

Fourth Edition

# ORGANIC COATINGS

Science and Technology



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

WILEY



# Organic Coatings



# Organic Coatings Science and Technology

**Fourth Edition**

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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

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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.



## 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  $\mu\text{m}$ .

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.

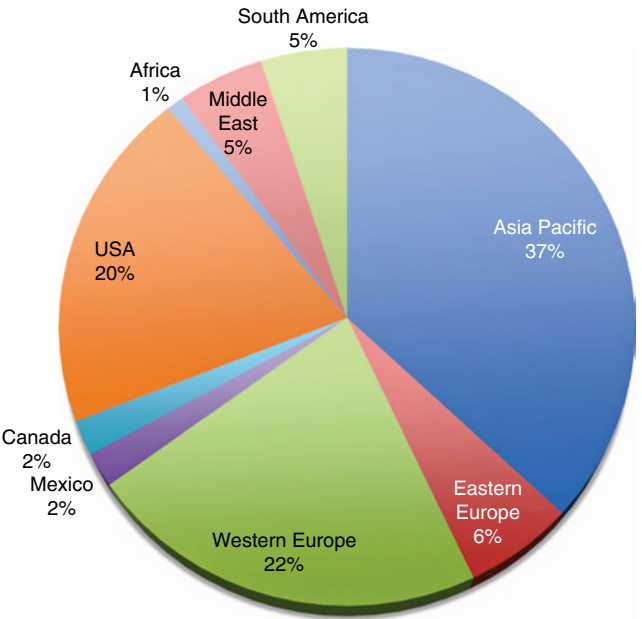
A confusing situation results from multiple meanings of the term *coating*. As a noun *coating* is used to describe both the material (usually a liquid) that is applied to a substrate and the resultant "dry" film. As a verb, *coating* means the process of application. Usually, the intended meaning of 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.

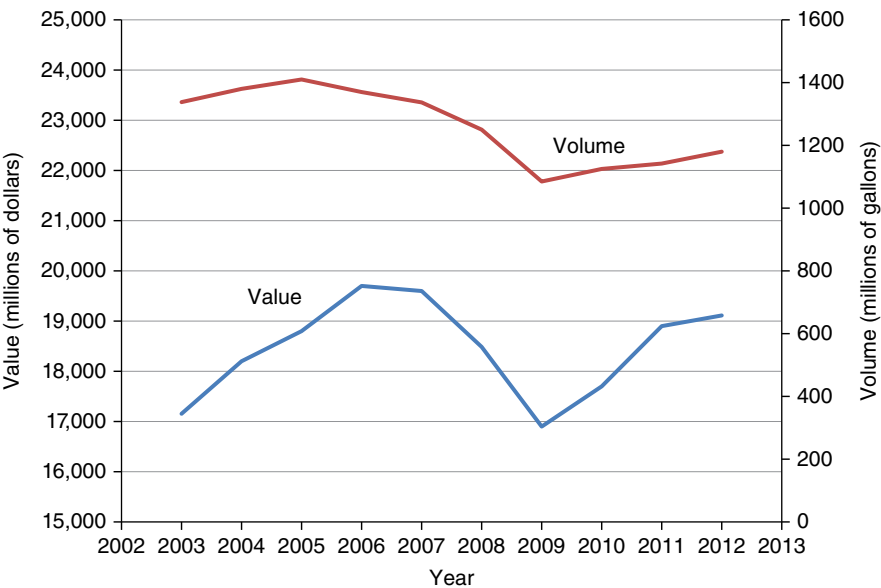
Because we are limiting the scope of this book to organic coatings that are historically associated with paints, we are also choosing not to cover important materials such as coatings applied to paper and fabrics, decals, laminates and cosmetics, and printing inks, even though one could argue that these 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  $\text{TiO}_2$ '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.

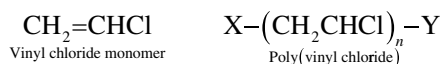
### 2.1 POLYMERS

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:

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

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

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:

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

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.

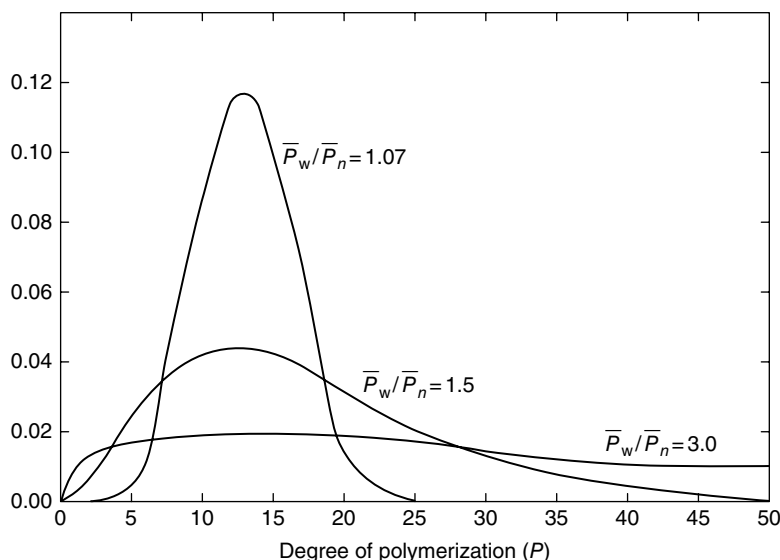
Figure 2.1 shows an idealized plot of weight fraction of molecules of each MW as a function of degree of polymerization for oligomers made from the same monomer by three different processes (Hill and Wicks, 1982). In relatively simple distributions of MWs, the value of  $\bar{P}_n$  is at, or near, the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

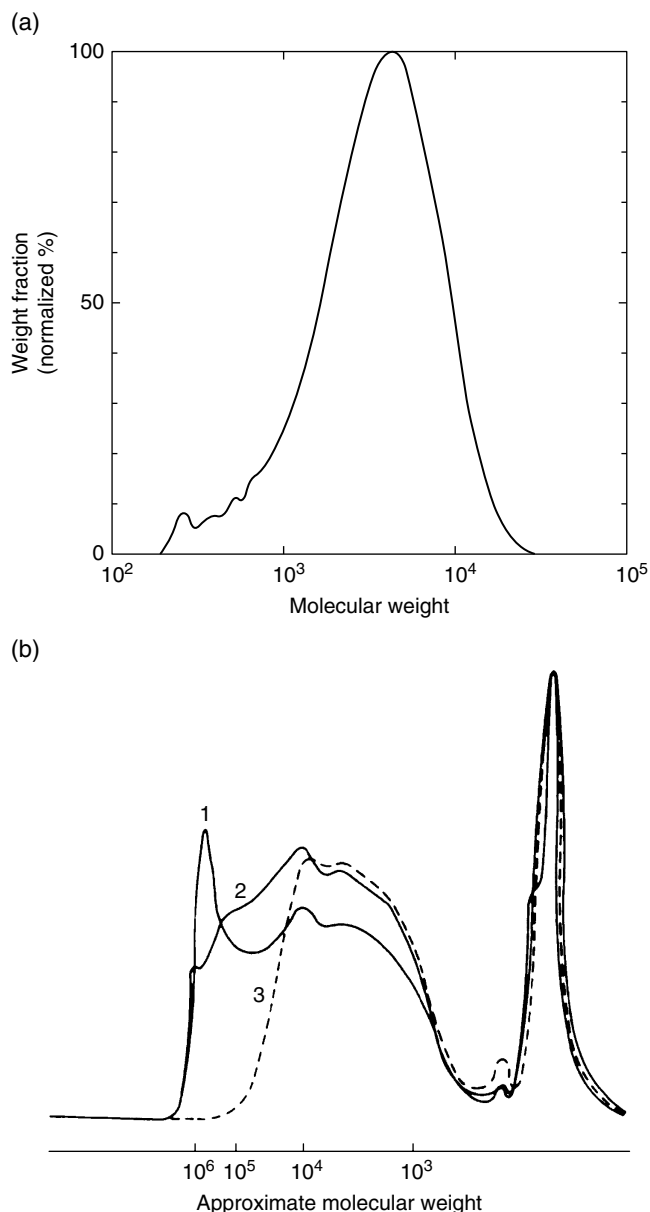
end groups can be significant and affect the equality of the ratios. These ratios are called *polydispersity* (PD), or sometimes, *polydispersity index* (PDI). We use the symbols  $\bar{M}_w/\bar{M}_n$  and  $\bar{P}_w/\bar{P}_n$ . The ratios provide a convenient way to compare the MW distributions of 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.

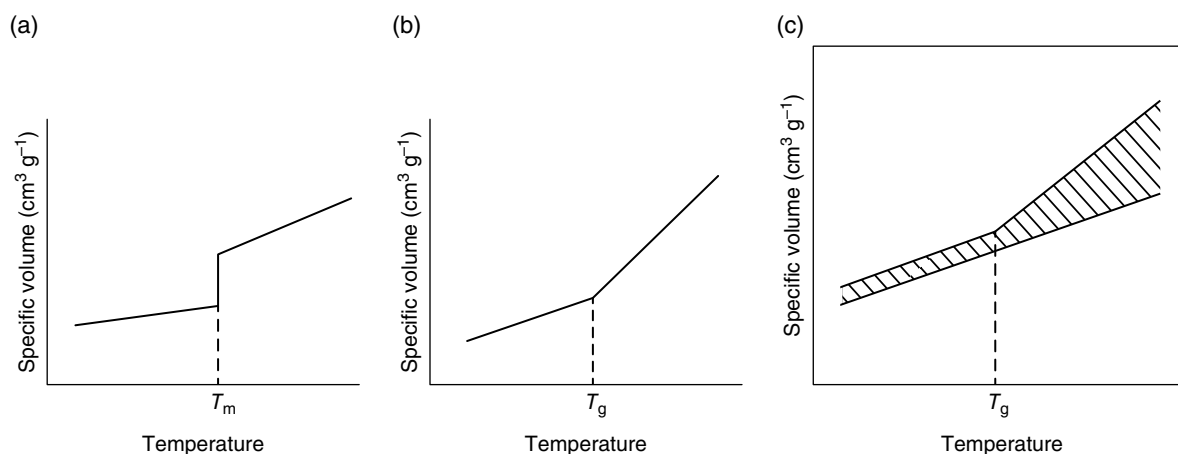
An important advantage of many waterborne coatings is that MW of the polymer generally does not directly affect viscosity, since the polymers are dispersed rather than dissolved in the solvent.

