, 3019 (1990).
51. Eur. Pat. 414102 (1991), U. Keppeler and M. Bobrich (to BASF); *Chem. Abstr.* **116**, 61, 329 (1992).
52. C. P. Smith, J. W. Reisch, and J. M. O'Connor, *J. Elast. Plast.* **24**, 306 (1992).
53. K. G. Spitler and J. J. Lindsey, *J. Cell. Plast.* **17**, 43 (1981).
54. U.S. Pat. 4761434 (1985), M. Dietrich (to Bayer A.G.).
55. H. W. Bonk and co-workers, *J. Elastom. Plast.* **3**, 157 (1971).
56. C. S. Schollenberger and F. D. Stewart, *Advances in Urethane Science and Technology*, Vol. I, Technomics, Stamford, Conn., 1971, p. 65.
57. *Chem. Eng. News* 10 (July 17, 1995).
58. Eur. Pat. 297444 (1989), M. Eggersdorfer and co-workers; *Chem. Abstr.* **111**, 77, 493 (1989).
59. G. Oertel, *Polyurethane Handbook*, 2nd ed., Carl Hanser Publishers, Munich, Germany, 1993.
60. W. F. Gum, W. Riese, and H. Ulrich, *Reaction Polymers*, Hanser Gardner Publications, Munich, Germany, 1992.
61. G. Woods, *The ICI Polyurethanes Book*, John Wiley & Sons, Inc., New York, 1987.
62. S. Neffgen, H. Keul, and H. Höcker, *Macromolecules* **30**, 1289 (1997).
63. H. Ulrich, R. Richter, and B. Tucker, *Synthesis* 277 (1979).
64. J. F. Kinstle and L. E. Sepulveda, *J. Polym. Sci., Polym. Lett.* **15**, 467 (1977).
65. N. D. Ghatke and J. Y. Jadhar, *J. Polym. Sci. A* **21**, 1941 (1983).
66. R. M. Versteegen, R. P. Sijbesma, and E. W. Meijer, *Angew. Chem. Int. Ed.* **38**, 2917 (1999).
67. W. Mormann, N. Tiemann, and E. Turuskan, *Polymer* **30**, 1127 (1989).
68. A. Kumar and S. Ramakrishnan, *J. Chem. Soc., Chem. Commun.* 1953 (1993).
69. Y. Chamberlin and co-workers, *J. Polym. Sci. A* **20**, 1445 (1982).
70. H. W. Bonk, H. Ulrich, and A. A. R. Sayigh, *J. Elast. Plast.* **4**, 259 (1979).
71. H. Ulrich, *J. Polym. Sci.: Macromol. Rev.* **11**, 93 (1976).
72. Y. Iwakura and co-workers, *Makromol. Chem.* **95**, 205 (1966).
73. D. W. House, W. M. Baumann, and R. V. Scott, in *Proceedings Polyurethane World Congress*, Aachen, Germany 1987, p. 340.
74. U.S. Pat. 4567236 (1986), D. J. Goldwasser and R. Oertel (to The Upjohn Co.).
75. H. W. Bonk, R. S. Drzal, G. N. Georgacopoulos, and T. M. Shah, in *Proceedings of the SPE 43rd Annual Technical Conference*, New York, 1985, p. 1300.
76. U.S. Pat. 3555071 (1971), D. V. Rao, A. A. R. Sayigh, and H. Ulrich (to The Upjohn Co.).
77. T. Burniana and co-workers, *J. Macromol. Sci., Pure Appl. Chem. A* **32**, 1397 (1995).

