

Fourth Edition

ORGANIC COATINGS

Science and Technology



Frank N. Jones • Mark E. Nichols • Socrates Peter Pappas

WILEY

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Zeno W. Wicks, Jr., 1920–2007

Zeno was the lead author of the first three editions of this book. Two of us (Jones and Pappas) remember him fondly as an outstanding scientist, a charismatic teacher, a mentor, a marvelous colleague, and a gentleman. Zeno influenced hundreds, more likely, thousands, of students, many of whom have made careers in coatings. His favorite advice to them was “Don’t park your brains at the door.”

Being in a younger generation, Mark Nichols missed out on meeting Zeno. “My loss,” he says, and he is right.

Zeno got his Ph.D. in Chemistry at the University of Illinois. He joined Inmont Corporation, where he advanced to vice president of research and development during a 28-year career. (Inmont was a leading coating and ink producer, acquired by BASF in 1985.) For the next 11 years, he was professor and chair of the Department of Polymers and Coatings at North Dakota State University (NDSU). He then became a consultant. Among other activities, he traveled worldwide to teach about coatings. He received the Mattiello Memorial Award, the Roy W. Tess Award, and four Roon Awards.

Zeno was the best teacher we ever saw. He could teach all day, and when he invited a class to return after dinner for optional discussion, they came. This book originated as a set of lecture notes Zeno prepared during his last year at NDSU, where he taught a full-year course in coatings for upperclassmen and graduate students. He thought, rightfully so, that the notes might be helpful to his successors.

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Preface

Coatings science and technology advance in a continuous stream of improvements with an occasional breakthrough. This year's house paint may look the same as that of 10 years ago, but it is a lot better. Thus, it is time to revise the third edition of *Organic Coatings: Science and Technology*, published in 2007. Here, the third edition has been completely updated. Our purpose remains the same—to provide a reference and textbook that interrelates coatings technology with current scientific understanding.

For the fourth edition, Mark Nichols joined the team of authors. For the first time, we have a real materials scientist involved—and a very good one. As editor-in-chief of the *Journal of Coatings Technology and Research*, Mark has a broad view of contemporary coatings technology and is a leading authority on automotive coatings. His contributions are reflected in major revisions. Entire books could be written about the subject of each chapter, and many have been. To be as comprehensive as possible in the limited space available, we have summarized each topic and have provided references for readers seeking more detailed information. We have striven to enhance the usefulness of this edition both as a classroom textbook on coatings science and as a reference book. The reader will benefit from having taken college level chemistry courses through organic chemistry, but no coursework in polymer or materials science is assumed.

Some chapters include brief descriptions of coating compositions and applications, supported by references, which could be omitted in a classroom or used for outside-of-class assignments, such as term papers. We hope that these specific examples enhance the value of the volume as a reference book and self-teaching text. We understand that the first three editions were widely used for this purpose. We have also defined the jargon of coatings to help newcomers to the field understand its specialized language. While this book is written specifically about coatings, many of the principles apply to the related fields of printing inks, adhesives, and parts of the plastics industry.

Coatings technology evolved empirically by trial and error. Directions on how to make and apply paint have been published for at least 2000 years. Since about 1900, scientific understanding of the applicable principles has evolved. In 1905 Einstein published an equation applicable to flow of pigmented paints, and before 1920, pioneers such as H. A. Gardner, E. Ladd, C. B. Hall, and M. Toch applied scientific methods to testing. However, the coatings field is extremely complex, and scientific understanding remains incomplete. Empirical formulation and experimentation is still essential in developing and using coatings. The often conflicting needs for sustainability, reduced impact on the environment and health, reasonable cost, and improved coating performance require continuing innovation. Our conviction is that understanding the underlying science can help formulators work more effectively and that an appreciation of the formulators' craft is essential for scientists and engineers working in the field. Knowledge should flow both ways.

A complete literature review for each chapter would fill much of the book. We only cite key references and those that support specific information. Many of the references in older editions were replaced with newer ones, but many old references remain because they describe significant contributions to the evolution of coatings technology. Various sources of additional information are available to investigators. These include refereed journals such as the *Journal of Coatings Technology and Research* and *Progress in Organic Coatings*, as well as books, trade journals, conference proceedings, academic dissertations, internal company reports, and information from suppliers and customers. Patents are sometimes overlooked, but they often include informative reviews of the "state of the art" and specific examples including formulas, test procedures, and results. Patents are also free and readily searchable online.

We thank Dean Webster and Carole Worth for their editorial assistance and helpful suggestions.

Chapter 1

Introduction to Coatings

Coatings have been used since prehistoric times to protect objects and convey information, and they are ubiquitous in modern society as they serve to both protect substrates and impart aesthetic qualities to improve objects' appearance. If you are reading this text in a traditional paper book, the paper is coated. Look up and the walls of your room are coated, as are the windows. If you are wearing glasses, the lenses are likely coated to improve the plastic's scratch resistance and absorb UV radiation. If you are reading this text on a computer screen, the screen is coated to prevent glare and perhaps reduce fingerprints. The CPU inside your computer exists because of coatings used during the printing of nanometer-sized circuits. If you are outside, the buildings, cars, airplanes, roads, and bridges are all coated. Objects without coatings are less common than those with coatings!

Just because coatings science is an ancient technology does not mean that innovation has ceased. Today many coatings scientists and formulators are working diligently to improve the performance of coatings, reduce the environmental impact of their manufacture and application, and create coatings that provide functionality beyond today's coatings.

1.1 DEFINITIONS AND SCOPE

Coatings are typically thought of as thin layers that are applied to an object, which is often referred to as the *substrate*. Thus, one of the defining characteristics of a coating is its thinness. While the thickness of a coating depends on the purpose it serves, typical coating thicknesses range from a few microns to a few hundred microns, but of course, exceptions to this are common. Historically, the thickness of a coating was often quoted in terms of mils, where 1 mil equals one thousandth of an inch or 25.4 μm .

While coatings can be made from any material, this book is primarily concerned with organic coatings. Thus, we leave for other books coatings such as the zinc coatings used to galvanize steel, ceramic coatings that are formed from metal oxides or when metals such as aluminum are anodized, and the many other inorganic coatings used to impart hardness, scratch resistance, or corrosion protection. While these coatings are both technically and economically important, they lie mostly beyond the scope of this book.

Organic coatings are often composite materials in that they are composed of more than one distinct phase. The matrix, called the *binder*, holds the other components of the coating composition together and typically forms the continuous phase in the dry coating. As stated previously, we are mostly concerned with organic coatings, where the binder is typically an organic polymer.

A confusing situation results from multiple meanings of the term *coating*. As a noun *coating* is used to describe both the material (usually a liquid) that is applied to a substrate and the resultant "dry" film. As a verb, *coating* means the process of application. Usually, the intended meaning of the word coating can be inferred from the context. The terms *paint* and *finish* often mean the same thing as *coating* and also are used both as nouns and verbs. What is the difference between a coating and a paint? Not much—the terms are often used interchangeably. However, it is fairly common practice to use "coatings" as the broader term and to restrict "paints" to the familiar architectural and household coatings and sometimes to maintenance coatings for bridges and tanks. Some prefer to call sophisticated materials that are used to coat automobiles and computer components "coatings," and others call them "paints." Consumers are often familiar with the terms *varnish* or *stain*. These are types of coatings that are used to protect and beautify wood

and are certainly within the scope of this book as they are typically made from polymeric binders with or without pigments.

Because we are limiting the scope of this book to organic coatings that are historically associated with paints, we are also choosing not to cover important materials such as coatings applied to paper and fabrics, decals, laminates and cosmetics, and printing inks, even though one could argue that these coatings share much in common with traditional paints. However, readers interested in those materials will find that many of the basic principles discussed in this text are applicable to such materials. Restrictions of scope are necessary if the book is to be kept to a reasonable length, but our restrictions are not entirely arbitrary. The way in which we are defining coatings is based on common usage of the term in worldwide business. For classification purposes, coatings are often divided into three categories: architectural coatings, original equipment manufacturer (OEM) coatings, and special purpose coatings.

As the coatings industry is a relatively mature industry, its growth rate typically paces that of the general economy. Like many other industries, growth has slowed in North America and Europe and has dramatically increased in Asia and South America as those economies have boomed. An estimate of the value of coatings used in each region is shown in Figure 1.1. The total value of the global coatings market was estimated to be approximately \$112 billion in 2014 (American Coatings Association and Chemquest Group, 2015).

Figure 1.2 summarizes the estimated value and volume of coating shipments in the United States for a recent 10-year period. The effect of the economic downturn in 2008–2009 is evident (Data from American Coatings Association and Chemquest Group, 2015).