## 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  $T_{g\infty}$  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),  $-(CH_2-CH_2-O)_n-$ , 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 <sup>a</sup>		−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			

<sup>a</sup> Mixture of C<sub>12–14</sub>.

- 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

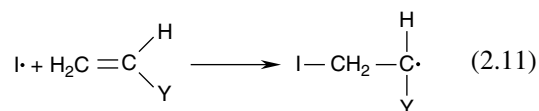
In coatings there are two major classes of polymerization reactions: *chain-growth* and *step-growth*. The mechanisms and kinetics of both classes have been extensively studied. The common denominator of chain-growth polymerization is that reactions are chain reactions. Frequently,

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.

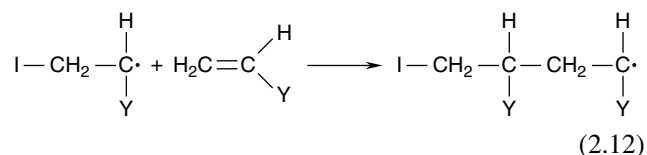
### 2.2.1 Chain-Growth Polymerization

*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):

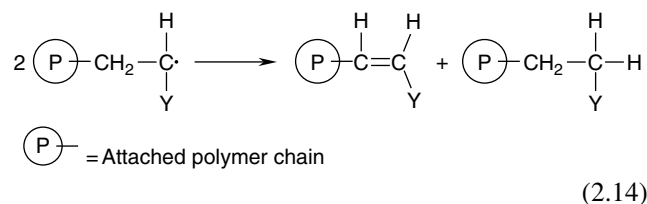
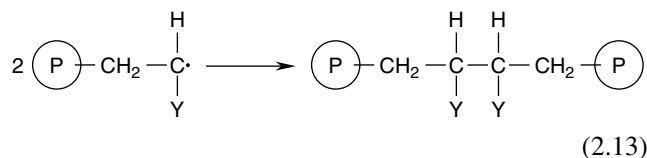


The polymer chain grows by the propagation reaction, in which the monomer free radical adds to a second monomer molecule to extend the chain and form a new free radical (Eq. 2.12):

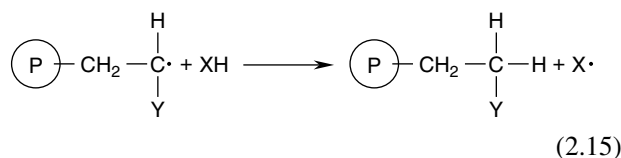


Propagation reactions are very fast—so fast that a chain with hundreds of mers can grow in a fraction of a second. At any moment, the concentrations of monomer and polymer greatly exceed the concentration of growing polymer molecules, which is about  $10^{-6}$  ML<sup>-1</sup>. (Exceptions are controlled 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:



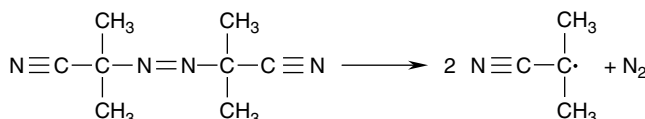
Side reactions also occur; among the most important are chain transfer reactions, in which the free radical on the end of the propagating polymer chain abstracts a hydrogen atom from some substance X—H present in the polymerization reaction mixture (Eq. 2.15):



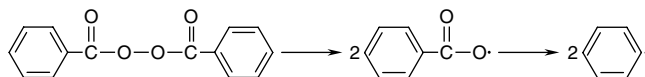
The net effect of chain transfer is to terminate the growing chain while generating a free radical, which may initiate a second chain. X—H may be a solvent, a monomer, a molecule of polymer, or a *chain transfer agent*, a reactant that is added to the polymerization reactants to cause chain transfer. 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 CH<sub>2</sub> 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.

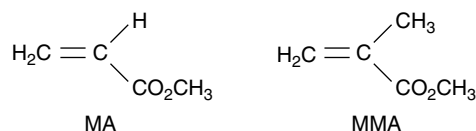
Initiators, sometimes, incorrectly called catalysts, are used in low concentration (usually in the range of 0.5–4 wt% (weight percent), but sometimes higher when low MW is desired). A variety of free radical sources has been used. Two common classes of initiators are azo compounds, such as azobisisobutyronitrile (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 CO<sub>2</sub>:



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).

3b. *Catalytic chain transfer polymerization (CCTP)*, which uses a conventional initiator, usually an azo type, in the presence of a chelated cobalt (or other) metal salt. CCTP is especially useful for preparing macromonomers having relatively low color (Chiefari et al., 2005; Smeets et al., 2012; Boyer et al., 2016).

Descriptions of CRP techniques are provided by Matyjaszewski (1999), Muller and Matyjaszewski (2009), and Lutz et al. (2014); Odian's (2004b) book includes a lengthy discussion about it. The subject has become so vast that not one book covers it all. Aspects of the subject have also been extensively reviewed, for example, by Boyer et al. (2016) and by Krol and Chmielarz (2014). The latter work emphasizes applications (realized and potential), including coatings. Journals and especially patents are rich with specific procedures for CRP synthesis of acrylic polymers having various structures. In some cases, the procedures are straightforward.

CRP development has largely been driven by applications in medical and biomedical technologies. In coatings, TMMLRP methods have been the focus of most researches. Block acrylic copolymers prepared by ATRP are useful aqueous pigment dispersants (White et al., 2002), as are graft copolymers made with CCTP (Viosscher and McIntyre, 2003). Krol and Chmielarz (2014) cite several more recent examples. CRP methods can be used in aqueous media, notably in emulsion polymerization. See Section 21.3.1 for further examples and discussion of the use of the copolymers in pigment dispersion. It is technically feasible to use CRP to synthesize desirable resins for large-scale uses such as automotive clear coats, where the technology is slowly making commercial inroads (Chapter 30).

Astonishing progress has been achieved in controlling polymer structures, but polymer chemists are still a long way from an answer to the chemists' prayer:

Oh Lord, I fall upon my knees,  
And pray that all my syntheses,  
Will not always be inferior,  
To those effected by bacteria.

## 2.2.2 Step-Growth Polymerization

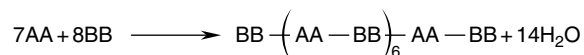
A second class of polymerization that is important in the coatings field is *step-growth polymerization*. As the name indicates, the polymer is built up a step at a time. The term *condensation polymerization* has been used for this process because early examples involved condensation reactions—reactions in which a small molecule by-product, such as water, is eliminated. While both terms are still used, *step-growth polymerization* is more appropriate because many step-growth polymerizations are not condensation reactions. Step-growth polymerization reactions are used in

two ways in coatings. One is to prepare resins for use as vehicles, and the other is for cross-linking after the coating has been applied to a substrate.

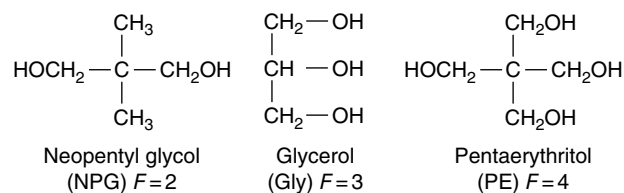
The formation of polyesters, which are discussed more broadly in Chapter 10, is used here to illustrate the principles involved. Of the many reactions that form esters, three are commonly used to prepare polymers and oligomers for coatings by step-growth polymerization: direct esterification of an acid with an alcohol, transesterification of an ester with an alcohol, and reaction of an anhydride with an alcohol. A fourth, less common, method is ring-opening polymerization of a lactone. The first two of these reactions proceed rapidly only at elevated temperature; and process temperatures of 200°C and higher are common.

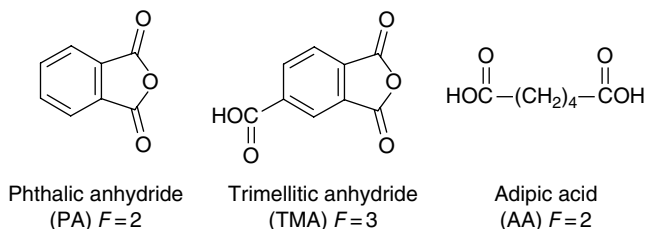
In order to form a polymer from two reactants, both must have two or more functional groups. When both reactants are difunctional, linear polymers form. High MW linear step-growth polymers are commonly used in fibers, films, and plastics. Most polyester resins used in coatings, however, have relatively low MWs and are branched, requiring that at least one reactant has at least three or more functional groups. After application of the coating, the terminal groups on the branch ends are reacted with a cross-linker to form the cured coating. Note that in this section, the terms *reactant* and *monomer* are used interchangeably.

When a difunctional acid (AA) reacts with a difunctional alcohol (BB) in a direct esterification reaction, the MW builds up gradually. Under ideal conditions, polymer chains averaging hundreds of mers per molecule can be made, but this can occur only if (a) the reactants AA and BB contain no monofunctional impurities, (b) the amounts of AA and BB are exactly equimolar, (c) the reaction is driven virtually to completion, and (d) side reactions are negligible. If one reactant is present in excess, terminal groups of the excess monomer predominate. The MW of the completely reacted system is progressively lower as the difference from equal equivalents is increased. For example, if 7 mol of dibasic acid are completely reacted with 8 mol of a dihydroxy compound (a diol), the *average* molecule will have terminal hydroxyl groups as shown in the following equation (here, for convenience, AA and BB represent both the reactants and the mers in the polymer):



Common monomers (reactants) are as follows:





The symbol  $F$  is used for the functionality of monomers, which is the number of reactive groups per molecule. The anhydride groups in PA and TMA count as two functional groups since they can form two ester groups during polymerization.

The average functionality, represented by  $\bar{F}$ , of a mixture of monomers containing equal equivalents of hydroxyl and carboxyl groups is calculated as follows:

$$\bar{F} = \frac{\text{total equivalents}}{\text{total moles}}$$

Most polyester resins for coatings are hydroxyl-functional and are made using monomer mixtures having excess hydroxyl groups. Since some of the hydroxyl groups, thereby, have no carboxyl groups to react with, the equation must be modified to reflect only the total number of equivalents that can react. In a resin having excess hydroxyl groups prepared from dicarboxylic acids, the total equivalents that can react correspond to twice the number of equivalents of carboxylic acid groups:

$$\bar{F} = \frac{\text{total equivalents that can react}}{\text{total moles}} = \frac{2(\text{equivalents of COOH})}{\text{total moles}}$$

A simple formulation for a polyester oligomer is given in Table 2.2.