78. M. Chen and co-workers, *Macromolecules* **25**, 4032 (1992).
79. M. F. Rubner, *Macromolecules* **17**, 2114 (1986).
80. Y. Shimura and D. Chen, *Macromolecules* **26**, 5004 (1993).
81. Y. X. Shen and H. W. Gibson, *Macromolecules* **25**, 2058 (1992).
82. D. Dietrich, W. Keberle, and H. Witt, *Angew. Chem.* **82**, 53 (1970).
83. Ger. Pat. 1237306 (1964), W. Keberle, D. Dietrich, and O. Bayer.
84. Ger. Pat. 922736 (1952), G. Pieper and co-workers; *Chem. Abstr.* **55**, 10, 912 (1961).
85. Brit. Pat. 1076909 (1965), W. Keberle and D. Dietrich.
86. H. A. Al-Salah and co-workers, *J. Polym. Sci. B* **24**, 2681 (1986).
87. H. Matsuda and S. Takechi, *J. Polym. Sci. A* **29**, 83 (1991).
88. S. K. Pollack and co-workers, *Macromolecules* **25**, 2381 (1992).
89. G. Smith and co-workers, *Macromolecules* **23**, 3389 (1990).
90. J. Back Lee and co-workers, *Macromolecules* **26**, 4989 (1993).
91. B. Szczepaniak and co-workers, *J. Polym. Sci. A* **31**, 3223 (1993).
92. M. Tanaka and T. Nakaya, *J. Macromol. Sci., A: Chem.* **26**, 1655 (1989).
93. M. Tanaka and T. Nakaya, *J. Macromol. Sci., A: Chem.* **24**, 777 (1987).
94. K. Diblitz and C. Diblitz, in *Proceedings of the Polyurethane World Congress*, Vancouver, Canada, 1993, p. 619.
95. H. Mispereuve and P. Knaub, in *Proceedings of the Polyurethane World Congress*, Vancouver, Canada, 1993, p. 297.
96. J. V. McClusky and co-workers, in *Proceedings of the Polyurethane World Congress*, Vancouver, Canada, 1993, p. 507.
97. D. R. Battice and W. J. Lopez, *J. Cell. Plast.* **23**, 158 (1987).
98. R. M. Hennington, V. Zellmer, and M. Klincke, in *Proceedings of SPI 33rd Annual Conference*, 1990, p. 492.
99. J. S. Hicks and A. K. Schrock, in *Proceedings of SPI 33rd Annual Conference*, 1990, p. 348.
100. A. C. M. Griffiths and P. Shreeve, *Cell. Polym.* 195 (1984).
101. J. Grimminger and K. Muha, in *Proceedings Polyurethane World Congress*, Vancouver, Canada, 1993, p. 279.
102. C. Cecchini, V. Cancellier, and B. Cellarusi, in *Proceedings Polyurethane World Congress*, Vancouver, Canada, 1993, p. 354.
103. H. Ulrich, *J. Cell. Plast.* **17**, 31 (1981).
104. A. K. Zhitinkina, N. A. Shibanova, and O. G. Tarakanov, *Russ. Chem. Rev.* **54**, 1104 (1985).
105. H. E. Reymore, R. J. Lockwood, and H. Ulrich, *J. Cell. Plast.* **14**, 95 (1978).
106. T. W. Bodnar, J. J. Koch, and J. D. Thornsberry, in *Proceedings Polyurethane World Congress*, Nice, France, 1991, p. 191.
107. T. P. Russell and co-workers, *Macromolecules* **26**, 1922 (1993).
108. H. Lee and S. C. Kim, *Macromolecules* **19**, 644 (1986).
109. W. L. Chang, K. C. Frisch, and K. Ashida, *J. Polym. Sci. A* **27**, 3619 (1989).
110. S. Schlick and co-workers, *Macromolecules* **22**, 822 (1989).
111. Y. S. Yang and L. J. Lee, *Macromolecules* **20**, 1490 (1987).
112. L. H. Sperling, D. Klempner, and L. A. Utracki, *Interpenetrating Polymer Networks*, American Chemical Society, Washington, D.C., 1994. Advances in Chemistry Series No. 239.
113. U.S. Pat. 4219502 (1980), K. G. Ihrman and M. Brandt.
114. H. G. Schmelzer and co-workers, *J. Prakt. Chem.* **336**, 483 (1994).
115. R. A. Smiley, S. Yang, H. X. Xiao, K. C. Frisch, and J. Kresta, in *Proceedings UTECH'90*, 1990, p. 205.
116. J. C. Lee and B. Kim, *J. Polym. Sci. A* **32**, 1983 (1994).
117. B. K. Kim, J. C. Lee, and K. H. Lee, *J. Macromol. Sci., Part A: Chem.* **31**, 1241 (1994).

118. D. Dietrich, *Proc. Org. Coat.*, **9**, 281 (1981).
119. R. J. Carson and A. Edwards, *Urethane Technology* 24 (Dec. 1999/Jan. 2000).
120. A. W. Musk, J. M. Peters, and D. H. Wegman, *Am. J. Ind. Med.* **13**, 331 (1988).
121. M. H. Karol, *CRC Crit. Rev. Toxicol.* **16**, 349 (1986).
122. I. F. Carney, *Toxicology of Isocyanates*, International Isocyanate Institute, Inc., New Canaan, Conn., 1980.
123. H. Ulrich and co-workers, *Polym. Eng. Sci.* **18**, 844 (1978).

HENRI ULRICH

POLYVINYL CARBAZOLE. See VINYL CARBAZOLE POLYMERS.

POLYVINYL PYRROLIDINONE. See VINYL AMIDE POLYMERS.

POM. See ACETAL RESINS.