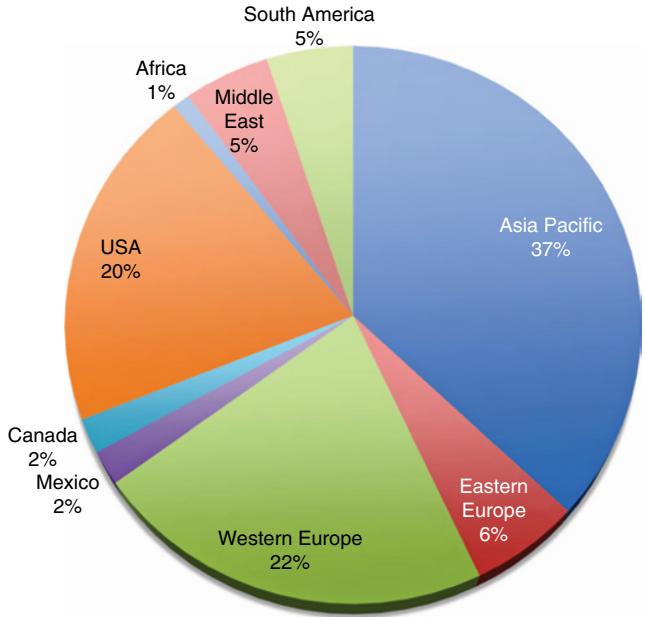


Figure 1.1 The value of coatings used in 2014. Source: Reproduced with permission of American Coatings Association.

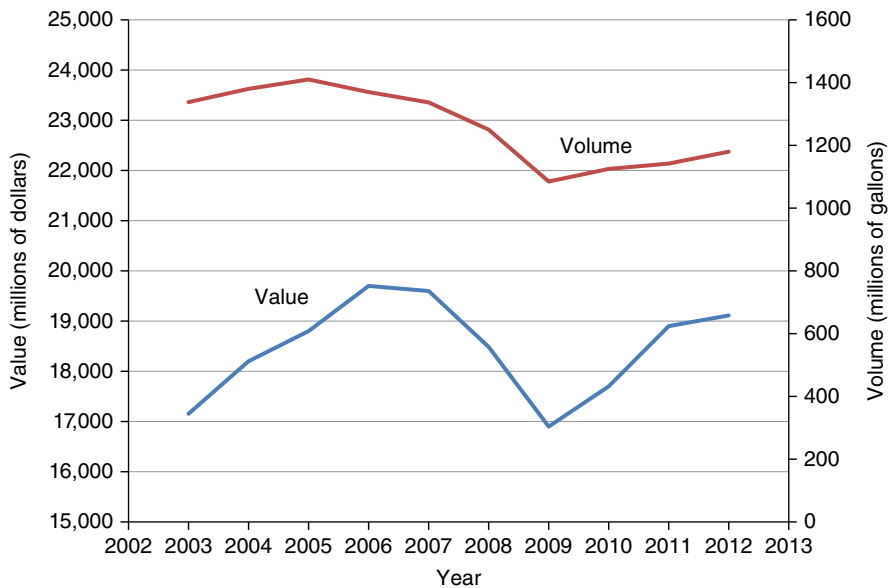


Figure 1.2 Ten-year trend in coating shipments in the United States (both gallons and dollar value). Source: Reproduced with permission of American Coatings Association.

1.2 TYPES OF COATINGS

Architectural coatings include paints and varnishes (transparent paints) used to decorate and protect buildings, outside and inside. They also include other paints and varnishes sold for use in the home and by small businesses for application to such things as cabinets and household furniture (not those sold to furniture factories). Architectural coatings are often called *trade sales paints*. They are sold directly to painting contractors and do-it-yourself users through paint stores and other retail outlets. In 2014 in the United States, architectural coatings accounted for about 60% of the total volume of coatings; however, the unit value of these coatings was lower than for the other categories, so they made up about 49% of the total value. This market is the least cyclical of the three categories. While the annual amount of new construction drops during recessions, the resulting decrease in paint requirements tends to be offset by increased repainting of older housing, furniture, and so forth during at least mild recessions. Latex-based coatings make up about 77% of architectural coatings. Interior paints are approximately 2/3 of all architectural coatings, exterior paints 23%, and stains 7%, with the remainder split among varnishes, clear coats, and others.

OEM coatings are applied in factories on products such as automobiles, appliances, magnet wire, aircraft, furniture, metal cans, and chewing gum wrappers—the list is almost endless. In 2014 in the United States, product coatings were about 29% of the volume and 31% of the value of all coatings. The volume of product coatings depends directly on the level of manufacturing activity. This category of the business is cyclical, varying with OEM cycles. Often, product coatings are custom designed for a particular customer's manufacturing conditions and performance requirements. The number of different types of products in this category is much larger than in the others; research and development (R&D) requirements are also high.

Special purpose coatings are industrial coatings that are applied outside a factory, along with a few miscellaneous coatings, such as coatings packed in aerosol containers. This category includes *refinish coatings* for cars and trucks that are applied outside the OEM factory (usually in body repair shops), *marine coatings* for ships (they are too big to fit into a factory), and striping on highways and parking lots. It also includes *maintenance paints* for steel bridges, storage tanks, chemical factories, and so forth. In 2012 in the United States, special purpose coatings made up about 11% of the total volume and 20% of the total value of all coatings, making them the most valuable class. Many of today's special purpose coatings are the product of sophisticated R&D, and investment in further improvements remains substantial.

Coatings are used for one or more of three reasons: (1) for decoration, (2) for protection, and/or (3) for some functional purpose. The low gloss paint on the ceiling of a room not only fills a decorative need but also has a function. It reflects and diffuses light to help provide even illumination. The coating on the outside of an automobile adds beauty to a car and also helps protect it from rusting. The coating on the inside of a beverage can have little or no decorative value, but it protects the beverage from the can. (Contact with metal affects flavor.) In some cases, the interior coating also protects the can from the beverage. (Some soft drinks are so acidic that they can dissolve the metal.) Other coatings reduce the growth of algae and barnacles on ship bottoms, protect optical fibers for telecommunications against abrasion and guide the light within the fiber, retard corrosion of bridges, protect wind turbine blades from erosion due to the impact of raindrops, and so on. While the public most commonly thinks of house paint when talking about coatings, all kinds of coatings are important throughout the economy, and they make essential contributions to most high-tech fields. As already mentioned, computer technology depends on microlithographic coatings to pattern the circuits in CPU and memory chips.

1.3 COMPOSITION OF COATINGS

Organic coatings are complex mixtures of chemical substances that can be grouped into four broad categories: (1) *binders*, (2) *volatile components*, (3) *pigments*, and (4) *additives*.

Binders are the materials that form the continuous film that adheres to the *substrate* (the surface being coated), bind together the other substances in the coating to form a film, and present an adequately hard outer surface. The binders of coatings within the scope of this book are organic polymers—some made via synthetic organic chemistry and some derived from plant oils. In some cases, these polymers are prepared and incorporated into the coating before application; in other cases, lower molecular weight organic materials (*monomers* or *oligomers*) are mixed with the other components of the coating, and final polymerization takes place after the coating has been applied. Binder polymers and their precursors are often called *resins*. The binder governs, to a large extent, the properties of the coating film. The major resin types used in coatings as percentages of the total are given in Table 1.1. These numbers should be taken as approximations as different coating suppliers name their resins somewhat differently, and some coating contain more than one resin type.

Volatile components are included in a large majority of coatings and are often referred to as *solvents*. They play a major role in the synthesis, mixing, and application of coatings. They are liquids that make the coating fluid enough for

Table 1.1 Breakdown of Major Resin Types for the US Coatings Market

Resin type	Percent
Acrylic	31
Vinyl	20
Urethane	14
Epoxy	8
Alkyd	7
Silane	5
Polyester	4
Amino	3
PVC	2
SBR	1
Phenolic	1
Cellulosic	1
Other	3

Source: Reproduced with permission of American Coatings Association.

application, and they evaporate during and after application. Until about 1935, almost all of the volatile components were low molecular weight organic compounds that dissolved the binder components. However, the term solvent has become potentially misleading because many coatings have been developed for which the binder components are not fully soluble in the volatile components but instead act as a carrier to reduce viscosity, but not fully solvate the binder. Because of the need to reduce the environmental impact of coating manufacture and application, a major continuing drive in the coatings field is to reduce the use of *volatile organic compounds* (VOCs) by making the coatings more highly concentrated (higher solids coatings), by using water as a major part of the volatile components (waterborne coatings), and by eliminating solvents altogether.

Vehicle is a commonly encountered term. It usually means the combination of the binder and the volatile components of a coating. Today, most coatings, including waterborne coatings, contain at least some volatile organic solvents. Exceptions are powder coatings, certain solventless liquid coatings (also called 100% solids coatings), radiation-curable coatings, and a small but growing segment of architectural coatings.

Pigments are finely divided, insoluble solid particles, ranging from a few tens of nanometers to a few hundred microns in size, that are dispersed in the vehicle and remain suspended in the binder after film formation. Generally, the primary purpose of pigments is to provide color and opacity to the coating film. Additionally, pigments can provide other functions, such as corrosion-inhibiting pigments, which enhance the corrosion protecting properties of the coatings. Pigments also play a major role in the application characteristics and the mechanical behavior of coatings.

While most coatings contain pigments, there are important types of coatings that contain little or no pigment, commonly called *clear coats*, or just *clears*. Clear coats for automobiles and transparent varnishes are examples. *Coating solids* typically refer to the proportion of binder and pigment and are the part of the paint that remains after the volatile components have left the coating. Pigments are distinct from dyes, which are typically soluble in their binder and/or solvent and exist as individual molecules in that vehicle. Dyes are rarely used in the types of coatings discussed in this book.

Additives are materials that are included in small quantities to modify some property of the coating. Examples are catalysts for polymerization reactions, light and heat stabilizers, rheology modifiers, defoamers, and wetting agents.