An additional important consideration in designing resins is the functionality of the resin. To distinguish the functionality of the resin from that of the monomers and the monomer mixture, the symbol  $f$  is used. Since almost all coating polyester resins are made using some trifunctional and/or tetrafunctional monomers, a number average functionality  $\bar{f}_n$  is more appropriate:

**Table 2.2** Polyester Formulation

Component	Moles	Equivalents
Adipic acid	0.9	1.8
Phthalic anhydride	0.9	1.8
Neopentyl glycol	1.0	2.0
Glycerol	1.0	3.0
	3.8	8.6
$F = 8.6/3.8 = 1.89$		

$$\bar{f}_n = \frac{\text{number of functional groups in a sample}}{\text{number of molecules in the sample}}$$

The value of  $\bar{f}_n$  can be calculated from  $\bar{M}_n$  and the number of functional groups per sample weight obtained by analysis.

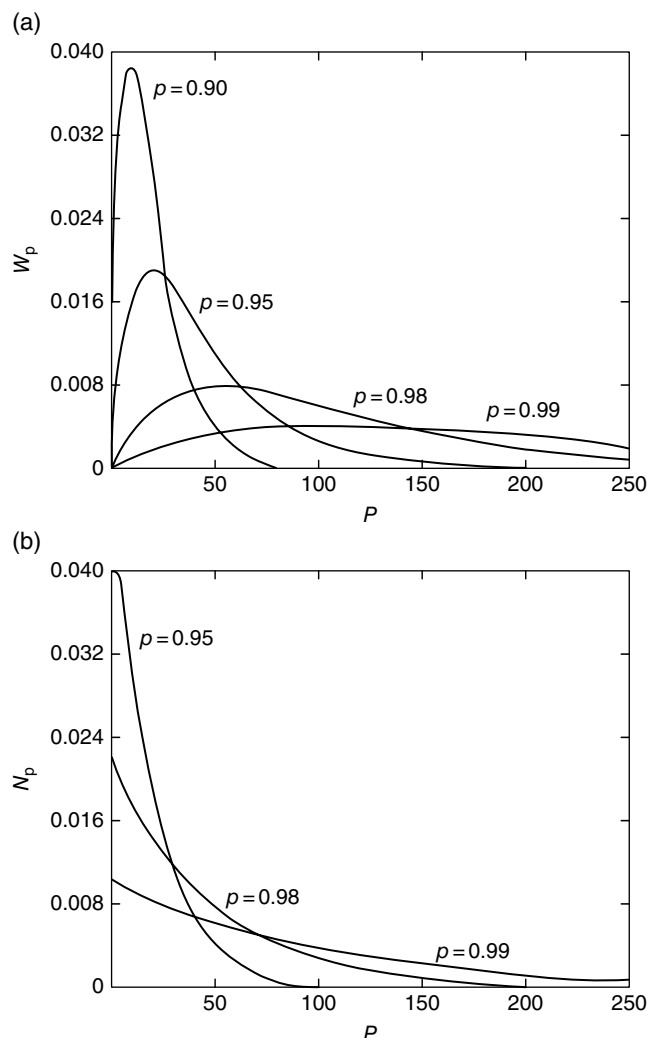
Esterification of a carboxylic acid with an alcohol is acid catalyzed. In the absence of a catalyst, the rate  $r$  is approximately of third order in reactants, as shown in Eq. 2.8, with one carboxyl group reacting with the alcohol and  $v$  second catalyzing the reaction. Since water is generally removed rapidly from the reaction mixture, it is reasonable to use Eq. 2.16, which disregards the reverse reaction:

$$r = k[\text{RCOOH}]^2[\text{R'OH}] \quad (2.16)$$

Because of the second-order dependence on acid concentration, the rate decreases precipitously as reaction proceeds. For example, polyesterification of equal moles of diethylene glycol with adipic acid at 160°C without a catalyst is 60% complete in 1 h, but requires 27 h to reach 94.5% conversion and would require years to reach 99.8% conversion (Flory, 1939). The reaction is accelerated by strong acid catalysts, but in many cases, conventional strong acids cause side reactions and discoloration. Therefore, the usual catalysts are organotin compounds, such as monobutyltin dioxide, or titanate esters. It has been shown that both the organotin compound and the carboxylic acid act as catalysts (Chang and Karalis, 1993).

The kinetics of ideal step-growth polyesterification for difunctional reactants can be analyzed in terms of  $p$ , the fractional extent of reaction;  $n_p$ , the number fraction of differing degrees of polymerization;  $P_n$ , the degree of polymerization; and  $w_p$ , the weight fraction of molecules. As  $p$  increases, the degree of polymerization builds up slowly at first—at  $p=0.5$  (corresponding to 50% conversion),  $\bar{P}_n$  is only 2. The  $\bar{P}_n$  is only 10 at  $p=0.9$ , and  $p=0.998$  is required to reach a  $\bar{P}_n$  of 500. Thus, with difunctional monomers, high MW can only be attained when the mole ratio of COOH/OH is 1.00 and when esterification is driven beyond  $p=0.99$ . This is difficult because of the decreasing reaction rate at high values of  $p$ . Note that, as shown in Figure 2.4a, the number of unreacted monomer molecules remains higher than that of any other single species in the reaction mixture, no matter how high  $p$  becomes. As shown in Figure 2.4b,  $\bar{P}_n$ , the peak of the  $P$  distribution curve, only reaches substantial values at high  $p$  values. In the case of high MW linear polymers, under ideal conditions, the  $\bar{M}_w/\bar{M}_n$  obtained in step-growth polymerizations is 2.





**Figure 2.4** (a) Weight fraction distribution  $w_p$  of molecules in a linear step-growth polymer for several extents of reaction  $p$ . (b) Number, or mole fraction, distribution  $n_p$ . Source: Odian (2004c) with permission.

## 2.3 FILM FORMATION

Most coatings are liquids having a viscosity appropriate for the application method, generally in the range of 0.05–1 Pa·s at high shear rates. After application, the liquid is converted to a “dry,” that is, solid film. In powder coatings, the powder is liquefied after application and then converted to a solid film. The chemical and physical changes that occur in these processes are called *film formation*, which critically determines the ultimate appearance and performance of the coating.

If the polymers of the applied coating were crystalline, there would be no difficulty in defining a solid film. The film would be solid if the temperature were below its freezing point; however, binders of coatings are almost always

amorphous, thereby having no melting point or sharp demarcation between a liquid and a solid. A useful definition of a solid film is that it is not significantly damaged under the pressures to which it is subjected during use. Thus, one can define whether a coating is a solid by stating the minimum viscosity required to resist flow sufficiently to satisfy a particular test requirement under a specified set of conditions. For example, it is reported that a film is *dry-to-touch* if its viscosity is greater than about  $10^3$  Pa·s (Burrell, 1962). However, if the definition of a solid is that the film resists *blocking*—that is, sticking together when two coated surfaces are put against each other for 2 s under a pressure of  $1.4 \text{ kg cm}^{-2}$  (20 psi)—the viscosity has to be greater than about  $10^7$  Pa·s.

For thermoplastic binders, we can use this information to predict polymer structures that could meet such tests. Using a simplified form (Eq. 2.17; in the equation  $T$  is in Kelvin) of the Williams–Landel–Ferry (WLF) equation (Section 3.4), using “universal constants” and assuming that the viscosity at  $T_g$  is  $10^{12}$  Pa·s, one can estimate the  $T_g$  of a binder required so that a film does not flow under some set of circumstances:

$$\ln \eta = 27.6 - \frac{40.2(T - T_g)}{51.6 + (T - T_g)} \quad (2.17)$$

Using Eq. 2.17, we can estimate the appropriate  $(T - T_g)$  value required for a film to be dry-to-touch, that is, to have a viscosity of  $10^3$  Pa·s. The calculated  $(T - T_g)$  value is  $54^\circ\text{C}$ , which corresponds to a  $T_g$  of  $-29^\circ\text{C}$  for a film to be dry-to-touch at temperature  $T$  of  $25^\circ\text{C}$ . The  $T_g$  calculated for block resistance (at  $1.4 \text{ kg cm}^{-2}$  for 2 s at  $25^\circ\text{C}$ , i.e., for a viscosity of  $10^7$  Pa·s) is  $4^\circ\text{C}$ . This is near the optimum  $T_g$  for many architectural paints. Because there is considerable variation in the WLF “universal constants,” these  $T_g$  values are not exact, but they can serve as a formulation guide. Since we have a reasonable idea of the relationships between structure and  $T_g$  (Section 2.1.2), we can approximate the requirements to make a binder with the viscosity necessary to pass a particular test. If the coating has to pass a test at a higher temperature than  $25^\circ\text{C}$ , the  $T_g$  of the binder must be higher, since the free volume dependence is on  $(T - T_g)$ . If the pressure to which the film is to be subjected is higher or the time under pressure is to be longer, the  $T_g$  must be higher.

### 2.3.1 Film Formation by Solvent Evaporation from Solutions of Thermoplastic Binders

Films can be formed in a variety of ways. One of the simplest methods is to dissolve a polymer in solvent(s) at a concentration needed for application requirements, apply

the coating, and allow the solvent to evaporate. Let us illustrate with a copolymer of vinyl chloride, vinyl acetate, and a hydroxyl-functional vinyl monomer with  $\bar{M}_n$  of 23 000 that is reported to give coatings having good mechanical properties without cross-linking (Mayer and Kaufman, 1984). The  $T_g$  of the copolymer is 79°C. A solution in methyl ethyl ketone (MEK) with a viscosity of 0.1 Pa·s required for spray application would have about 19 NVW (nonvolatile weight, i.e., weight percent solids) and about 12 NVV (nonvolatile volume, i.e., volume percent (vol%) solids). MEK has a high vapor pressure at room temperature and evaporates rapidly from a thin layer. In fact, a sizable fraction of the MEK evaporates from the atomized spray droplets between the time they leave the spray gun and reach the substrate. As solvent evaporates from a film, viscosity increases, and the film will be dry-to-touch soon after application. Also, in a short time, the coating will not block under the conditions mentioned previously. Nevertheless, if the film is formed at 25°C, the “dry” film contains several percent of retained solvent. Why?

