Polyurethanes
Science, Technology, Markets, and Trends

Mark F. Sonnenschein
POLYURETHANES
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WILEY
Dedicated to my wife Geraldine Franklin Sonnenschein for her beauty, kindness, and endless support, and to my children Matthew, Anne, and Susan for the inspiration and the laughs.
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1

INTRODUCTION

In the early 1900s, there were very few of the synthetic polymers we have grown accustomed to now. During succeeding years, polymer science experienced explosive growth with the invention of polyvinyl chloride (PVC, 1913), polyethylene (1933), polyvinylidene chloride (Saran, 1933), polyamides (nylon, 1934), and polytetrafluoroethylene (Teflon, 1938). In addition, during the 1930s, the polymer family known as polyurethanes was invented. Now, of course, polyurethanes, and all the polymers developed during this period, have become an integral part of modern life. As you read this, you may not be aware of how many ways polyurethanes surround you. They are present in the shoes you stand in, the seat cushion you sit upon, the carpet backing and foam pad underlay you walk upon, the fibers of your clothing, insulation of your walls and roof, your refrigerator, dishwasher, water heater, automotive seating, automotive structural foam, automotive paints and coatings, furniture coatings, your bed mattress, and the adhesive holding this book together—the list just goes on. This book’s purpose is to explain polyurethane science, technology, applications, trends, and markets in virtually all of its forms and relate those structures to the properties that make them so suited for so many uses. It is not an overstatement to say that polyurethanes are, if not the most versatile class of materials, then certainly one of the most versatile polymer categories in existence.

Discovery of polyurethane chemistry is attributed to the efforts of Otto Bayer and the research team he led at the now defunct I.G. Farben AG chemical company. The first patent associated with polyurethanes was filed in 1937, and numerous other patents, most notably the production of flexible foams resulting from isocyanate–water reactions,
were filed thereafter. I.G. Farben was broken up following World War II for complicity in war crimes, and the company’s top leaders were convicted for crimes against humanity (exploitation of slave labor and production of nerve gas). The largest surviving components of I.G. Farben, Bayer AG and BASF SE, remain very large and respected global chemical concerns and very large producers of polyurethane chemicals.

After the initial discovery and expositions of basic chemistry, mostly based on short-chain diols and polyester polyols, industrial polyurethanes saw immense growth following the development of polyether polyols by E.I. DuPont de Nemours and Co. and The Dow Chemical Co. While Dow Chemical remains one of the world’s largest manufacturers of polyurethane chemicals, DuPont has exited its polyurethane businesses that were primarily textile and coating related. While polyesters remain prominent components of polyurethane chemistry, it was the superior processing, low-temperature flexibility, and hydrolytic stability of polyether polyols that expanded polyurethane polymers into their current acceptance in every aspect of modern life.

As ubiquitous as polyurethanes are, it is perhaps surprising that they represent a relatively minor (but still significant) fraction of the overall volume of plastics global consumption (Fig. 1.1). Structures of the listed commodity polymers are relatively simple repeating units (Fig. 1.2). Their simplicity is in part responsible for their high level of utility and low-cost positions. The plastics industry has generated variants of the structures shown in Figure 1.2 by introducing branching, for instance, but those complexities do not fundamentally alter the basic polymer structure.

Polyurethane is the largest volume commodity polymer that cannot be characterized by a simple structure such as shown in Figure 1.2. Instead, polyurethane represents a class of polymers, and any polymer with a urethane repeat unit is classified as a polyurethane regardless of the other functional or polymer structures incorporated (Fig. 1.3).

**FIGURE 1.1** Percentage global consumption of plastics in 2012. Polyethylene encompasses all densities; styrenics includes all copolymers along with atactic polystyrene.
Specific polyurethane structures used for making mattress foam, or insulation foam, or shoe foam, can be significantly different from one another and cannot be neatly represented like the structures in Figure 1.2. In fact, even structures of different insulation foams can vary so widely that they also cannot be easily represented by a single structure. Another difference with other commodity polymers is that large
volume polyurethane applications require the mixing of two reactive liquid components rather than the processing of a pellet into a molded or extruded object. Given these complexities, it is remarkable that polyurethanes have developed into a commodity plastic category and is a testament to polyurethane versatility and performance that polyurethanes are so difficult to replace in their favored applications.

Polyurethane polymers as a class are made from commodity building block reagents and short-chain polymers (or oligomers). These building blocks include categories: polyisocyanates, polyethers, polyesters, water, and amines, for example (Fig. 1.4). As building block categories, they also cannot be represented by unique structures and are denoted “R” to allow designers to insert any conceivable chemically allowable unit.