1.4 COATING HISTORY

The chemistry of most coatings used today bears little resemblance to the coatings used prior to the industrial revolution. For centuries coatings were based on naturally occurring oils and pigments. 40000 years ago ochre was processed for use as a pigment in Africa (Rosso et al., 2016). Cave paintings in northern Spain date from over 40000 years ago and contain depictions of animals and people. While their true purpose is impossible to ascertain, the paintings demonstrate that even in prehistoric times people were using coatings to decorate their surroundings and to convey information to others.

In Asia, a traditional coating made from urushiol, the resin from a native tree, has been used since at least 1200 B.C. to produce beautiful clear lacquers for art objects. Egg yolk was often used as the binder for paintings in the West until the fourteenth or fifteenth century, when certain plant oils, such as linseed (also known as flax) and walnut oils, were introduced to protect and beautify wood. Those oils were also used as the binder for many of the great oil paintings made by famous artists such as Michelangelo, and they continue to be favored by many artists today. During the nineteenth and early twentieth centuries, most architectural coatings employed linseed oil as the binder.

Early pigments were made from ground bones or charcoal and other minerals such as iron oxide, ochre, and calcium carbonate. Simple chemical reactions were later used to produce other pigments such as lead white (lead carbonate) and red lead (lead oxide). More chromatic pigments such as ultramarine blue were rare and expensive for centuries owing to their limited supply.

These simple binders and pigments formed the basis for almost all coatings up until the twentieth century when an explosion in our knowledge of synthetic organic chemistry multiplied the number of binders, pigments, and additives that were used in coatings. Naturally sourced binders

gave way to nitrocellulose lacquers and later enamels based on synthetic polymers. Other organic and synthetic inorganic pigments displaced some, but not all, of the naturally occurring pigments. For example, white lead carbonate gave way to titanium dioxide due to TiO_2 's superior *hiding* and reduced toxicity; and highly chromatic red pigments based on quinacridone chemistry were developed to provide colors that were previously difficult to achieve. *Hiding* refers to the capability of a coating to screen or hide the substrate from view, which is generally desirable from both aesthetic and protective standpoints.

Most people's interaction with coatings occurs when they paint the walls of their house or refinish an old piece of furniture; and they likely believe that coatings have changed little over the course of their lives. In many ways their thoughts are justified, as the process of painting with a brush has changed little over the past 100 years. However, as shown previously, advances in chemistry have resulted in dramatic changes in the formulation of paints. In addition, since 1965 the reduction of VOCs has been a major driving force because of the detrimental effect of VOCs on air quality. Coatings have been second only to the gasoline–automobile complex as a source of VOC pollutants responsible for excess ozone in the air of many cities on many days of the year. This situation has resulted in increasingly stringent regulatory controls on such emissions. The drive to reduce VOC emissions has also been fueled by the rising cost of organic solvents. Other important factors have also accelerated the rate of change in coatings. In particular, the increasing concern about toxic hazards has led to the need to change many raw materials that were traditionally used in coatings.

1.5 COMMERCIAL CONSIDERATIONS

The person who selects the components from which to make a coating is a *formulator*, and the overall composition he or she designs is called a *formulation*. Throughout history, formulators have been trying to understand the underlying scientific principles that control the performance of coatings. Most coating systems are so complex that our understanding of them today is still limited. Real progress has been made, but the formulator's art is still a

critical element in developing high performance coatings. Demands on suppliers of coatings to develop new and better coatings are accelerating. Therefore, time is now too limited to permit traditional trial-and-error formulation. Understanding the basic scientific principles can help a formulator design better coatings more quickly. In the chapters ahead, we present, to as great an extent as present knowledge permits, the current understanding of the scientific principles involved in coatings science.

We also identify areas in which our basic understanding remains inadequate and discuss approaches to more efficient and effective formulation despite inadequate understanding. In some cases, in which no hypotheses have been published to explain certain phenomena, we offer speculations. Such speculations are based on our understanding of related phenomena and on our cumulative experience acquired over several decades in the field. We recognize the risk that speculation tends to increase in scientific stature with passing time and may even be cited as evidence or adopted as an experimentally supported hypothesis. It is our intent, rather, that such speculations promote the advancement of coatings science and technology by stimulating discussion that leads to experimentation designed to disprove or support the speculative proposal. We believe that the latter purpose outweighs the former risk, and we endeavor to identify the speculative proposals as such.

Cost is an essential consideration in formulation. Novice formulators are inclined to think that the best coating is the one that will last the longest time without any change in properties, but such a coating may be very expensive and unable to compete with a less expensive coating, which provides adequate performance for particular application. Furthermore, it is seldom possible to maximize all of the performance characteristics of a coating in one formulation. Some of the desirable properties are antagonistic with others; formulators must balance many performance variables while keeping costs as low as possible.

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Rosso, D. E., et al., *PLoS ONE*, **2016**, *11(11)*, e0164793.

Polymerization and Film Formation

This chapter introduces basic concepts of polymer chemistry and film formation with particular emphasis on aspects related to organic coatings. Many excellent books (Sperling (2001), Odian (2004d), Billmeyer (2007), Young (2014), Young and Lovell (2001), and Fried (2014), among others) provide more comprehensive coverage.

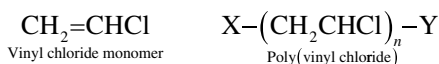
2.1 POLYMERS

A polymer is a substance composed of large molecules. Some authors reserve the term *polymer* to describe a substance and use the term *macromolecule* for the molecules making up the substance. This usage distinguishes between the material and the molecules but is not common in the coatings field. We use the term polymer for both meanings. Depending on the context, the term refers to either the molecules or the substance. The structure of polymers is a multiple repetition of units (mers) derived from molecules of relatively low molecular weight (MW) (monomers). (The more rigorous designation of MW is *molar mass*, but we use MW because it is much more commonly used in the coatings field.)

There is disagreement about how high the MW has to be for a material to qualify as a polymer. Some people refer to materials with MWs as low as 1 000 as polymers; others insist that only materials with MWs over 10 000 (or even 50 000) qualify. The term *oligomer*, meaning “few mers,” is often used for materials having MWs of a few hundred to a few thousand. This additional term does not help the definition problem much because there is no clear-cut boundary between an oligomer and a polymer, but the term can be useful because it provides a name with which most can agree for materials containing 2 to about 20 mers.

Polymers occur widely in nature; *biopolymers* are produced by living organisms. Examples are proteins, starch, cellulose, and silk. In the coatings field, we are concerned mainly with synthetic polymers, although some chemically modified biopolymers are also used.

Synthetic polymers and oligomers are prepared by *polymerization*, a sequence of chemical reactions in which small molecules are joined by covalent bonds. A polymer made from a single monomer is called a *homopolymer*. If it is made from a combination of monomers, it is often, but not always, called a *copolymer*. An example of a homopolymer is provided by the polymerization of vinyl chloride:



In this example, the $-(\text{CH}_2\text{CHCl})-$ repeating unit is the mer, and n represents the number of mers joined together in the molecule. X and Y represent terminal groups on the ends of the chain of mers.

Polymers are described by the chemical compositions of their monomers. In addition, they can be synthesized in various structures (*topologies*) (Krol and Chmielarz, 2014). Three topologies are especially important in coatings:

- When the mers are linked in chains, the polymers are called *linear polymers*, a term that is potentially misleading because the large molecules seldom form a straight line, but rather twist and coil. In linear copolymers, the different monomers may be distributed more or less at random throughout the chain (*random copolymers*), they may tend to alternate (*alternating copolymers*), or they may be separated into groups of the same monomer (*block copolymers*).

- If there are forks in the chains, the polymers are called *branched* polymers. A polymer chain of one type of monomer having polymer branches of a different monomer is called a *graft copolymer*. *Comb* and *brush polymers* have a large number of branches.
- A third topology results from the bonding of chains with each other at several sites to form *cross-linked*, or *network*, polymers, also called *gels*. These are branched polymers where the branches are covalently bound to other molecules, so the mass of polymer consists mainly of a single, interconnected molecule.

Other topologies, such as *dendritic* and *hyperbranched* polymers, are gaining importance in coatings.

Reactions that join polymer or oligomer molecules together are called *cross-linking reactions*. Polymers and oligomers that can undergo such reactions are frequently called *thermosetting* polymers. Some confusion can result because the term *thermosetting* is applied not only to polymers that cross-link when heated but also to those that can cross-link at ambient temperature or even below. A polymer that does not undergo cross-linking reactions is called a *thermoplastic polymer*, because it becomes plastic (softens) when heated.

Polymers can also be formed from mers that contain multiple H-bonding sites, in which case the mers are held together by H-bonds rather than by covalent bonds. Such polymers are called *supramolecular* polymers, which are of particular interest when the H-bonding sites, are four-centered owing to greatly enhanced strength relative to three-center H-bonds (Brunsveld et al., 1999). Coatings compositions in which multicenter H-bonds complement covalent cross-links can enhance coatings properties owing to thermal reversibility of the H-bonds, as observed for polyurethanes (Chapter 12). Unlike covalent bonds, H-bonds are readily broken and readily reestablished.