In the first stage of solvent evaporation from a film, the rate of evaporation is essentially independent of the presence of the polymer. Evaporation rate depends on the vapor pressure of the solvent at the particular temperature, the ratio of surface area to volume, and the rate of air flow over the surface. However, as solvent evaporates, viscosity increases,  $T_g$  increases, free volume decreases, and the rate of loss of solvent is no longer dependent on its vapor pressure, but rather becomes limited by how rapidly solvent molecules can diffuse to the surface of a film. The solvent molecules must jump from one free-volume hole to another to reach the surface. As solvent loss continues,  $T_g$  increases, free volume decreases further, and solvent loss slows. If the film is formed at 25°C from a solution of a polymer that, when solvent free, has a  $T_g$  greater than 25°C (in this example, it is 79°C), the film retains considerable solvent even though it is a hard “dry” film. Solvent slowly leaves such a film, but it has been shown experimentally that 2–3% of solvent remains after several years at ambient temperature. To assure nearly complete removal of solvent in a reasonable period of time requires baking at a temperature significantly above the  $T_g$  of the solvent-free polymer. Solvent loss from films is discussed in more detail in Section 18.3.4.

### 2.3.2 Film Formation from Solutions of Thermosetting Resins

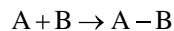
High MW thermoplastic polymers are required for good film properties, which, in turn, require high solvent levels (often on the order of 80–90 vol% solvent) to achieve the necessary viscosity for application. Considerably less solvent is needed for coatings based on solutions of lower MW thermosetting resins. After application, the solvent

evaporates, and chemical reactions occur resulting in polymerization and cross-linking, which imparts good film properties. A goal is to attain an optimal XLD in the film. Many combinations of chemical reactions are used in thermosetting coatings, as discussed in Chapters 8–17. A critical aspect of the design of a coating is the selection of components that provide required mechanical properties (Chapter 4). In this section, we discuss the general principles of cross-linking reactions.

A dilemma with thermosetting systems is the relationship between coating stability during storage and the time and temperature required to cure a film after application. Generally, it is desirable to be able to store a coating for many months, or even several years, without a significant increase in viscosity resulting from a reaction during the storage period. On the other hand, after application, one would like to have the cross-linking reactions proceed rapidly at the lowest possible temperature.

As formulations are shifted to higher solids to reduce volatile organic compound (VOC) emissions, there are higher concentrations of functional groups, resulting in greater difficulty in formulating storage stable coatings. The problem results not only from the presence of less solvent but also from the lower MWs and lower equivalent weights needed to achieve an acceptable XLD. Both factors increase the concentration of functional groups in a stored coating. Concentration of reactants in a film increases after application and evaporation of solvent, which increases reaction rates; but, since the MW is lower, more reactions must occur to achieve the desired cross-linked film properties.

What controls the rate of a reaction? We can consider this question broadly as a reaction between two groups, represented by the symbols A and B that react to form a cross-link A–B:



In the simplest cases, one can express the rate of reaction  $r$  of A and B by Eq. 2.10, where  $k$  is the rate constant for the reaction between A and B at a specified temperature, and [A] and [B] represent the concentration of the functional groups in terms of equivalents per liter. The rate constant is the reaction rate when  $[A] \times [B]$  equals 1 equiv.<sup>2</sup>L<sup>-2</sup>:

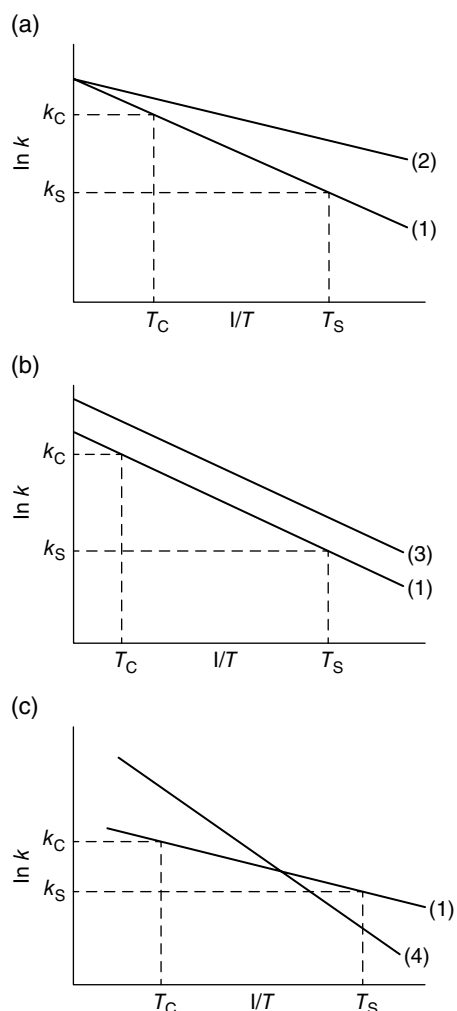
$$r = k[A][B] \quad (2.18)$$

To minimize the temperature required for curing while maintaining adequate storage stability, it is desirable to select cross-linking reactions for which the rate depends strongly on temperature. This dependence is reflected in the rate equation by the dependence of  $k$  on temperature. It is commonly taught in introductory organic chemistry

classes that rate constants double with each 10°C rise in temperature. That generalization is true for only a limited number of reactions within a narrow temperature range near room temperature. A better estimate, but still an estimate, of the temperature dependence of  $k$  is given by the empirical Arrhenius equation, Eq. 2.19, where  $A$  is the *pre-exponential term*,  $E_a$  is the thermal coefficient of reactivity (commonly labeled *activation energy*),  $R$  is the gas constant, and  $T$  is temperature (in Kelvin):

$$\ln k = \ln A - \left( \frac{E_a}{RT} \right) \quad (2.19)$$

Reaction rate data that fit this equation give straight lines when  $\ln k$  is plotted against  $1/T$ , as illustrated in Figure 2.5. As seen in plot *a* of competing reactions (1) and



**Figure 2.5** Arrhenius plots for competing reactions: (a)  $A(1)=A(2)$ ,  $E_a(1)>E_a(2)$ ; (b)  $A(3)>A(1)$ ,  $E_a(1)=E_a(3)$ ; (c)  $A(4)>A(1)$ ,  $E_a(4)>E_a(1)$ . Source: Pappas and Feng (1984). Reproduced with permission of Technology Marketing Corporation.

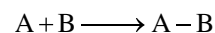
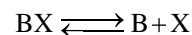
(2), where  $A(1)=A(2)$  and  $E_a(1)>E_a(2)$ , the temperature dependence of the reaction rate increases with increasing values of  $E_a$ . However, the rate of reaction (2) is slower than that of reaction (1) at all temperatures. This effect can be counteracted by selecting a reaction having a higher  $A$  value, as shown in plot *b*, where  $A(3)>A(1)$  and  $E_a$  for the two reactions is equal. If both  $A$  and  $E_a$  are sufficiently greater for one reaction than for another, the rate constant at storage temperature would be smaller, while the rate constant at a higher temperature would be larger, as shown schematically in plot *c*.

Term  $A$  is controlled predominantly by entropic factors, or more specifically, by changes in randomness or order, as the reaction proceeds to the activated complex in the transition state. Three important factors to consider in selecting appropriate reactions are as follows:

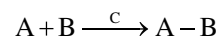
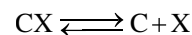
1. Unimolecular reactions tend to exhibit larger  $A$  values than those with a higher molecular order.
2. Ring opening reactions tend to have high  $A$  values.
3. Reactions in which reactants become less polar exhibit larger  $A$  values.

The importance of these factors—in particular, factor (3)—depends on the reaction medium; accordingly, solvent selection can have a significant effect on storage stability.

While unimolecular reactions are desirable for high  $A$  values, cross-linking reactions are necessarily bimolecular. A way around this problem is to use a *blocked* reactant  $BX$  that thermally releases a reactant  $B$  by a unimolecular reaction—most desirably, with ring opening and decreasing polarity—followed by cross-linking between  $A$  and  $B$ :



Another approach is to use a blocked catalyst  $CX$ , where  $C$  catalyzes the cross-linking of  $A$  and  $B$ :



Here an important consideration is that the cross-linking reaction, which follows unblocking, should be faster than the reverse reaction, which regenerates the blocked reactant or catalyst. While one often encounters “threshold” or “unblocking” temperatures for reactions in the literature, such minimum reaction temperatures do not exist in the kinetics of reactions. Reactions proceed at some rate at any temperature. Threshold or unblocking temperatures are actually the temperatures at which some observable extent of reaction has occurred within a specified time interval.

These concepts are helpful for understanding the differences we see between storage stabilities, but another reason for understanding these kinetic considerations is that they can be used to predict whether any chemical reaction will ever be found to meet some combination of stability and cure schedule that might be desired for a coating. Pappas and Hill (1981) carried out calculations to permit such predictions. They made reasonable assumptions about reactive group concentrations during storage and in the applied film, permissible degrees of reaction during storage, and required extents of reaction during curing. Using these assumptions, they calculated the ratio of rate constants needed to permit any specified time of storage together with any specified cure time. In turn, this allowed calculation of  $E_a$  and  $A$  values as a function of any combination of storage and curing temperatures. Kinetic parameters calculated for unimolecular blocked reactant systems that proceed at 5% over a 6 month period at 30°C (storage temperature) and 90% in 10 min at various curing temperatures are listed in Table 2.3 (Pappas and Feng, 1984).

Rate constants and kinetic parameters are independent of concentration for unimolecular, but not for bimolecular reactions. Kinetic parameters calculated for bimolecular (i.e., second order) reactions using concentrations corresponding to high solids coatings were of similar magnitude to those for unimolecular reactions. Although the values in Table 2.3 represent order of magnitude calculation, they provide useful guidelines for avoiding development projects aimed at impossible goals and provide insights for design of thermosetting coatings. Kinetic parameters are known for many chemical reactions. As a point of reference, a reasonable upper limit of  $A$  values for unimolecular reactions is  $10^{16} \text{ s}^{-1}$ , which corresponds to an upper value for the frequency of simple vibrations. For bimolecular reactions,  $A$  values tend to be less than  $10^{11} \text{ l mol}^{-1} \text{ s}^{-1}$ , an upper limit for the rate constant of diffusion, which must precede reaction. However, as shown in Table 2.3, a coating stable at 30°C would require an  $A$  value of  $10^{24} \text{ s}^{-1}$  if it were to cure within 10 min at 100°C. No such reaction is known or even conceivable. Users would like to have package stable coatings that cure in a short time at 80°C, a convenient temperature for low pressure steam heat, but it is

pointless to pursue this goal via kinetic control. That is not to say that it is impossible to make such a coating, it means that the problem must be solved by an approach other than kinetic control.