The polyurethane unit is easily mistaken for the related polyester, polyurea, or polyamide (nylon) structures (Fig. 1.5). In fact, polyureas, polyesters, and polyurethanes are often joined into polyurethane materials and still broadly classified as polyurethane (polyamides are not a part of polyurethane chemistry due to vastly different processing characteristics).

As commodity products, polyurethanes have achieved a certain establishment status in academic science. However, activity in polyurethane science shows no sign of abating, due to its high potential for design and innovation [1–14]. Figure 1.6 shows total global publication activity including patents, journal articles, reviews, meeting abstracts, governmental documents, etc. for the years 2003–2014 for all commodity plastics named in Figure 1.1. While many plastics exhibit activity approximately in proportion to their production, polyurethane activity is more than double its production. Figure 1.7 shows the annual growth of polyurethane publishing for publications where a polyurethane polymer property is the focus of the document. The steady growth of activity appears independent of general global economic activity. Figure 1.8 quantifies the kinds of publications over this time period showing that open literature publications predominate but that patent activity is nearly as prevalent.
FIGURE 1.6  Publication activity focused on commodity plastics for the years 2003–2013. The total includes all public literature, patent filings, conference proceeding, and books where the subject focus is the plastic. The total number of publications for all listed plastics = 1,265,554.

FIGURE 1.7  Publication activity for the years 2003–2013 where the subject focus is polyurethane polymer properties. Graph shows steady increase and no apparent dip in the global recession years 2008–2010. Only publications in English are collated. Addition of other languages does not materially change the distribution but does change the number.
This book also covers markets and commercial aspects of the polyurethane industry. The market and commercial activities overlap, but they are not synonymous. The overlap in how the words “marketing” and “commercial” are used reflects their conflation in meaning. Polyurethane market concepts are broader, more strategic, and more theoretical than commercial concepts. Marketing encompasses the equilibrium and nonequilibrium driving forces that make one material attractive to a consumer and another unacceptable. They take into consideration regional preferences, regional access to feedstocks, and the underlying cultural and societal influences that make a product useful or desirable or possess value. They also include the advantages a particular competitor in a market may possess from all facets including intellectual (i.e., patents).

The commercial aspects of an industrial product include those aspects that are important to specific customers or groups of customers such as advantages or value a product may have versus a competitive material or a competitive company. Probably the most prominent commercial aspect, especially for commoditized products, is price and price movement. Without doubt, thorough and confident knowledge of pricing in commerce is essential and can distinguish a profitable enterprise from one that fails. A commercial move to raise prices when there is excess capacity, or failure to raise prices when there are shortages or feedstock prices are rising, is common commercial failure, and the ability to shrewdly navigate price movements is the hallmark of well-run companies.

FIGURE 1.8 Type of publications where the focus of the work is polyurethane polymer properties for the years 2003–2013. The high level of open literature and patent activity demonstrates the continuing intellectual and commercial interest in these materials. The logarithmic scale may exaggerate the importance of items at the low end of the distribution. Only publications in English are collated, which partially skews the distribution. Addition of other languages would include a significant amount of work in Chinese.
In recent years, the polyurethane industry has been subject to significant macroeconomic forces. The overriding force has been the expansion of polyurethane feedstock manufacturing capacity in China. In particular, this capacity growth has injected chemical production during a period of global economic stagnation (especially in Europe) and slow growth environments in North America. Figure 1.9 shows the extent of isocyanate overproduction. The deteriorating demand/capacity ratio can have a very material impact on price expectations and influence decisions on additional capacity expansions. It is not always the case that manufacturers flee a market in response to temporary price declines resulting from overexpansion. It has occurred in the past that manufacturers with a strong financial base will wait out the failure of financially weaker producers. The closure of these weak assets will reduce production volumes, called “tightening the market.” It has also occurred in the past that manufacturers with a particularly strong financial position and a strong commitment to the market will increase production in the face of overcapacity to further drive down prices and drive weak manufacturers into untenable production economics. The anticipated response is for weak producers to shutter poorly performing manufacturing assets or sell their business to one of their competitors. Following these closings, production can regain a capacity/demand balance and prices can rise. This kind of “game” is not seen very often now in the chemical industry. In part, this is due to the relatively small number of global manufacturers and their similar financial strengths, maturity, and experience. Additionally, regulation of monopolistic behavior has become more stringent, and the potential gain by this kind of predatory practice may not be worth the potential reputational risk. Lastly, many manufacturers see the
benefit of strong and rational competition in the marketplace. Rational and mature competition can provide ballast to minimize market fluctuations and provide a stimulus to improve business performance. In contrast to rational industrial practices, the recent haphazard expansion of polyurethane elastic fiber production has witnessed rapid capacity expansion concomitantly with falling prices. Very few major manufactures from the year 2000 are still in the market, and commercial profitability and market value have probably been permanently destroyed. This is covered in detail in Chapter 9.