Another term commonly, but loosely, used in the coatings field is *resin*. This term overlaps the meanings of polymer and oligomer. Historically, the term meant hard, brittle materials derived from tree exudates, such as rosin, dammar, and elemi. A variety of these naturally occurring resins were used since prehistoric times to make coatings. In the nineteenth and early twentieth centuries, such resins were dissolved in drying oils to make *varnishes* (Section 14.3.2). The first entirely synthetic polymers used in coatings were phenol-formaldehyde polymers (Section 13.6), which replaced naturally occurring resins in many applications. Accordingly, they were called *phenol-formaldehyde resins* or *phenolic* resins. As more synthetic products were developed to replace naturally occurring resins, these products were also called resins.

When words do not have precise meanings, it is important to understand the context in which they are placed. Commonly, it is assumed, without much thought, that

information that has been learned about high MW polymers is also applicable to low MW polymers or oligomers, because all are often called polymers. Many characteristics, however, depend on MW. While much of the information available from studies of high MW polymers can be useful in the coatings field, it must be used with caution, because the resins used in making coatings are commonly low MW polymers or oligomers, even though they are frequently called polymers. In the next set of subsections, we describe some of the key characteristics of synthetic polymers and oligomers.

2.1.1 Molecular Weight (MW)

For most pure organic compounds, the concept of MW is straightforward—each compound has a MW. For synthetic polymers, however, the situation is more complex. All methods of synthesis lead to mixtures of molecules with different numbers of mers and, therefore, with different MWs. Even relatively simple thermoplastic homopolymers, such as polystyrene or poly(vinyl chloride), contain molecules with hundreds of different chain lengths. With copolymers, the number of different molecules present is much larger. There is a distribution of MWs in a synthetic polymer; accordingly, MWs can be defined only by a statistical calculation. In the simplest cases, the distribution of the number of molecules of each MW resembles a skewed Gaussian distribution, but in other cases, the distribution may be quite complex. While many types of average MW can be calculated, the two most widely used are number and weight average MWs.

Number average MW (\bar{M}_n) is the MW average based on summing the products of the numbers of molecules and their MWs and dividing by the sum of the number of molecules in the sample. Mathematically, it is expressed by Eq. 2.1, where M_1 , M_2 , and M_i are the MWs of the first, second, and i th species, respectively, and the N values are the numbers of molecules of each species present:

$$\bar{M}_n = \frac{\sum N_i M_i + N_2 M_2 + \dots}{\sum N_1 + N_2 + \dots} = \frac{\sum_i N_i M_i}{\sum_i N_i} \quad (2.1)$$

$$\bar{P}_n = \frac{\sum_i N_i P_i}{\sum_i N_i} \quad (2.2)$$

A similar equation (Eq. 2.2) represents the *number average degree of polymerization* \bar{P}_n , where P is the number of mers in a molecule and P_i is the number of mers in the i th polymer. For homopolymers, $\bar{M}_n = \bar{P}_n$ times the MW of each mer; for copolymers, a weighted average MW of the mers is used. The differing weights of end groups can

be neglected in calculating \bar{M}_n/\bar{M}_w of high polymers, but not of oligomers, for which the effect can be appreciable.

Weight average MW (\bar{M}_w) is defined by Eq. 2.3, in which w_1 , w_2 , and w_i are the weights of molecules of species 1, 2, and i th; since $w_i = N_i M_i$, \bar{M}_w can also be calculated from the numbers of molecules of the different species, as shown in the equation. *Weight average degree of polymerization* \bar{P}_w is defined by analogous equations:

$$\bar{M}_w = \frac{w_1 M_1 + w_2 M_2 + \dots}{w_1 + w_2 + \dots} = \frac{\sum_i w_i M_i}{\sum_i w_i} = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i} \quad (2.3)$$

Higher-order MWs such as M_z and M_{z+1} give additional weight to the larger molecules. M_v correlates with solution viscosity of many polymers.

Figure 2.1 shows an idealized plot of weight fraction of molecules of each MW as a function of degree of polymerization for oligomers made from the same monomer by three different processes (Hill and Wicks, 1982). In relatively simple distributions of MWs, the value of \bar{P}_n is at, or near, the peak of the weight fraction distribution curve. \bar{M}_w and \bar{P}_w are always larger than \bar{M}_n and \bar{P}_n .

The breadth of the MW distribution can have an important effect on the properties of a polymer and is often critical to achieving satisfactory performance of a coating. The ratio \bar{M}_w/\bar{M}_n is widely used as an index of the breadth of distribution. In the case of high MW polymers, $\bar{M}_w/\bar{M}_n = \bar{P}_w/\bar{P}_n$, but in the case of oligomers, differences in

end groups can be significant and affect the equality of the ratios. These ratios are called *polydispersity* (PD), or sometimes, *polydispersity index* (PDI). We use the symbols \bar{M}_w/\bar{M}_n and \bar{P}_w/\bar{P}_n . The ratios provide a convenient way to compare the MW distributions of different polymers. However, one must be cautious in the use of a single value to describe a possibly complex distribution. As shown in Figures 2.1 and 2.2, synthetic polymers commonly have broad distributions of MWs. As \bar{M}_w/\bar{M}_n increases, the fractions of polymer at the extremes above and below the number average MW increase. Even the oligomer with a number average of 12 mers and with $\bar{M}_w/\bar{M}_n = 1.07$ has substantial numbers of molecules containing 7–18 mers, and a polymer with a more typical $\bar{M}_w/\bar{M}_n = 3$ has molecules spanning several orders of magnitude of MW.

\bar{M}_n is the MW of most importance for relating stoichiometric ratios of reactants and for comparing certain physical properties. \bar{M}_w often proves more useful than \bar{M}_n when considering the relationship between MW and many physical properties of polymers, including some of the properties that are crucial to coating performance. M_z and even M_{z+1} provide useful correlations with certain film properties in some thermoset coatings.

The classical ways of measuring \bar{M}_w and \bar{M}_n are difficult and are beyond the scope of this book; Elias (1984) is but one of many books that describe them. In practice, most scientists in the coatings field use *gel permeation chromatography* (GPC), more properly called *size exclusion chromatography* (SEC), to measure MWs. In this convenient

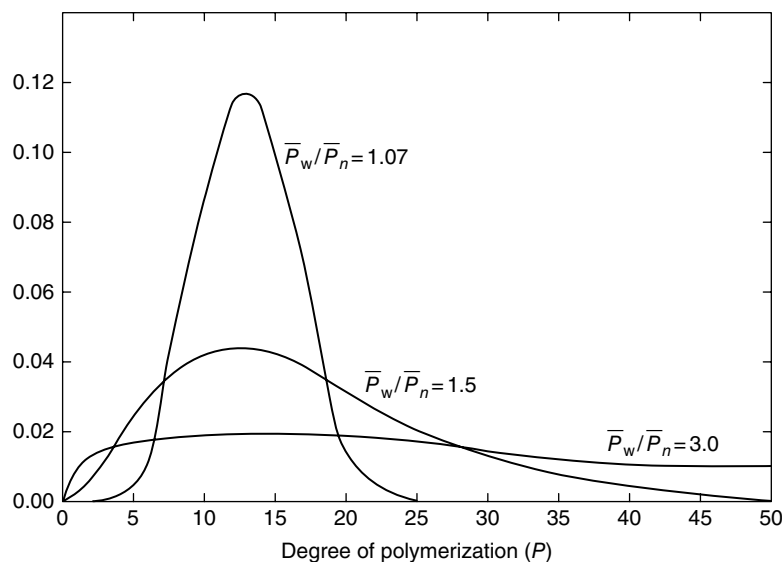


Figure 2.1 Degree of polymerization distribution plots calculated for three types of chain-growth polymers. $\bar{P}_w/\bar{P}_n = 1.07$ is for an ideal anionic polymerization, \bar{P}_w/\bar{P}_n is 1.5 for an ideal free radical polymerization with termination by combination, and \bar{P}_w/\bar{P}_n is 3.0 for a typical free radical polymerization. \bar{P}_n is 12 for all plots, and \bar{P}_w is 12.84, 18, and 36, respectively. Source: Hill and Wicks (1982). Reproduced with permission of Elsevier.