Storage life can be extended by refrigeration, but users are seldom willing to incur the expense. More reactive combinations can be used in *two package coatings*, in which one package contains a resin with one of the reactive groups and the second package contains the component with the other reactive group. Alternatively, the second package could contain a catalyst for the reaction. The packages are mixed shortly before use. Two package coatings are often called *2K coatings* and single package coatings are sometimes called *1K coatings*. The K stands for the German word for component. Two package coatings are used on a large scale commercially, but they pose substantial additional problems for the user; mixing and cleaning equipment take extra time, some of the material is usually wasted, they are generally more expensive, and error may occur in mixing. Even 2K coatings have the analogous problem of *pot life*, corresponding to the length of time after the two packages are mixed that the viscosity stays low enough for application. Pappas and Hill (1981) made similar calculations of  $A$  and  $E_a$  values for the shorter times involved.

There are several approaches to increasing package stability while permitting cure at ambient or moderately elevated temperature. One or more of these approaches are included in the discussions of many of the cross-linking reactions that are covered in later chapters. The following list gives some of the approaches to solving this “impossible” problem:

1. Use of a radiation-activated cross-linking reaction instead of a thermally activated reaction.
2. Use of a cross-linking reaction requiring an atmospheric component as a catalyst or reactant; reactions involving oxygen or water vapor in the air are examples. (In a way, these are 2K coatings, but the second component is free.) A similar principle is involved in passing a coated article through a chamber containing a catalyst vapor.
3. Use of a volatile component that inhibits the reaction when the coating is stored in a closed container, but volatilizes after application as a thin film, permitting the reaction to proceed. Examples include use of a volatile antioxidant in a coating that dries by oxidation and use of oxygen as an inhibitor in a composition that cures anaerobically.
4. Use of a cross-linking reaction that is a reversible condensation reaction involving loss of a volatile reaction product. If the volatile reaction product is included in the solvent mixture of the coating, the noncross-linked

**Table 2.3** Kinetic Parameters as a Function of Cure Temperature

$T$ (°C)	$A$ ( $\text{s}^{-1}$ )	$E_a$ ( $\text{kJ mol}^{-1}$ ) <sup>a</sup>
175	$10^{10}$	109
150	$10^{12}$	121
125	$10^{17}$	146
100	$10^{24}$	188

Source: Pappas and Feng (1984).

<sup>a</sup> 1 kJ = 0.239 kcal.

side of the equilibrium is favored during storage but shifts to the cross-linked side after application, when the solvent evaporates. A similar approach can be used with blocked reactants and catalysts in which the blocking group is volatile.

5. Use of an encapsulated reactant or catalyst, whereby the capsules are ruptured during application. Encapsulation has been useful in adhesives, but applications in coatings are limited because residual capsule shells interfere with appearance and/or performance. An extension of this idea is to put encapsulated reactants in the coating that do not break during application but break later when the coating suffers mechanical damage; the goal is to make the coating *self-healing* (Section 34.3).
6. Use of a reactant that undergoes a phase change. While there are no threshold temperatures for kinetic reactions, phase changes can occur over narrow temperature ranges. A crystalline blocked reactant or catalyst, insoluble in the vehicle, could give an indefinitely stable coating; heating above the melting point permits the unblocking reaction to occur, releasing a soluble reactant or catalyst. Over a somewhat wider temperature range, the same idea can be used for an amorphous blocked reactant, having a  $T_g$  about 50°C above the storage temperature and, perhaps, 30°C below the desired cure temperature.

*Mobility considerations.* Another consideration in selecting components for thermosetting coatings is the potential effect of the availability of free volume on reaction rates and reaction completion. For reactions to occur, the reacting groups must diffuse into a reaction volume to form an activated complex that can then form a stable bond. If the diffusion rate is greater than the reaction rate, the reaction will be kinetically controlled. If the diffusion rate is slow compared with the kinetic reaction rate, the rate of the reaction will be mobility controlled. The major factor controlling the diffusion rate is the availability of free volume. If the reaction is occurring at a temperature well in excess of  $T_g$ , the free volume is large and the rate of reaction is controlled by concentrations and kinetic parameters. If, however, the temperature is well below  $T_g$ , the free volume is so limited that the polymer chain motions needed to bring unreacted groups close together are very slow, and reaction virtually ceases. At intermediate temperatures, the reaction can proceed, but the reaction rate is controlled by the rate of diffusion, that is, by the mobility of the reactants.

Since cross-linking often starts with low MW components,  $T_g$  increases as the reaction proceeds. If the reaction temperature is well above the  $T_g$  of the fully reacted polymer, there will be no mobility effect on the reaction rate. However, if, as is often the case in ambient cure coatings,

the initial  $T_g$  is below the ambient temperature and the  $T_g$  of the fully reacted polymer is above the ambient temperature, the reaction rate will become mobility controlled as cross-linking proceeds. As further reaction occurs, cross-linking may essentially stop before reaching completion. As  $T_g$  approaches the temperature ( $T$ ) at which the reaction is occurring, reactions become slower. When  $T_g$  equals  $T$ , reactions become very slow and *vitrification* (glass formation) is said to occur. Unless the experiment is continued for a relatively long time, the reactions have been said to cease (Aronhime and Gilham, 1984). However, with extended reaction times, it can be seen that reactions continue slowly. Blair (1985) reports that reaction rate constants drop by about three orders of magnitude when  $T_g$  equals  $T$ , but that the reaction continues at a slow rate until  $T_g$  increases to  $T+50^\circ\text{C}$ . It is interesting to consider the similarity of this value to the universal  $B$  constant of 51.6 in the WLF equation (Eq. 2.9).  $T_g - B$  is the temperature at which viscosity goes to infinity and free volume theoretically approaches zero, corresponding to a  $T_g$  of  $T+B$ . Dusek and Havlicek (1993) studied the effect of variables on mobility control of reaction rates. In the reaction of bisphenol A diglycidyl ether and 1,3-propanediamine, they determined the effects of temperature, polymer-solvent interaction, and solvent volatility on reaction rates and extent of reaction. They also reviewed the theories involved.

It seems reasonable for a formulator to assume that cross-linking reactions begin to slow as  $T_g$  increases to about 10°C below the curing temperature and get progressively slower until  $T_g$  is about 50°C above the curing temperature, where reaction essentially ceases. The slow rates of reaction mean that properties of many ambient cure coatings can change substantially for several weeks, and change may continue indefinitely. Caution is required, since  $T_g$  values are dependent on the method of determination and the rate of heating used. For this purpose,  $T_g$  values obtained at very slow rates of heating and at low rates of application of stress are most appropriate. Dusek and Havlicek (1993) point out that, if reactions are very fast, equilibrium  $T_g$  may not be reached. Another factor that may affect the development of mobility control is the size of the diffusing reactants. Small molecules may diffuse more readily to reaction sites than functional groups on a polymer chain. Yet another consideration is that water plasticizes coatings such as polyurethanes and epoxy-amines, lowering their  $T_g$ .

If the initial reaction temperature is well below the  $T_g$  of the solvent-free coating, it is possible that little or no reaction can occur after solvent evaporation and that a "dry" film forms merely due to solvent evaporation without much cross-linking. The result is a weak, brittle film. One must be careful when defining what is meant by a dry film, especially when dealing with ambient temperature cure coatings. One consideration is whether the film is dry to

handle. This stage could be reached with little cross-linking if the  $T_g$  of the solvent-free binder is high enough. Another consideration is whether the required extent of cross-linking has occurred. This must be tested by some method other than hardness, most easily by determining resistance to solvent rubbing or by the extent of solvent swelling (Section 4.2).

Mobility limitations are less likely to be encountered in baking coatings because in most cases, the final  $T_g$  of the film is below the baking temperature. Furthermore, the  $T_g$  is usually well above ambient temperatures so even if there are some unreacted groups, reactions essentially stop after cooling to ambient temperature. In moderate temperature cure powder coatings, mobility control of reaction can be a limitation, since the initial  $T_g$  of the reactants has to be above 50°C so that the powder will not sinter during storage (Section 28.3). To achieve a high extent of reaction, the baking temperature must be above the  $T_g$  of the fully reacted coating. Gilham and coworkers extensively studied factors influencing reaction rates in high  $T_g$  epoxy-amine systems; Simon and Gilham (1993) summarize Gilham's work and, in particular, point out its applicability to powder coatings.

Other complications arise from the likelihood that cross-linking does not yield uniform films. Formation of gel particles early in the process can cause inhomogeneities. Also, surface effects may alter structures of parts of the cross-linked network near the film's surfaces and near the surfaces of pigments, fillers, and nanoparticles. Such complications are difficult to study experimentally but can be addressed by computer modeling. An example has been provided by Song et al. (2015), who modeled the cure of nanoparticle-filled automotive clear coats and demonstrated the model's effectiveness in a case study.

### 2.3.3 Film Formation by Coalescence of Polymer Particles

In contrast to the processes of film formation from solutions of thermoplastic or thermosetting polymers, dispersions of insoluble polymer particles form films by *coalescence* (fusion) of particles. After application and loss of volatile components, the particles form a continuous film. How does this happen? It is a very complex process; here we will outline the key considerations. Readers seeking more detail are referred to a book by Keddie and Routh (2010) and books edited by Provder et al. (1996) and Provder and Urban (2001). The largest volume of coatings that form films by coalescence is latexes, which are a dispersion of high MW polymer particles in water (Chapter 9).

For a given latex, the lowest temperature at which coalescence occurs sufficiently to form a continuous film is called its *minimum film formation temperature* (MFFT);

some authors call it the *minimum filming temperature* (MFT). MFFT is measured by placing samples on a heated metal bar with a temperature gradient. A major factor controlling MFFT is the  $T_g$  of the polymer in the particles. The  $T_g$  of PMMA is about 105°C, and one cannot form a useful film from a PMMA latex at room temperature; instead, one gets a layer of material that powders easily. Many latexes are designed to have layers of material with different  $T_g$ s within each particle (Sections 9.1.3 and 9.2), making it difficult to directly relate MFFT to  $T_g$ .