The trends in polyurethane manufacturing reflect global competitive pressures and global opportunities. This has resulted in expansion of manufacturing assets close to raw material feedstocks and also close to geographies with increasing economic growth. It is not immediately clear whether it is cheaper to ship commodity feedstocks to centers of economic activity or ship finished polyurethane chemicals from low-cost manufacturing sites. However, low feedstock cost manufacturing is probably less prone to geopolitical factors and will always maintain a low-cost position. On the other hand, market and commercial flexibility is enhanced by proximity to customers.

There is continuing movement toward manufacturing innovation using processes that reduce usage of solvents and reagents and involve less purification and environmental impact. There is probably little incentive for production of new families of polyurethane building blocks, particularly for new polyisocyanates. It would appear that the regulatory burden of new isocyanate production inhibits innovation, and currently available products perform adequately and at acceptable cost. In the same regard, there has been relatively weak growth of polyols derived from new DMC catalysts despite the performance advantages of the polyol product (see Chapter 2). Again, this is probably due to insufficient performance/cost incentive for manufacturers or customers resulting in slow adoption. On the other hand, improvements in established products, such as production of copolymer polyols with ever higher solid content, lower viscosity, and smaller particle size, will undoubtedly continue and find success in the market.

The trend for polyurethane applications is being driven by overriding trends in the industries in which polyurethanes find purpose. Thus, automotive trends toward lighter weight dictate a trend toward higher performance at lower foam density. Higher performance includes achieving required comfort factors with lower vibration and noise transmission. In construction markets, the trend is toward improved thermal insulation with new blowing agents that exhibit lower ozone depletion potential and now lower global warming potential as well. Restrictions on acceptable flame retardant packages for both flexible foams and rigid foams are also a driver of polyurethane industrial innovation. Thus, blowing agents and flame retardants score highly in the intensity of industrial activity associated with polyurethanes. Industrially, reactive catalyst innovation has been consistently pursued (to reduce fugitive catalyst emissions). This trend may intensify in the future due to governmental and consumer pressures, particularly in Europe. The trend toward further employment of renewable feedstocks has been slow and based on patent activity will probably remain so for the near future.

The science of polyurethanes is ongoing and will continue a high level of activity in the future. While a great deal is known about the fundamentals of polyurethane
structure–property relationships, the control of these relationships is still being actively pursued. Most understanding of polyurethanes is based on equilibrium properties; however, due to kinetic limitations of reaction-induced phase separation, theory and reality are often in conflict. Exponential increases in computing power allow for finer-grained simulations of larger volumes that can be harnessed by modern self-consistent field theoretical techniques to better predict or simulate experimental results.

REFERENCES

Polyurethane Building Blocks

The versatility of polyurethanes is derived in large part from the wide selection of building blocks available to materials designers. The growth of polyurethanes has been highly dependent on the cheap and available feedstock polyisocyanates, polyols, and chain extender coreactants such as water, alcohols, and amines. However, this paradigm has recently been challenged as substitutions are made for purposes of avoiding health and safety issues associated with isocyanates. A detailed discussion of substitute chemistries to urethane structures will be handled in Chapter 12 [1–3]. This chapter provides an overview of building blocks for conventional polyurethane polymerization.

In principle, there is as much potential for design of isocyanate structures as there is for alcohol and amine coreactants. In reality, while there are numerous polyisocyanates to choose from, most of the innovation in polyurethane performance comes from the broad range of choices available in the coreactant alcohols and amines. To a great extent, this reflects complications (both industrial and regulatory) associated with making isocyanates and the comparative ease of making polyol and polyamine structures. It also reflects the fact that for most polyurethanes, nonisocyanate reactants comprise more than 50% of the polyurethane volume. Thus, for the purpose of obtaining any particular outcome, varying the polyol and the chain extender components is the most straightforward way to begin.
2.1 POLYOLS

The term polyol refers simply to polymer backbones containing nominally two or more hydroxyl groups. Polyols are the largest volume raw material used in polyurethane applications with weight fractions in applications ranging from 90 wt% in low modulus flexible sealants, 70 wt% in flexible foams, and as low as 30 wt% in rigid insulation foams. As implied by these values, the polyols in urethane formulations tend to provide softness and flexibility, while isocyanates and low-molecular-weight chain extenders provide hardness and stiffness to the resulting polymer structures.