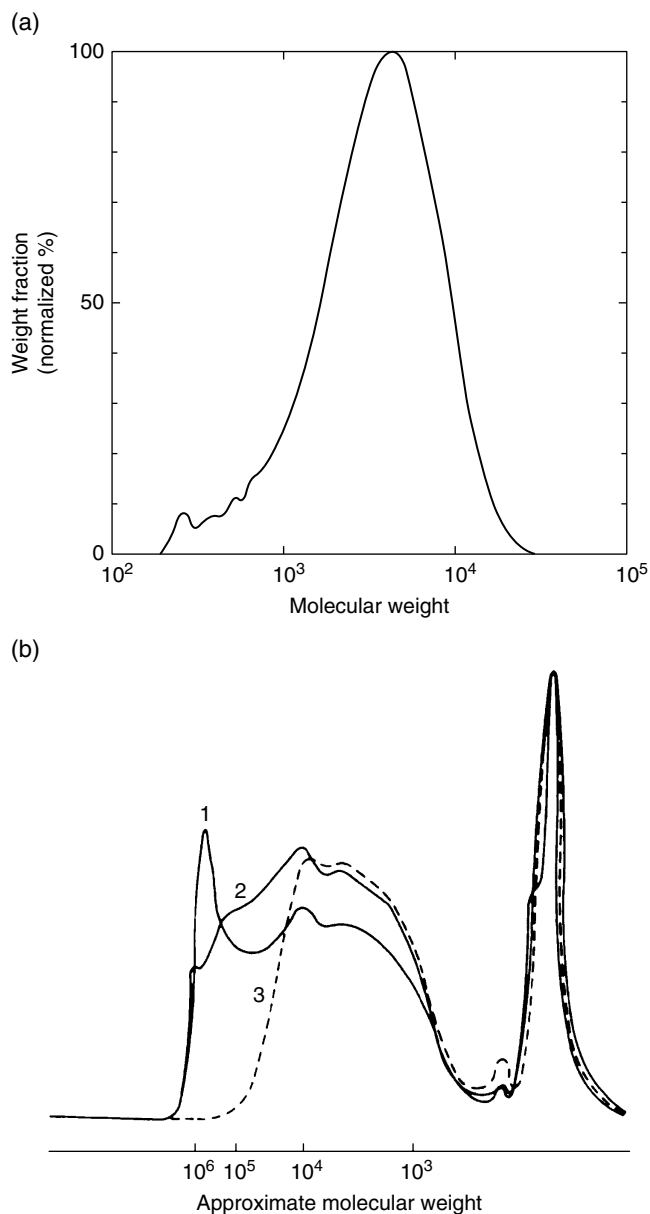


Figure 2.2 (a) Molecular weight distribution of a typical polyester resin. Source: Sullivan et al. (1990) Reproduced with permission of American Coatings Association. (b) Molecular weight distributions of three alkyd resins, as measured by GPC with a UV detector. Source: Kumanotani et al. (1984). Reproduced with permission of Marcel Dekker Inc.

method, a dilute solution of an oligomer or a polymer is pumped at high pressure through a series of columns containing porous gels. The molecules are “sorted” by sizes, wherein the largest ones elute first and the smaller ones, which are slowed by entering and leaving more of the gel pores, elute later. The concentration of polymer in the solvent is analyzed as it leaves the column and is plotted as a function of time. A computer program compares the plot to

plots of standard polymers of known MWs and calculates \bar{M}_n , \bar{M}_w , M_z , and M_{z+1} of the entire polymer sample. The results appear precise, but they may not be accurate; errors of +10% are common, and much larger errors are possible. Errors can result because the MW is not measured directly. Rather, the size of the polymer molecules in solution is measured, and the calculations are based on differences in detector response to different compositions. Despite its inaccuracy, GPC is a standard tool, especially valuable for comparing polymers of similar structure. Instrumentation is steadily improving.

The \bar{M}_n of oligomers can be accurately measured by colligative methods, such as freezing point depression and vapor pressure osmometry. However, the accuracy decreases as MW increases, and colligative methods are of little use above $\bar{M}_n = 50\,000$. Mass spectroscopic methods are available that can accurately measure the MWs of individual molecules in oligomers, and even in fairly high polymers (Section 10.2 gives examples).

Some polymers and oligomers have MW distributions approaching the idealized distributions shown in Figure 2.1, as illustrated by the GPC trace of a polyester oligomer in Figure 2.2a. However, many polymers used in coatings have complex distribution patterns as exemplified by the alkyd resins in Figure 2.2b. The \bar{M}_w and \bar{M}_n can be calculated for the entire trace or for portions of complex traces. But, such PD numbers must be used with caution for complex traces.

The MW of resins is an important factor affecting the viscosity of coatings made with solutions of the resins: generally, the higher the MW, the higher the viscosity. The MW of oligomers used in higher solids coatings is especially critical. It is often desirable to prepare oligomers with as narrow a range of MW as possible, in order to minimize the proportions of very low and very high MW molecules. The low MW fraction is generally undesirable from the standpoint of film properties, whereas the high MW fraction increases the viscosity of a resin solution disproportionately. However, alkyd resins having broad, complex MW distributions often perform better than alkyds with similar compositions having less broad distributions (Kumanotani et al., 1984).

MW is often a critical factor controlling the strength of films that are not cross-linked. In general, the higher the MW, the higher the tensile strength of such films, at least up to a point. The acrylic copolymer in automotive acrylic lacquers must have an \bar{M}_w greater than about 75 000 for acceptable film properties, but less than 100 000 for acceptable application properties. For other lacquers the required MWs depend on polymer composition and application methods. Film property considerations favor using high MW polymers in formulating solution coatings, but viscosity considerations favor low MWs. As is often the case in coatings, compromises are needed.

An important advantage of many waterborne coatings is that MW of the polymer generally does not directly affect viscosity, since the polymers are dispersed rather than dissolved in the solvent.

2.1.2 Morphology and Glass Transition Temperature, T_g

Morphology is the study of the physical forms of materials. Like MW, morphology is more complex with polymers than with smaller molecules. Pure small molecules generally solidify to crystals if the temperature is sufficiently low. In contrast, few synthetic polymers crystallize completely, and many do not crystallize at all. Non-crystalline materials that appear to be solids are called *amorphous solids*. There are at least two reasons that synthetic polymers are at least partly amorphous. In general, synthetic polymers are not pure compounds, so it is difficult to achieve the completely regular structure characteristic of a crystalline material. In addition, the molecules are so large that the probability of complete crystallization is low. Part of a molecule can associate with a part of a different molecule or with another part of the same molecule, reducing the probability of pure crystal formation. However, small crystalline domains are common in synthetic polymers; polymers with fairly regular structures, usually homopolymers, are most likely to crystallize partially. In these crystalline domains, fairly long segments of molecules associate with each other in a regular way. The remaining parts of the same molecules are unable to fit together regularly and remain amorphous. While polymers used in fibers and films (e.g., polyethylene and nylon) are often partly crystalline, polymers used in coating applications are, with few exceptions, amorphous.

An important difference between crystalline and amorphous materials is shown in Figure 2.3a and b, which schematically compare the changes in specific volume of these materials with temperature. In the case of a pure crystalline material (Figure 2.3a), as temperature increases, initially there is a slow increase in specific volume, owing to increasing vibrations of the atoms and molecules. Then, at a specific temperature, the substance melts. The melting point T_m is the lowest temperature at which the vibrational forces pushing molecules apart exceed the attractive forces holding them together in crystals. With almost all substances, the molten compound occupies more volume at the same temperature than the crystals; because the molecules are freer to move in a molten compound, they “bounce” their neighbors out of the way, leading to an abrupt increase in specific volume at T_m . Above T_m , the specific volume of a liquid slowly increases with further increase in temperature. Water is a notable exception to this behavior—what might be the consequences if ice was denser than water?

Amorphous materials behave differently, as shown in Figure 2.3b. Starting from a low temperature, there is a slow increase in specific volume as temperature increases, but there is no temperature at which an abrupt change in volume occurs because there is no melting point. Rather, there is a temperature at which there is a change in the rate of increase of specific volume with temperature. Above that temperature, the thermal expansion coefficient is larger than below it. This change of slope is not a phase change; it is a second-order transition, that is, there is a discontinuity in a plot of the *derivative of volume change* as a function of temperature. The temperature at which it occurs is called the *glass transition temperature* (T_g). T_g is properly defined as the temperature at which there is an increase in the thermal expansion coefficient. By comparison, T_m is a

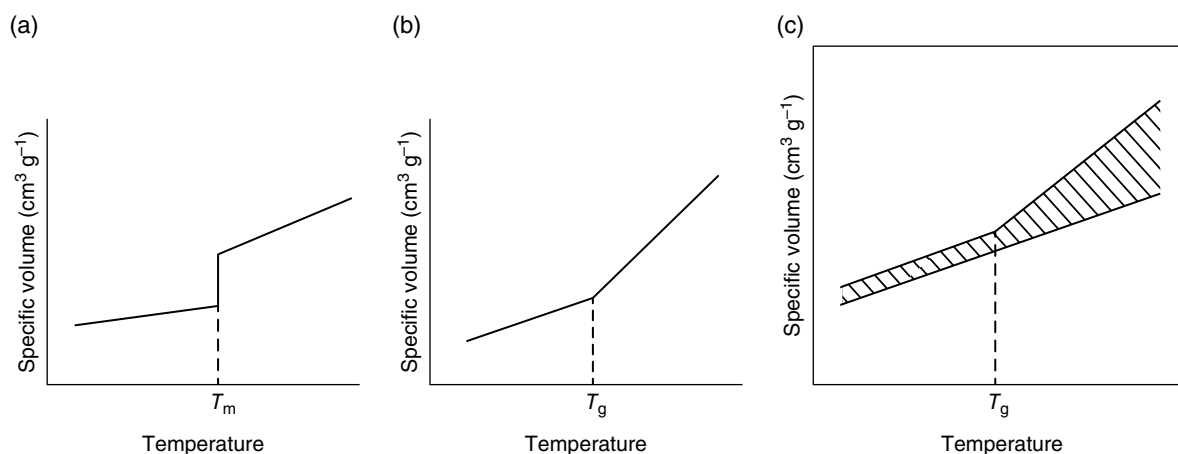


Figure 2.3 Specific volume as a function of temperature (a) for a crystalline material and (b) for an amorphous material; (c) shows free volume within an amorphous material as a function of temperature. Units of specific volume are volume per mass (usually cubic centimeter per gram). Source: Hill and Wicks (1982). Reproduced with permission of Elsevier.

first-order transition, that is, there is a discontinuity in change of volume as a function of temperature, corresponding to the solid–liquid phase change. Unfortunately, T_g is often improperly defined as the temperature below which a material is brittle and above which it is flexible. While there are many cases when this is true, there are other cases when this definition is misleading (Section 4.2). Perhaps, part of the reason for the misunderstanding is the connotation of the word *glass*, which we associate with a brittle material. Like all amorphous materials, glasses undergo a second-order transition. In fact, the phenomenon was first observed in the study of glasses—hence, the name *glass transition temperature*. The idea has proliferated that T_g is a phenomenon associated only with polymers. This is not true. Many small molecules can be supercooled without crystallization to form amorphous glasses that have a T_g . For example, the T_g of *m*-xylene is 125 K (Wicks, 1986). The T_g is always lower than T_m . Partially crystalline polymers show both a T_m and a T_g (Chapter 4).