The mechanism of film formation from latexes has been extensively studied but still is not fully understood. A simplified picture of the steps in film formation used by many authors is as follows:

1. *Evaporation* of water and water-soluble solvents that leads to a close-packed layer of latex particles
2. *Deformation* of the particles from their spherical shape that leads to a more or less continuous, but weak, film
3. *Coalescence*, a relatively slow process in which the polymer molecules *interdiffuse* across the particle boundaries and entangle, strengthening the film

It should be emphasized that these steps, especially 2 and 3, overlap during the process. This picture is called *vertical drying*. *Horizontal drying* is discussed in the following text. A further complication is that different authors use different terms for the three steps: some call step 2 “coalescence” and step 3 “diffusion” or “interpenetration.”

During step 1, repulsive forces between the particles favor uniform packing, but other forces, such as convection, may cause irregularities (Gromer et al., 2015). The close-packed array of particles usually still contains water. The internal phase volume at this stage depends on particle size distribution: the broader the distribution, the higher the internal phase volume.

If the particle size distribution of the latex particles is narrow, the end result of step 1 can be formation of ordered *colloidal crystals*. In such cases, small angle X-ray scattering (SAXS) can be used to study step 2 by measuring the rate of disappearance of the crystalline structure (Sulyanova et al., 2015).

As the polymer particles come together, they begin to deform.  $T_g$  of the latex particles is an important factor controlling the rates of particle deformation. Lower  $T_g$  particles have a lower modulus—that is, they are softer (Section 4.2) and, hence, are more easily deformed. Surfactant stabilizers can increase water absorption and also act as plasticizers for the polymer (Vandezande and Rudin, 1996). In general, higher surfactant content reduces MFFT. Structure of the surfactant also affects MFFT; for example, nonyl phenol ethoxylates having fewer than 9 ethoxylate units reduced MFFT further than those with 20 or 40 units. Furthermore, MFFT can be reduced by as much

as 5°C by forming the film in a humid atmosphere (Eckersley and Rudin, 1990). Reduction of  $T_g$  by water is largest with hydrophilic polymers.

Deformation of the close-packed particles increases the area of contact between particles and promotes coalescence. For deformation to occur it is necessary overcome the stabilizing repulsion. What are the driving forces for deformation? Since 1950, various plausible theories have been advanced (Dobler and Holl, 1996). These theories include the following:

- Dry sintering driven by particle–air interfacial tension
- Wet sintering driven by particle–water interfacial tension
- Capillary pressure within the still-wet close-packed particles
- Compression forces caused by evaporation of water after a surface film has formed
- Reduction of surface free energy of the particles (Another name for sintering?)

Each of these theories is supported by experimental evidence in some cases. Furthermore, different deformation mechanisms have been observed for the same latex under different conditions (Gonzales et al., 2013). Thus, it seems likely that, in a given situation, several driving forces may be at work to differing extents during film formation (Routh and Russel, 2001). Furthermore the contributions of different forces probably vary as drying conditions change.

Lin and Meier (1996) strongly adhere to the position that capillary pressure is the dominant driving stress for film formation. Croll (1987) estimated that capillary forces could generate pressure as much as 3.5 MPa (5000 psi), but he pointed out that they act only briefly. His data on drying rates support a proposal of Kendall and Padget (1982) that a major driving force for coalescence is surface free energy reduction. The surface area of a coalesced film is only a small fraction of the surface area of the particles, so the driving force resulting from reduction in surface area must be significant.

Consistent with the differences in surface area, small particle size latexes often form films at somewhat lower temperatures than larger particle size ones (Eckersley and Rudin, 1990). However, Kan (1999) showed that this is not always the case—with other latexes, larger size promotes deformation. Still other work indicates that in some cases there is no effect of particle size on MFFT. Since broader distribution of particle size increases close-packed volume fraction, it leads to more rapid film formation. Possibly, these different conclusions are caused not just by particle size but also by particle size distribution and differences in the compositions of the latexes used. It is speculated that the larger proportion of surface active material in small particle size latexes may also play a role.

The third step, coalescence, begins during the process of deformation. With the large number of variables involved in coalescence, one would expect interactions among the different variables. The rate of interdiffusion is primarily driven by  $T - T_g$ . Adequate interdiffusion will occur only when the  $T_g$  of the particles is lower than the temperature at which the film is to be formed. Theoretical and experimental studies of coalescence suggest that molecules only need to interdiffuse a distance comparable to the radius of gyration of one molecule to develop maximum film strength (Winnik, 1997). This distance is considerably less than the diameter of a typical latex particle. The rate of interdiffusion is directly related to  $T_g$  and is, therefore, controlled by free volume availability (Winnik, 1997). The major factor affecting free volume is the difference between the temperature of film formation and the  $T_g$  of the particles. Presumably, the  $T_g$  of the material near the surface of the original particle is most important. As a general rule, coalescence will be very slow unless the temperature is at least slightly higher than  $T_g$ . Latexes for paints are generally copolymers of acrylic and vinyl esters that have a  $T_g$  well below room temperature so that they can coalesce readily within the usual range of application temperatures.

Most studies of the mechanism of film formation use carefully prepared uniform films that are dried in a laboratory under conditions of intermediate humidity and little air flow over the surface. Real-life conditions are quite different: the latex has been formulated into a paint with pigments and many additives, and dried under a wide variety of conditions. In many cases film thickness is not uniform. A further complication is that water evaporation is seldom uniform across the whole area of a film. The result is often *horizontal* (or *lateral*) *drying* in which a drying front starts, perhaps at a thin spot or edge, and spreads laterally across the panel (Salamanca et al., 2001). When this happens, both water and polymer particles move sideways near the drying front, and smaller particles appear less likely to give uniform films. The practical implications of this finding are only partly understood. It may partly explain why film formation is poor when exterior house paint is applied on a hot windy day with low humidity.

*Plasticizers*, which dissolve in the polymer, can be added to lower  $T_g$  and MFFT of the formulation. Since non-volatile plasticizers permanently reduce  $T_g$ , most latex paints contain volatile plasticizers, which are called *coalescing solvents*, although they accelerate deformation as well as coalescence. A coalescing solvent must be soluble in the polymer and have a low, but appreciable, evaporation rate. The coalescing solvent acts as a plasticizer to lower the MFFT, but after the film has formed, it diffuses to the surface of the film and evaporates. Since free volume in the film is relatively small, the rate of loss of the last of the coalescing solvent is very slow. Though the films feel dry in a short time, they will still block for days, or even weeks,

after application. Effects of coalescing solvents on film formation have been quantitatively studied by fluorescence decay measurements to follow the extent of polymer diffusion in films as they coalesce (Winnik et al., 1992). The efficiency of coalescing solvents varies over a wide range; an example of a relatively efficient solvent is the acetate ester of propylene glycol monobutyl ether (PnBA) (Geel, 1993). The rate of evaporation from films also varies. For example, dipropylene glycol dimethyl ether leaves a film more rapidly than PnBA, but somewhat more is required for film formation. A widely used coalescing solvent is Texanol®, the isobutyric ester of 2,2,4-trimethylpentane-1,3-diol. Some of the common coalescing solvents are counted as VOC in North America but not in Europe (Chapter 18).

While films form rapidly from latexes when the temperature is above MFFT, complete coalescence is a relatively slow process; in many cases, the film probably never equilibrates to become completely uniform. The rate of equilibration is affected by  $(T - T_g)$ . From the standpoint of rapid coalescence, it is desirable to have a latex having  $T_g$  well below the temperature at which the film is to be formed. Review papers discuss factors affecting the development of cohesive strength of films from latex particles (Daniels and Klein, 1991; Winnik, 1997). The extent of coalescence has been studied by small angle neutron scattering, direct energy transfer of particles labeled with fluorescent dyes, and scanning probe microscopy (Butt and Kurovka, 1995; Rynders et al., 1995). Berce et al. (2015) employed electrochemical impedance spectroscopy (EIS) and atomic force microscopy (AFM) to observe the course of deformation and coalescence in styrene/acrylic and acrylic latexes.

Usually, architectural paints are formulated so that film formation occurs at temperatures as low as 2°C. Film formation at such a low temperature requires a low  $T_g$  latex. However, as discussed in the introductory paragraphs of Section 2.3,  $(T - T_g)$  also affects whether the film obtained will be solid. It was estimated that for a film to withstand the relatively mild blocking test described,  $(T - T_g)$  would have to be on the order of 21°C. If the film is to be exposed to the blocking test when the temperature is 50°C (not an unreasonable expectation during direct exposure to summer sun), the  $T_g$  should be about 29°C or higher. Thus, the paint formulator is faced with a difficult challenge to design a system that can form a film when applied at 2°C and yet resist blocking at 50°C.

Coalescing solvents help solve this problem, but environmental regulations are limiting permissible emissions of VOC. A second approach is to design latex particles so that there is a gradient of  $T_g$  from a relatively high  $T_g$  in the center of the particles to a relatively low  $T_g$  at the outer periphery (Hoy, 1979; Sections 9.1.3 and 9.2). The low  $T_g$  of the outer shell permits film formation at low temperature.

Over time, the  $T_g$  of the coalesced film approaches the average  $T_g$  of the total polymer. The higher average  $T_g$  reduces the probability of blocking. Relatively small amounts of coalescing solvents can be sufficient with such a latex.

A third approach is to use blends of high and low  $T_g$  latexes, which can reduce MFFT without the presence of coalescing solvents (Winnik and Feng, 1996). It has been proposed that the films contain particles of high  $T_g$  polymer dispersed in a matrix of lower  $T_g$  polymer, reinforcing the matrix, increasing its modulus, and, hence, decreasing blocking. There must be enough soft polymer to form a continuous film enclosing the hard particles. These studies were done without pigment, which can also reinforce a film. A fourth approach involves use of core-shell latexes (Juhue and Lang, 1995; Section 9.1.3).

Another complication is the potential for development of stresses within the coalesced films. Price et al. (2014) showed that stresses in films derived from core-shell latex particles can influence important film properties.