Polyols are produced with a range of backbones and hydroxy functionalities that can be tailored to best meet application processing and property requirements. The most industrially significant polyol backbones are ether and ester based, while a number of specialty backbones including carbonate, acrylic, and ethers derived from tetrahydrofuran (THF) are used in high-performance coating, adhesive, and elastomer applications. Figure 2.1 shows their relative global volumes as of 2011 [4, 5]. For comparison, the relative global volume for polyether polyols in 1992 was 2654 thousand metric tons and for PTMEG was 100,000 metric tons [4]. In the case of polyether polyols, this translates to roughly 4% annual growth rate. The volume growth of PTMEG has also been a long-term trend of approximately 4% [6]. Despite continuity of the long-term trend, the growth in these categories has not been linear over time and not uniform over all geographies. For instance, it is estimated that while the current growth rate for polyether polyols in China is nearly 8%, it is only about 2.5% in North America. While the polyol industry as a whole has grown, the relative size of each category reflects the integrated underlying dependence on global economic growth in various regions.

![Figure 2.1](image-url)  
**FIGURE 2.1** Relative volumes of polyols produced in 2011.
Polyols vary markedly in structure, manufacture, function, and price. While each occupies a particular price/performance niche, for many of them, there is an overlap, and the choice of which polyol to use in any particular application depends on the history and experience of the chemist and the end user. In general, polyols all begin with low-cost commoditized building blocks. Final cost depends on factors related to volume of production, cost of polymerization process, and perceived value in an application. The structures of several commonly utilized polyols are provided in Figure 2.2. The structure to a great extent defines the properties of the resulting polyurethane, as well as the compromises each structure demands of the final product performance. For instance, while polyethers generally provide good low temperature performance, an easily processed backbone, and a good cost position, the low ceiling temperature (the temperature at which the rate of depolymerization is equal to the rate of polymerization) is relatively low for these structures [7]. While many factors may influence the exact degradation temperature, these polyether polyols should not be considered stable above 220°C. Polyether polyol flammability results from the high volatility of the monomers and the combination of oxygen and hydrocarbon fuel that the monomer represents and is a fundamental limitation to these structures [8, 9]. This problem has in turn created a demand for flame retardants in many polyether containing systems, especially foam systems having high surface to volume ratios [10]. Similarly, the well-known hydrolytic instability of polyesters is a compromise that must be accommodated if taking advantage of their low cost (in some instances) and high thermal stability (Table 2.1).

2.1.1 Polyether Polyols

2.1.1.1 Building Blocks Polyether polyols are the class of polymers formed from the exothermic reaction of ethylene oxide (oxirane), 1,2-propylene oxide (methyloxirane), or 1,2-butylene oxide (ethyloxirane). Other materials could be considered (i.e., epichlorohydrin), but these monomers are the largest volume of this class and of the most use in polyurethane chemistry. Additionally, the related cyclic ether THF is another important building block for polyether synthesis (Fig. 2.3). Although the molecules are structurally related, each one is prepared by significantly different procedures.

Ethylene oxide is prepared directly from the catalyzed oxidation of ethylene [11, 12]. 1,2-Propylene oxide and 1,2-butylene oxide are prepared from a 2-step reaction consisting of reaction of the 1,2-alkene with chlorine and water to form the chlorohydrin followed by ring closure to form the cyclic ether by reaction with base [13, 14]. Figure 2.4 is an illustration of the synthesis of 1,2-butylene oxide.

A more recent innovation produces propylene oxide (PO) by direct oxidation of propylene using hydrogen peroxide (HPPO process) [15, 16] (Fig. 2.5). The HPPO process is simpler and less energy consuming but requires the coproduction of hydrogen peroxide on a massive scale to make PO economically. A third industrial route to propylene oxide involves peroxidation of ethyl benzene to form ethyl benzene hydroperoxide followed by reaction with propylene to produce the desired propylene oxide and the side product methyl phenyl carbitol, which can
Figure 2.2 Comparison of basic polyol structures.
### TABLE 2.1 Comparison of polyol general properties