What is physically happening at T_g ? As an amorphous material is heated, atoms in the molecules vibrate with increasing energy, colliding with neighbors and shoving molecules apart for very short periods of time. At T_g , a few of the short-lived “holes” between the molecules become large enough such that an adjacent molecule or a segment of a polymer molecule can fit between two molecules. Thus, T_g can be considered the lowest temperature at which segments of polymer molecules can move with facility in cooperation with neighboring segments. The increase of the coefficient of thermal expansion above T_g results from the greater degree of freedom available to the molecule segments. The larger volume between molecules gives more degrees of freedom, so the same increase in temperature gives a greater increase in volume. As temperature rises, specific volume increases, but there is no more material—just the same material occupying more space. What is in this “extra” volume? Nothing. It is called *free volume*, represented by the hatched area in Figure 2.3c. The molecular motions involved can be detected by spectroscopic techniques, such as solid-state nuclear magnetic resonance (NMR), and change as polymers are heated through T_g (Dickinson et al., 1988; Mathias and Colletti, 1989).

While it is difficult to overemphasize the importance of the concepts of T_g and free volume in coatings science, our understanding of these parameters and our ability to measure them are limited. Salez et al. (2015) describe recent progress toward theoretical understanding, but according to Philip Anderson (a Nobel Prize winner in solid-state physics), “the deepest and most interesting unsolved problem in solid-state physics is probably the glass transition” (Salez et al., 2015). Coatings scientists who do not fully understand T_g are in good company.

T_g values of a material that are measured by different methods may not agree with each other by 20°C or even

higher. Obviously, one must be careful in comparing T_g values of different materials to be sure they are based on consistent test methods. The classical method of measuring T_g is *dilatometry* (measurement of specific volume as a function of temperature). Nowadays, T_g is usually measured as described in Section 4.5 by *differential scanning calorimetry* (DSC), by *dynamic mechanical analysis* (DMA), or by *thermal mechanical analysis* (TMA). Roe (1987) and Mengqiu and Xin (2015) introduce these and other methods. The measured T_g depends on the measurement method and the conditions under which the measurement was made. Heating rate is an important variable. The faster the rate of heating during the determination, the higher the apparent T_g . When free volume is small, the rate of movement of molecules or segments is slow. If the rate of heating is slow, there is more time for movement and, hence, the expansion, and the measured T_g is lower.

Some scientists argue that T_g is not a real thermodynamic parameter. They point out that if the determination of specific volume were done at a slow enough heating rate, no transition would be observed and that rather than two straight lines, as shown in Figure 2.3c, there would be a smooth curve. Despite this controversy, T_g is a very useful concept and is well understood in qualitative terms. Relationships between polymer structure and T_g are understood well enough that it is often possible to make reasonable predictions of T_g from knowledge of composition and \bar{M}_n . Beyond that, knowing the T_g tells a lot about the film properties expected of a polymer. Important factors affecting the T_g of thermoplastic polymers include the following:

1. *Number average MW.* T_g increases with increasing \bar{M}_n , approaching a constant value at \bar{M}_n in the range of 25 000–75 000, depending on the polymer structure. It is logical that T_g is related to \bar{M}_n because decreasing \bar{M}_n results in an increasing proportion of chain ends to chain middles, since chain ends have more freedom of movement than the middles. The relationship of T_g to \bar{M}_n is approximated by Eq. 2.4, where T_{g^∞} is the T_g at infinite MW and A is a constant (T_g is in Kelvin).

$$T_g = T_{g^\infty} - \frac{A}{\bar{M}_n} \quad (2.4)$$

2. *Polymer backbone flexibility.* T_g is affected by the ease of rotation about bonds in the polymer backbone. For example, the siloxane bond, Si—O—Si, rotates easily; the T_g of poly(dimethylsiloxane) is 146 K (–127°C) (Andrews and Grulke, 1999). Aliphatic polyethers, such as poly(ethylene oxide), $-(\text{CH}_2-\text{CH}_2-\text{O})_n-$, also have low T_g , generally in the range of 158–233 K, because there is considerable ease of rotation around the ether bond. The T_g of polyethylene varies because,

although we commonly think of polyethylene as being just chains of methylene groups, the backbone is actually substituted to varying degrees with alkyl side chains, such as ethyl groups. Also, most grades of polyethylene are partially crystalline; only the amorphous areas show a T_g . However, all would agree that the T_g of a long linear aliphatic chain is low, perhaps less than 200 K. The presence of rigid aromatic or cycloaliphatic rings in the polymer backbone substantially increases T_g .

3. *Side chains.* Pendant aromatic rings also lead to high T_g , for example, 373 K for polystyrene, since ease of rotation is decreased. Similarly, pendant methyl groups and carboxymethyl groups increase T_g . For example, T_g increases from 281 K for poly(methyl acrylate) to 378 K for poly(methyl methacrylate), which has both methyl and carboxymethyl groups on alternate carbons of the chain. If the side chains are several atoms long and flexible, T_g is reduced, for example, to 219 K for poly(*n*-butyl acrylate). However, if the side chain is short, bulky, and inflexible, it has less effect and, in some cases, raises T_g , for example, to 314 K for poly(*t*-butyl acrylate).

Care must be taken when comparing T_g values to be sure that the determinations have been carried out under consistent conditions and that the MWs are high enough to eliminate MW effects. Table 2.1 provides the T_g of high MW homopolymers of a group of acrylic and methacrylic esters, as well as other monomers often used as comonomers in polymers for coatings (Lesko and Sperry, 1997; Andrews and Grulke, 1999; Neumann et al., 2004).

Synthetic copolymers often have a disorderly distribution of mers within the chain, in which case, they are called *random copolymers*, although few of them are strictly random in the pure mathematical sense. Such copolymers have T_g values intermediate between those of the homopolymers. It is common to use the *Fox equation* (Eq. 2.5) to

estimate the T_g of “random” copolymers, where w_1, w_2, w_3 , and so on are the weight fractions of the various monomers in the copolymer and T_{g1}, T_{g2}, T_{g3} , and so on are the T_g (Kelvin) of their high MW homopolymers:

$$\frac{1}{T_{g(\text{copolymer})}} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} + \frac{w_3}{T_{g3}} + \dots \quad (2.5)$$

Somewhat better approximations can be calculated using a different mixing equation, 2.6, also devised by Fox, in which v_1, v_2, v_3 , and so on are the volume fractions of the various monomers in the copolymer; this equation is not widely used because some of the homopolymer densities needed to calculate v_1, v_2, v_3 , and so on are not readily available:

$$T_{g(\text{copolymer})} = v_1 T_{g1} + v_2 T_{g2} + v_3 T_{g3} + \dots \quad (2.6)$$

Gupta (1995) reports an extensive study on estimating the T_g of acrylic copolymers. He recommends the use of the van Krevelen equation, 2.7, for estimation of T_g , where M is the MW of the repeat unit and Y_g is a molar glass transition factor. Gupta’s values for the T_g of *n*-butyl methacrylate (10°C) and of 2-ethylhexyl acrylate (−63°C) vary considerably from the values given in Table 2.1, illustrating that different values are often found in the literature:

$$T_g = \frac{Y_g}{M} \quad (2.7)$$

Block copolymers sometimes have two or more distinct T_g s.

The T_g of cross-linked polymers is controlled by several factors and their interactions:

- T_g of the segments of polymer between the cross-links
- The cross-link density (XLD)

Table 2.1 Glass Transition Temperatures (°C) for Homopolymers of Various Monomers

Monomer	Methacrylate	Acrylate	Monomer	Methacrylate	Acrylate
Free acid	185	106	<i>n</i> -Tridecyl ^a		−46
Methyl	105	9	<i>iso</i> -Tridecyl		−39
Ethyl	65	−23	2-Hydroxyethyl	55	
Isopropyl	81	−8	2-Hydroxypropyl	73	
<i>n</i> -Butyl	20	−54	Other monomers		
Isobutyl	53	−40	Styrene	100	
<i>t</i> -Butyl	114	74	Vinyl acetate	29	
<i>n</i> -Hexyl	−5	−57	Vinyl chloride	81	
2-Ethylhexyl	−10	−50	Vinylidene chloride	−18	
<i>iso</i> -Decyl		−30			

^a Mixture of C_{12–14}.