*Polyurethane dispersions* (PUDs; Section 12.7.1) have low MFFT values in relation to dry film  $T_g$  owing to the plasticizing effect of H-bonding with water. Accordingly, coalescing solvents are not needed with PUDs. When PUDs are blended with high  $T_g$  acrylics, MFFT is reduced without reducing hardness (Section 12.7.2).

Cross-linkable (thermosetting) latexes are another approach to the problem of film formation at low temperatures and block resistance. This topic will be introduced here and discussed fully in Section 9.4. In general, a lower  $T_g$  latex can be used in such coatings, which permits coalescence with less or even no coalescing solvent. The cross-linking may not increase  $T_g$  significantly but does improve mechanical properties and solvent resistance of the films. Taylor and Winnik (2004) reviewed the subject in detail, describing the theory as well as a variety of possible cross-linking chemistries. At that time, two package coatings were often required, and they were only useful for industrial applications.

Chemists and formulators have now learned to make package stable cross-linking latex coatings that are suitable as architectural and special purpose coatings. These are often called *self-cross-linking paints*. While this terminology suggests that the cross-linking reactants are copolymerized into the latex, this is often not the case. Typically, the cross-linking results from reaction of one reactive group within the latex and a separate bi- or polyfunctional cross-linker. An example of such a combination is a latex copolymer that includes a ketone or aldehyde functional monomer and a separate, water-soluble dihydrazide cross-linker (Section 17.11).

For such systems to be practical, rates of many different processes must be controlled. In addition to the rates of evaporation, deformation, and coalescence (polymer molecule interdiffusion) required of thermoplastic latexes, the



rates of cross-linker diffusion into the polymer and the rates of the chemical cross-linking reactions must be properly timed (Winnik, 2002). Premature cross-linking is avoided by having the cross-linker in the aqueous phase and coreactant imbedded in the polymer particles. In order to develop good properties, significant interdiffusion of polymer molecules during coalescence and diffusion of cross-linker into the polymer must occur before extensive cross-linking reaction occurs. The rates of interdiffusion and diffusion are governed by  $(T - T_g)$  and the chain lengths of the latex molecules. Thus, thermosetting latexes are designed with somewhat lower  $T_g$  and MW to facilitate interdiffusion.  $T_g$  and shortens chain length. Straight chains diffuse more rapidly than branched chains.

Caution: Most studies of the mechanism of film formation have been done with latexes, not with fully formulated paints. It is to be expected that other components of paints, such as pigments, pigment dispersing agents, and water-soluble polymers used as thickening agents, among others, affect MFFT, rate of film formation, and blocking resistance. See Chapter 31 for further discussion of latex paints.

Other types of coatings that involve coalescence of particles are discussed in later chapters, including aqueous PUDs, organosols, water-reducible resins, and powders.

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# Chapter 3

## Flow

*Rheology* is the science of flow and deformation. This chapter deals only with the flow of relatively liquid materials; deformation of relatively solid materials, another aspect of rheology, is discussed in Chapter 4.

The flow properties of coatings are critical for proper application and appearance of films. For example, in brush application of a paint, the flow properties govern settling of pigment during storage, how much paint is picked up on the brush, film thickness applied, leveling of the applied film, and control of sagging of the film. Depending on how stress is applied to a fluid, there are several types of flow. Of major importance in coatings is the flow under a shear stress. We consider shear flow first and then, more briefly, other types of flow.

### 3.1 SHEAR FLOW

To understand and define *shear flow*, consider the model shown in Figure 3.1 (Patton, 1979). The lower plate is stationary, and the upper parallel plate is movable. The plates are separated by a layer of liquid of thickness  $x$ . Lateral force  $F$  is applied to the top movable plate of area  $A$ , so the plate slides sidewise with velocity  $v$ . The model assumes that there is no slip at the interfaces and that there is no fluid inertia. When the plate moves, the liquid near the top moves with a velocity approaching that of the movable plate and the velocity of the liquid near the bottom is close to zero. The velocity gradient  $dv/dx$  for any section of the liquid is constant and, therefore, equals  $v/x$ . This ratio is defined as *shear rate*,  $\dot{\gamma}$ . The units of shear rate are reciprocal seconds,  $s^{-1}$ :

$$\dot{\gamma} = \frac{dv}{dx} = \frac{v}{x}; \quad \frac{\text{cm s}^{-1}}{\text{cm}} = \text{s}^{-1}$$

Force  $F$  acting on the top plate of area  $A$  results in *shear stress*  $\tau$ . The units of shear stress are pascals (Pa):

$$\tau = \frac{F}{A}; \quad \text{units: m kg s}^{-2} \text{m}^{-2} = \text{Nm}^{-2} = \text{Pa}$$

A liquid exerts a resistance to flow called *viscosity*,  $\eta$ , defined as the ratio of shear stress to shear rate. This type of viscosity is more correctly called *simple shear viscosity*, but since it is the most widely encountered type of viscosity, it is usually just called viscosity. The separation of molecules in flow dissipates energy, primarily as heat. Thus, viscosity is the energy per unit volume dissipated to attain a unit velocity gradient. The units are pascal seconds (Pa·s). The older, and still commonly used, unit is the poise (P). One Pa·s equals 10 P, and 1 mPa·s equals 1 cP:

$$\eta = \frac{\tau}{\dot{\gamma}}; \quad \frac{\text{Pa}}{\text{s}^{-1}} = \text{Pa} \cdot \text{s}$$

When a liquid flows through a hole or a capillary, part of the energy is diverted into kinetic energy; then the resistance to shear flow is called *kinematic viscosity*,  $\nu$ , with units of  $\text{m}^2 \text{s}^{-1}$ , formerly called stokes, where  $1 \text{ m}^2 \text{s}^{-1} = 10^4$  stokes. When the acceleration results from gravity, kinematic viscosity equals simple shear viscosity divided by the density,  $\rho$ , of the liquid:

$$\nu = \frac{\eta}{\rho}$$

### 3.2 TYPES OF SHEAR FLOW

When the ratio of shear stress to shear rate is constant, liquids are *Newtonian*; and viscosity is independent of shear rate (or shear stress). A plot of shear rate as a function of shear stress is linear (Figure 3.2a), and the slope equals the inverse of viscosity. Such plots sometimes appear in the literature with axes opposite to those shown; then the slope is the viscosity. Newtonian flow is exhibited by liquids composed of miscible small molecules. Many solutions of oligomeric resins also approximate Newtonian flow.

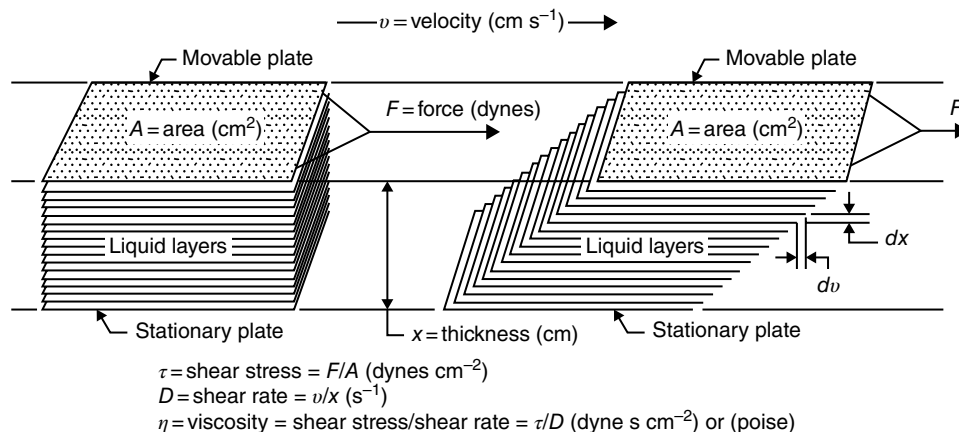
Many liquids are non-Newtonian; that is, the ratio of shear stress to shear rate is not constant. One class of non-Newtonian liquids exhibits decreasing viscosity as shear rate (or shear stress) increases; these liquids are *shear thinning*. As stress is applied, the molecules line up parallel to the direction of the flow, reducing the energy required to displace them further. In the case of liquids having a disperse phase, the particles line up as bead chains, again reducing the energy required to displace them further. Shear thinning has been called *shear-induced order*. When the molecules or particles are all aligned in the direction of the flow, the viscosity is again independent of shear rate and the curve becomes linear (Figure 3.2b).

With some liquids, no detectable flow occurs unless a minimum shear stress is exceeded. Such materials exhibit *plastic flow* and are sometimes called *Bingham bodies*. The minimum shear stress required is called the *yield value*, or *yield stress*, and is designated by the symbol  $\tau_0$ :

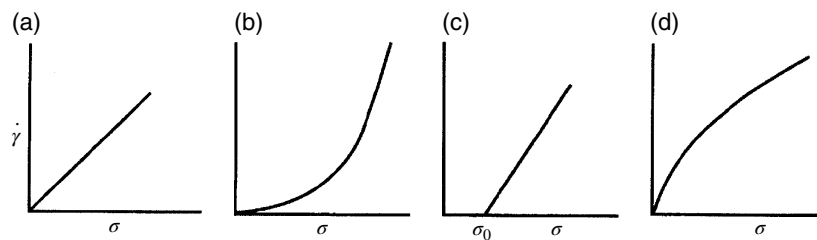
$$\tau - \tau_0 = \eta_p \dot{\gamma}$$

A schematic plastic flow diagram is shown in Figure 3.2c. The yield value depends strongly on the rate at which stress is increased. The faster the rate of stress is increased, the higher the measured value that is obtained. It is fairly common to extrapolate the linear part of the curve to the intercept with the shear stress axis and call the intercept a *yield value*.

Another class of liquids exhibits increasing viscosity as shear rate (or shear stress) increases. A schematic plot of such behavior is given in Figure 3.2d. Such liquids are *shear thickening*. Shear thickening has been called *shear-induced disorder*. If shear thickening liquids also increase in volume under shear, they are called *dilatant fluids*. Dilatant fluids have dispersed phases that become less ordered and, hence, occupy more volume. Examples are



**Figure 3.1** Model of shear flow of an ideal liquid. (In current usage, the symbol for shear stress is  $\tau$  and its units are Pa; the symbol for shear rate is  $\dot{\gamma}$  and the units of  $\eta$  are Pa·s.) Source: Patton (1979). Reproduced with permission of John Wiley & Sons.