<table>
<thead>
<tr>
<th>Polyol backbone</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyether polyols based on propylene oxide and ethylene oxide</td>
<td>Hydrolytic stability, cost, viscosity, flexibility</td>
<td>Oxidative stability, modulus/strength, thermal instability, flammability</td>
</tr>
<tr>
<td>Aliphatic polyester polyol</td>
<td>Oxidative stability, modulus/strength</td>
<td>Viscosity, hydrolytic stability</td>
</tr>
<tr>
<td>Aromatic polyester polyol</td>
<td>Flame retardance, modulus/stiffness</td>
<td>Viscosity, low flexibility</td>
</tr>
<tr>
<td>Polyether polyols based on tetrahydrofuran</td>
<td>Hydrolytic stability, modulus/stiffness</td>
<td>Oxidative stability, viscosity, cost</td>
</tr>
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<td>Polycarbonate polyols</td>
<td>Hydrolytic stability, oxidative stability, modulus/strength</td>
<td>Viscosity, cost</td>
</tr>
<tr>
<td>Acrylic polyols</td>
<td>Hydrolytic/oxidative stability, hardness</td>
<td>Viscosity, cost, low flexibility</td>
</tr>
<tr>
<td>Polybutadiene polyol</td>
<td>Low temperature flexibility, solvent resistance</td>
<td>Viscosity, thermal oxidizable (unless hydrogenated), cost</td>
</tr>
</tbody>
</table>

**FIGURE 2.3** Building blocks for polyether polyol synthesis.

**FIGURE 2.4** Synthesis of butylene oxide via chlorohydrin route.

**FIGURE 2.5** Synthesis of propylene oxide via hydrogen peroxide (HPPO) process.
be dehydrated to styrene [17]. Other methods also are practiced commercially [18]. Figure 2.6 details the share of each process to PO as of 2008.

The last feedstock for polyether production is THF. The great majority of THF is produced by dehydration of 1,4-butanediol [19]. Two alternative processes are practiced industrially. One route oxidizes butane to maleic anhydride followed by hydrogenation of the anhydride to THF [20]. A second route reacts butadiene with acetic acid and oxygen to form 1,4-diacetoxy butane, which can be hydrolyzed to 1,4-butanediol or THF by deacetoxy cyclization [21, 22]. While this route has the benefit of flexibly producing either the diol or the furan product, it creates increased demand for the valuable butadiene monomer with implications for those products requiring synthetic rubber. A new process produces THF from biosourced sugars by separation of succinic acid from the bacterial broth and reduction to butanediol and THF from the dehydration of butanediol [23] (Fig. 2.7).

2.1.1.2 Polymerization of Alkoxides to Polyethers While ethylene oxide is an important building block for synthesis of polyurethane polyether soft segments, there are only a few exceptions where polyethylene glycol (PEG) is utilized as the sole soft
segment. This is because of the crystallinity of PEG and because of its affinity for water. The affinity for water limits PEGs use since the properties of the polyurethane can be strongly dependent on the humidity of the environment. Instead, for polyurethanes, ethylene oxide is usually used as a coreactant with other alkylene oxides, usually propylene oxides, to create block or random copolymers.

Propylene oxide is polymerized to polypropylene oxide by two industrially dominant processes. Both processes are defined by the catalyst that is used. The dominant method employs an initiator or starter molecule with active hydrogens such as water, ethylene glycol, glycerine, ethylene diamine, or sorbitol and a base catalyst like potassium hydroxide [24]. This approach is usually referred to as the base-catalyzed process. The other process to polypropylene oxide uses a class of heterogeneous metal-based catalysts termed “double-metal cyanide” catalysts (aka DMC catalysts) [25]. Each process has unique attributes including differences in cost, process flexibility, and even structure of the final product. The base-catalyzed process follows the simplified path given in Figure 2.8.

The functionality of the final product is determined by the functionality of the initiating alcohol (see Table 2.2) and the final molecular weight influenced by the ratio of initiating alcohol to oxirane monomer. The base resides in a molecularly dispersed state with the oxirane and is termed a homogeneous catalyst. In actuality, the process is more complicated than expressed in Figure 2.8. The reaction mechanism of Figure 2.8 suggests that the result of the reaction is all secondary hydroxyl end groups. However, this is not in fact observed. In the synthesis of polypropylene oxide, there are also observed a population of primary hydroxyl end groups and a population with vinyl termination. The vinyl termination is a particular concern since it is not reactive with the other components of polyurethane chemistry and so degrades the polymer network structure. The actual chemistry that occurs within the reactor is explicitly given in Figure 2.9. The reaction resulting in secondary hydroxyls predominates, but the other structures do form and the process and specific product influence the product distribution.

The primary product in base-catalyzed (or explicit in these reactions—base initiated) polymerization is the product predominated by secondary hydroxyls due to the relative ease of nucleophilic attack on the less hindered carbon of the oxirane. Alkoxide attack on any of the methyl hydrogens results in unsaturation given