- The presence of dangling ends
- The presence of cyclic segments (Stutz et al., 1990)
- The structure of the cross-links when XLD is high

While generalized equations showing the relationships of the first four of these factors with T_g have been developed, the complex relationships are not fully understood. The T_g of the polymer segments between cross-links is governed by the chemical structures of the resin and the cross-linking agent, by the ratio of these components, and by the extent of the cross-linking reaction. The factors discussed in connection with thermoplastic polymers apply in terms of their effects on the T_g of the chain segments between cross-links. Since cross-links restrict segmental mobility, T_g increases as XLD increases. On the other hand, T_g decreases with an increasing proportion of dangling ends—that is, chain segments that are connected to the cross-linked network at only one end.

Solutions of polymer in solvent and of solvent in polymer have T_g values intermediate between the T_g of the polymer and that of the solvent. The T_g of solutions increases with increasing polymer concentration. When the weight fraction of solvent w_s is less than about 0.2, a simple mixing equation (Eq. 2.8) gives reasonable correlation between experimental and predicted results (Ferry, 1980). Over a wider range of concentrations, this simple equation gives poor correlations:

$$T_{g(\text{solution})} = T_{g(\text{polymer})} - kw_s \quad (2.8)$$

For solutions of oligomeric *n*-butyl methacrylate in *m*-xylene (Wicks et al., 1986), Eq. 2.9 gave a good fit between observed and predicted data over the whole range from pure solvent to solvent-free oligomer. Here, w_s and w_o are weight fractions and T_{gs} and T_{go} are the T_g of the solvent and the oligomer, respectively. While Eq. 2.1 accurately describes a limited number of oligomer and polymer solutions, its generality is not fully established:

$$\frac{1}{T_{g(\text{solution})}} = \frac{w_s}{T_{gs}} + \frac{w_o}{T_{go}} + Kw_s w_o \quad (2.9)$$

T_g is discussed further in Section 4.2 in the context of film mechanical properties.

2.2 POLYMERIZATION

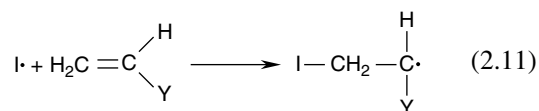
In coatings there are two major classes of polymerization reactions: *chain-growth* and *step-growth*. The mechanisms and kinetics of both classes have been extensively studied. The common denominator of chain-growth polymerization is that reactions are chain reactions. Frequently,

chain-growth polymerization is called *addition polymerization*, but this terminology is inadequate. While all chain-growth polymerizations involve addition reactions, not all addition polymerizations involve chain-growth reactions—some are step-growth reactions.

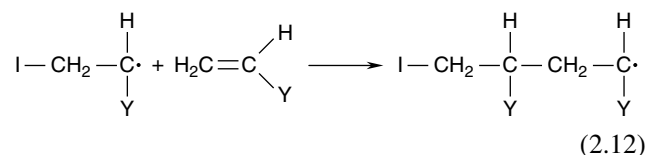
2.2.1 Chain-Growth Polymerization

Chain-growth polymerization, initiated by free radicals, is the most commonly used chain-growth polymerization for making vinyl copolymers (often acrylics) for coatings. Odian (2004a) provides an extensive review of the topic, particularly the kinetics of the reactions. Free radical chain-growth polymerizations of most interest to coating applications are *solution polymerization* (Chapter 8) and *emulsion polymerization* (Chapter 9). A related process of importance in coatings is the autoxidation involved in cross-linking drying oils and drying oil derivatives (Chapters 14 and 15). The discussion in this section applies to solution polymerization, although many of the principles are apply to emulsion polymerization as well.

Three types of chemical reactions—*initiation*, *propagation*, and *termination*—are always involved in chain-growth polymerization; and a fourth, *chain transfer*, often plays a significant role. Initiation occurs when an *initiator* (I) reacts to form an initiating free radical (I·) (Eq. 2.10), which, in turn, adds rapidly to a monomer molecule to form a second free radical (Eq. 2.11):

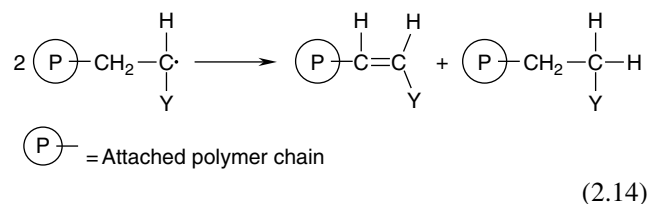
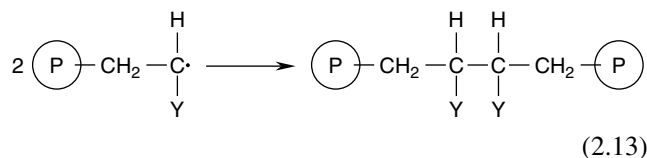


The polymer chain grows by the propagation reaction, in which the monomer free radical adds to a second monomer molecule to extend the chain and form a new free radical (Eq. 2.12):

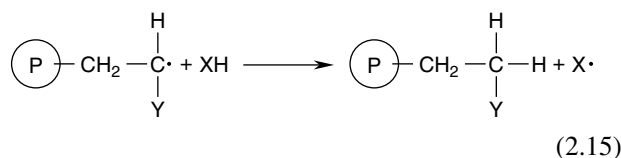


Propagation reactions are very fast—so fast that a chain with hundreds of mers can grow in a fraction of a second. At any moment, the concentrations of monomer and polymer greatly exceed the concentration of growing polymer molecules, which is about 10^{-6} ML⁻¹. (Exceptions are controlled radical polymerizations (CRP), Section 2.2.1.1.)

The final stage is termination of the growing chain. Two common types of termination reactions are *combination* (Eq. 2.13) and *disproportionation* (Eq. 2.14). In most free radical initiated polymerizations, the rate of propagation (Eq. 2.12) is faster than the rate of initiation, which is limited by the rate of Eq. 2.10:



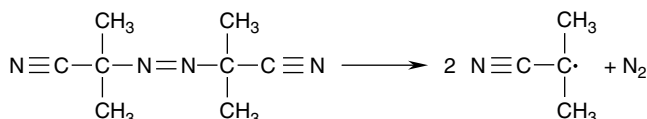
Side reactions also occur; among the most important are chain transfer reactions, in which the free radical on the end of the propagating polymer chain abstracts a hydrogen atom from some substance X—H present in the polymerization reaction mixture (Eq. 2.15):



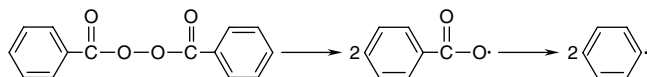
The net effect of chain transfer is to terminate the growing chain while generating a free radical, which may initiate a second chain. X—H may be a solvent, a monomer, a molecule of polymer, or a *chain transfer agent*, a reactant that is added to the polymerization reactants to cause chain transfer. When chain transfer is to a solvent or a chain transfer agent, MW is reduced. When chain transfer is to a polymer molecule, growth of one chain stops, but a branch grows on the polymer molecule; the result is a higher \bar{M}_w/\bar{M}_n .

Note that the structures of the propagating polymer chains show substitution on alternate carbon atoms. This structure results from the favored addition of free radicals to the CH₂ end of most monomer molecules, corresponding to *head-to-tail addition*. Head-to-tail addition predominates in almost all monomers, but a small fraction of *head-to-head addition* also occurs. The result is a polymer with most of the substitution on alternating carbons in the chain, but with a few chain segments having substitution on adjacent carbons. The effect of a small fraction of head-to-head structure is generally negligible, but it sometimes has significant consequences with regard to exterior durability and thermal stability.

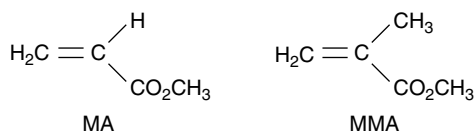
Initiators, sometimes, incorrectly called catalysts, are used in low concentration (usually in the range of 0.5–4 wt% (weight percent), but sometimes higher when low MW is desired). A variety of free radical sources has been used. Two common classes of initiators are azo compounds, such as azobisisobutyronitrile (AIBN) and peroxides such as benzoyl peroxide (BPO) or *t*-amyl peracetate. AIBN is fairly stable at 0°C but decomposes relatively rapidly when heated at 70–100°C to generate free radicals. A substantial fraction of the resulting radicals initiate polymerization, although some combine to form a coupling product. The half-life of AIBN is about 5 h at 70°C and about 7 min at 100°C:



BPO decomposes at similar temperatures—its half-life is about 20 min at 100°C. The reactive benzoyloxy free radical generated can initiate polymerization; also, it can dissociate (rapidly at higher temperatures, such as 130°C) to yield a very highly reactive phenyl free radical and CO₂:



A range of monomers is capable of propagating a radical initiated chain reaction. Most are alkenes having an electron-withdrawing group; methyl acrylate (MA) and methyl methacrylate (MMA) are important examples:



Copolymers containing a preponderance of acrylic and methacrylic ester monomers are called *acrylic polymers*, or often, just *acrylics*. They are extensively used in coatings. Control of MW and MW distribution is critical in preparing polymers for coatings. There are three major factors that affect MW when using the same monomer, initiator, and solvent:

1. *Initiator concentration.* Higher initiator concentration reduces the MW. When the initiator concentration is higher, more initiating free radicals are generated to react with the same total amount of monomer. More chains are initiated and terminated, thereby reducing both the \bar{M}_n and \bar{M}_w of the resulting polymer.
2. *Temperature.* At higher temperatures, more initiator is converted into initiating free radicals in a given time,

thereby increasing the concentration of growing chains and the probability of termination. As with increasing initiator concentration, the result is lower \bar{M}_n and \bar{M}_w .

3. *Monomer concentration.* Higher monomer concentration increases \bar{M}_n and \bar{M}_w . The highest MW is obtained in a solvent-free reaction mixture. With the same concentration of growing free radical ends, a higher monomer concentration increases the probability of chain-growth relative to termination.

To the extent that any of these factors change during a polymerization process, \bar{M}_n and \bar{M}_w of the polymer molecules also change. The usual result is a broader MW distribution. Changes in monomers also change MW distribution. Consider the difference between MA and MMA. Since the free radicals at the ends of growing chains of poly(methyl methacrylate) (PMMA) are sterically hindered, termination by combination is impeded, and termination by disproportionation predominates. On the other hand, with poly(methyl acrylate) (MA), a major fraction of the termination reactions occur by combination. Theoretical calculations show that for high MW polymers, the lowest \bar{M}_w/\bar{M}_n attainable with termination by combination is 1.5, while the minimum with termination by disproportionation is 2.0, corresponding to higher PD. In actual polymerization processes, \bar{M}_w/\bar{M}_n is usually higher, although with very high initiator concentrations, polydispersities tend to be lower. No basic studies have been reported to account for the low PDs with high initiator concentrations.

Chain transfer to polymer must also be considered. This reaction occurs to a degree in the polymerization of MMA but is more important in the polymerization of MA. The tertiary hydrogen on the carbon to which the carboxymethyl group is attached in PMA is more susceptible to abstraction by free radicals than any other hydrogen in PMA or PMMA. When this H atom is abstracted, growth of the original chain is terminated, and a new free radical on a PMA chain is formed. This free radical can now add to a monomer molecule, initiating growth of a branch on the polymer molecule. The result is a polymer containing branched molecules and having a larger \bar{M}_w/\bar{M}_n than predicted for ideal linear polymerization. In extreme cases, chain transfer to polymer results in very broad MW distributions and, ultimately, to formation of gel particles through cross-linking. The preceding discussion supposes that chain transfer to polymer occurs mainly between different molecules. Another possibility is that the growing radical may abstract a nearby hydrogen from the same molecule, a process called *back biting*, as discussed further in Chapter 8.

Branching can also result from the abstraction of hydrogen atoms from a polymer chain by initiating free radicals. Phenyl free radicals from high temperature decomposition of BPO are so reactive that they will abstract

almost any aliphatic hydrogen, leading to substantial branching. Accordingly, if branching is desired, initiation using BPO at high temperature (e.g., 130°C) is a good choice. However, in most cases, minimization of branching is more desirable. In these cases, azo initiators, such as AIBN, or aliphatic peroxy initiators are preferred over BPO.

Since initiator residues remain attached to the polymer chain ends, they may affect polymer properties. For high MW polymers, the effect on most properties is usually negligible. Exterior durability (Chapter 5) is an exception. However, for oligomers, the effect may be appreciable, particularly on exterior durability (Section 8.2.1).

MW and MW distribution also depend on solvent structure. For example, substituting xylene for toluene, with other variables constant, leads to a decrease in MW. Since each xylene molecule has six abstractable benzylic hydrogen atoms, while toluene has only three, the probability of chain transfer is higher for xylene and \bar{M}_n decreases.

To prepare a low MW polymer or oligomer, one can add a compound that undergoes facile hydrogen abstraction as a chain transfer agent. If the hydrogen atoms are readily abstracted, the addition of even relatively low concentrations of a chain transfer agent can lead to a substantial reduction in MW. Mercaptans (RSH) are widely used as chain transfer agents owing to the readily abstractable SH hydrogen atom, as well as the high initiating capability of the resulting thiyl radical.

Other variables affecting MW and MW distribution are the decomposition rate of the initiator and the reactivity of the resulting free radicals. To achieve a low \bar{M}_w/\bar{M}_n , concentrations of reactants must be kept as constant as possible throughout the polymerization. It is undesirable to simply charge all of the monomers, solvents, and initiators into a reactor and heat the mass to start the reaction. This procedure is sometimes used in small-scale laboratory reactions, but almost never in production. At best, it yields a high \bar{M}_w/\bar{M}_n ; at worst, the reaction may run violently out of control, because free radical polymerizations are highly exothermic. Instead, one charges some of the solvent into the reactor, heats to reaction temperature, and then adds monomer, solvent, and solutions of initiator to the reactor at rates such that the monomer and initiator concentrations are kept as constant as possible. Adding monomer at a rate that maintains a constant temperature leads to a fairly constant monomer concentration. The appropriate rate of addition of the initiator solution can be calculated from the rate of its decomposition at the temperature being used. Maintaining constant solvent concentration is more complex since as the polymerization proceeds, polymer is accumulating; in a sense, the polymer becomes a part of the "solvent" for the polymerization. Solvent is added at a decreasing rate so that the other concentrations stay as constant as possible. Perfect control is not possible, but careful

attention to details makes an important difference in the \bar{M}_w/\bar{M}_n of the polymer produced.

Bulk copolymerization of mixtures of unsaturated monomers further complicates the situation. The rates of reaction involved in the various addition reactions depend on the structures of the monomers. If the rate constants for all of the possible reactions were the same, the monomers would react randomly and the average composition of molecules of substantial length would all be the same. However, the rate constants are not equal. If polymerization is carried out by putting all of the reactants in a flask and heating, the first molecules formed would contain more than proportional amounts of the most reactive monomer, and the last molecules formed would have an excess of the least reactive monomer. This situation is usually undesirable. Such effects have been extensively studied, and equations have been developed to predict the results with different monomer combinations. (See Odian (2004a) for a detailed discussion of copolymerization.)

In actual practice, the problem is less complex, since reactions are not run in bulk. Rather, as mentioned earlier, monomers, solvent, and initiator solution are added gradually to the reaction mixture. If the additions are carefully controlled so that the rate of addition equals the rate of polymerization, copolymers having reasonably uniform composition corresponding to the feed ratio are obtained with most monomers. This procedure, called *monomer-starved conditions*, results in copolymerization under conditions in which the concentration of monomers is low and fairly constant. Further process refinements are possible by adding individual reactants or mixtures of reactants in two or three streams at different rates. Computer modeling of the processes can help achieve the desired results.

2.2.1.1 Living Polymerizations: Controlled Radical Polymerizations (CRP)

For several decades, considerable effort has been directed to the preparation of acrylic and other chain-growth (co) polymers with narrow MW distributions and controlled structures. Narrow MWD can only be accomplished when the rate of initiation is much faster than the rate of propagation and when the rates of termination reactions are slow, which corresponds to the opposite of the kinetics described in Section 2.2.1. Under these circumstances, almost all polymer chains start growing early in the process and grow at about the same rate under about the same conditions. In these processes the polymer chain ends often remain reactive even after all monomer has been consumed, in which case they are called *living polymers* (Darling et al., 2000).

Early living polymerizations included *anionic polymerizations* and *group transfer polymerizations* (Sogah et al., 1987; Webster, 2000). These methods require highly purified monomers and very dry conditions, as well as the

absence of proton donor (active hydrogen) groups such as —OH groups on the monomers. GTP can produce polymers with PDIs as low as 1.03; however, because of process costs, commercial use in coatings has been limited to specialty applications, such as pigment dispersants.

Attention has shifted to CRP. We prefer using CRP to the frequently used acronym CFRP for *controlled free radical polymerization*, since CFRP is also a common acronym for carbon fiber reinforced *plastics*.

Boyer et al. (2016) reviewed the history of CRP starting in 1982 by pioneers such as Otsu and Georges and their coworkers. Since then researchers have produced many thousands of papers and patents on the subject because of its great scientific interest and its enormous potential for diverse applications.

In general, CRP methods mediate the rates of propagation and termination by including some substance that reversibly bonds to the radical at the growing end of the polymer chain. By this means, it is possible to slow the propagation rate by many orders of magnitude, satisfying the kinetic requirements for living polymerization. Since these polymerizations are free radical processes, they are relatively insensitive to impurities, and they can be used to copolymerize monomers with proton donor (active hydrogen) groups. These methods enable the preparation of block, alternating block, sequence-controlled, and gradient copolymers by sequential addition of monomers; they can also be adapted to synthesize an enormous variety of linear, graft, and star polymers, copolymers, and *macromonomers* (polymerizable oligomers) from many of the common acrylic and styrenic monomers. The literature about CRP processes lacks consistency about how the processes are named. One possible classification follows:

1. *Stable free radical polymerization* (SFRP), also called *nitroxide-mediated polymerization* (NEM), in which polymerization is mediated by nitroxide compounds (Auschra et al., 2002). This method works well with monomers having hydroxyl functionality.
2. *Reversible addition–fragmentation chain transfer* (RAFT) polymerization, which involves mediation by certain dithioesters or xanthates (trithiocarbonates) (Perrier et al., 2004).
3. *Transition metal-mediated living radical polymerizations* (TMMLRP); several methods can be distinguished, although some authors lump them together. Here is a simple classification:

3a. *Atom transfer radical polymerization* (ATRP) where the mediator is a metal salt, often of copper, with a carefully chosen organic ligand and an organic halide that can undergo a redox reaction with the metal to trigger the polymerization (Matyjaszewski, 2012; Krol and Chmielarz, 2014; Boyer et al., 2016).