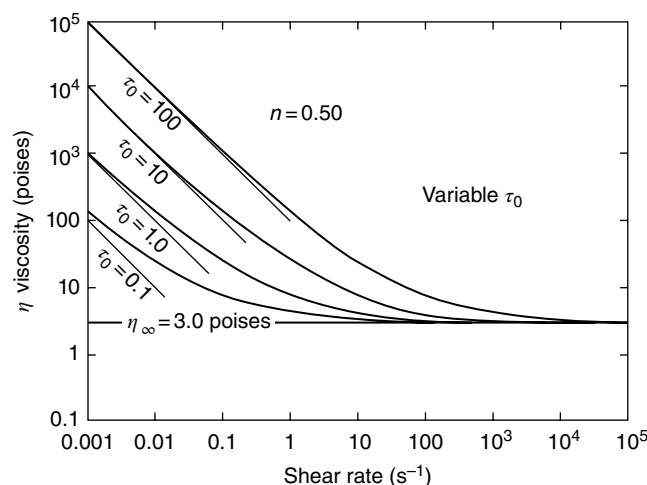
**Figure 3.2** Plots of the flow of various types of liquids. (a) Newtonian; (b) shear thinning; (c) plastic; (d) shear thickening.

pigment and resin dispersions in which the dispersed phase is sufficiently concentrated so that the particles approach being randomly close packed. If sufficient stress is applied for flow, microscopic voids are created, increasing the volume and increasing the energy necessary to induce flow. Thus, the viscosity increases. Another example is quicksand. Mewis and Vermant (2000) further describe the factors affecting dilatant flow.

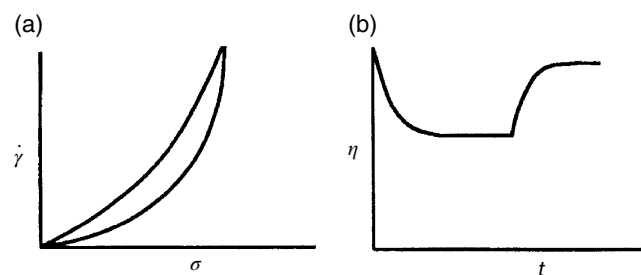
The Casson equation, Eq. 3.1, linearizes viscosity/shear rate data of shear thinning or thickening fluids; the slope of the line is the yield stress, and extrapolation gives the viscosity at infinite shear rate  $\eta_\infty$ . In many cases, the value of  $n$  is 0.5, and commonly, the Casson equation is shown with just the half-power relationship. In plots of log viscosity against shear rate, the degree of curvature is related to the value of  $\tau_0$ . In Figure 3.3, the values of  $\eta$  and  $\eta_\infty$  are held constant to show the effect of changes in  $\tau_0$  on flow response (Hester and Squire, 1997). For a Newtonian fluid,  $\tau_0$  equals zero and the plot is a straight line parallel to the shear rate axis:

$$\eta^n = \eta_\infty^n + \left( \frac{\tau_0}{\dot{\gamma}} \right)^n \quad (3.1)$$

Some fluids show time history dependence of viscosity, as illustrated in Figure 3.4a. The curves in the figure result from shear stress readings taken at successively higher shear rates to some upper limit (right-hand curve), followed immediately by shear stress readings taken at successively lower shear rates (left-hand curve). At any shear rate on the initial curve, the stress would decrease with time to an equilibrium value between the two curves; that is, the viscosity would decrease. On the other hand, if such a system



**Figure 3.3** Casson plot of viscosity as a function of shear rate showing the dependence  $\tau_0$  with constant  $\eta$  and  $\eta_\infty$ . Source: Patton (1979). Reproduced with permission of John Wiley & Sons.



**Figure 3.4** Schematic plots of systems exhibiting thixotropic flow. (a) The curve to the right is based on readings taken as shear rate was being increased, and the curve to the left is based on readings taken as shear rate was then being decreased. (b) The viscosity drops as shear continues and then increases as the shear rate is decreased.

had been exposed to a high rate of shear and then the shear rate decreased, the shear stress would increase to an equilibrium value as the measurement was continued; that is, the viscosity would increase with time. This behavior is called *thixotropic* flow.

Armstrong et al. (2016) define thixotropy as “... the continuous decrease of viscosity with time when flow is applied to a sample that has been previously at rest, and the subsequent recovery of viscosity when the flow is discontinued.” Thixotropic fluids are shear thinning fluids. In addition, their viscosity depends on time and prior shear history. All thixotropic fluids are shear thinning fluids, but not all shear thinning systems are thixotropic. Unfortunately, the term thixotropy is often improperly used as a synonym for shear thinning.

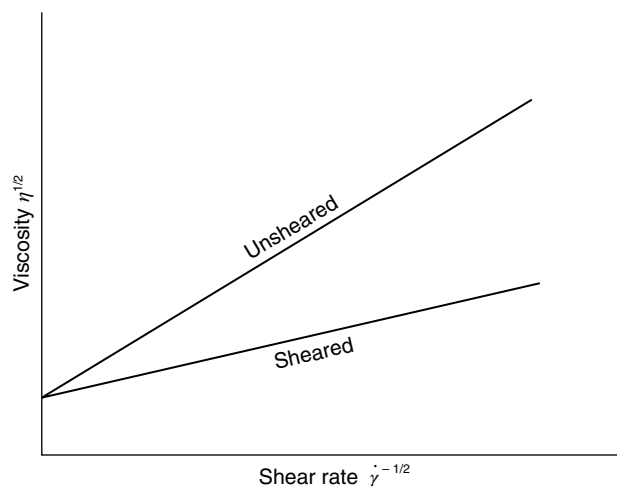
Thixotropy is a desirable attribute of many paints because it enables paint formulators to retard settling, optimize the application characteristics, and minimize sagging and dripping after application. Thixotropy usually results from reversible formation of a structure within a fluid; an example is association of dispersed particles held together by weak forces. Thixotropic structure is broken down by applying shear for a sufficient time and re-forms over time when shear is stopped. Some thixotropic fluids undergo viscosity reduction to equilibrium values in short time periods and recover their viscosity rapidly when shearing is stopped; others change more slowly with time. In early work, areas within hysteresis loops, as shown in Figure 3.4a, were compared to estimate the degree of thixotropy. However, such comparisons may be misleading because the areas of such loops depend on the shear history, the peak shear, and the time intervals between successive measurements. A more appropriate way to represent the effect is to plot the viscosity at a series of shear rates as a function of time ( $t$ ), as illustrated in Figure 3.4b. The time for recovery after shifting from a high shear rate to a lower shear rate is a useful method for comparing different paints. It is generally desirable to formulate such coatings so that

the rate of recovery is rapid enough to avoid sagging but slow enough to permit leveling.

Additives to impart thixotropy to coatings include clays treated with quaternary ammonium compounds, which form salts with the clay platelets and make them organophilic. Such additives are widely used in solvent-borne coatings. Attapulgite clay is used in both solvent-borne and waterborne coatings. The needles of this clay associate with each other, providing an increase in viscosity that reverses with agitation. In waterborne coatings, the clay also acts by absorbing water to make swollen particles that distort in shape with stress. Fine particle size silica has also been used for many years. Castor oil derivatives and powdered polyethylene are effective thixotropic agents in baking coatings. Polyamides such as alkyds partly gelled with aminoalcohols are used as thixotropes. Basic calcium sulfonate derivatives are liquid thickeners that do not reduce gloss and retain their effectiveness when a coating is heated. They are particularly useful in moisture-curable urethane coatings since their basicity neutralizes the  $\text{CO}_2$  produced by reaction isocyanates with water, thereby reducing the bubbling problem as well as imparting thixotropy. In latex-based paints, water-soluble polymers and associative thickeners are used as discussed in Section 3.5.1. Hare (2001) provides a review of thixotropes and additives for modifying paint flow.

Rheologists frequently discuss the properties of thixotropic fluids in terms of *viscoelasticity* and consider that they flow by a combination of viscous flow and elastic deformation (viscoelasticity is discussed in Section 4.2.2). Such interpretations are valid and useful, but historically they have been seldom applied in the coatings industry. Time dependency can best be measured in terms of viscoelasticity; see Hester and Squire (1997) and Boggs et al. (1996) for such analyses. The physics of thixotropy is quite complicated; for a recent overview see Armstrong et al. (2016), where various models are described and tested experimentally.

Another way to show the effect of shear on a thixotropic fluid is by a different type of Casson plot, as shown in Figure 3.5 (Schoff, 1988). The square root of the viscosity is plotted against the square root of the reciprocal of the shear rate; the steeper the slope, the greater the degree of shear thinning. If the sample had been sheared until all of the thixotropic structure was broken down, and if the measurements could be made before any structure buildup occurred, the sheared plot would be linear and parallel to the  $x$  axis. Although comparisons of the differences between the slopes of such lines give a qualitative expression of the extent of thixotropy, the slopes of the curves may depend on prior shear history, the rate of acceleration of shear, and the length of time that the sample was exposed to the highest shear rate.



**Figure 3.5** Schematic Casson plots of a sheared and unsheared thixotropic coating. The degree of divergence gives an estimate of the degree of thixotropy. Source: Schoff (1988). Reproduced with permission of John Wiley & Sons.

### 3.3 DETERMINATION OF SHEAR VISCOSITY

A variety of instruments is available to determine viscosity. They vary in cost, time required for measurements, operator skill required, sturdiness, precision, accuracy, and ability to measure shear rate variability or time dependency effects. Data obtained on the same sample with different instruments and by different operators with the same instruments can vary substantially, especially for shear thinning liquids at low rates of shear (Anwari et al., 1989). Some of the variation can result from lack of attention to details, especially temperature control and possible solvent evaporation; major errors can result from comparing samples that have had different shear histories. Recent improvements in instrumentation have helped the situation, but care is still needed.

Temperature must be carefully controlled. Since viscosity depends strongly on temperature (Section 3.4.1), it is critical that the measurement is made while the sample is at a constant, known temperature. When high viscosity fluids are sheared at high shear rates, heat is evolved and the temperature of the sample increases unless the heat exchange efficiency of the viscometer is adequate. If viscosity is determined while both shear rate and temperature are increasing, it may be impossible to tell whether or not the fluid is shear thinning.

Mezger (2014) describes dozens of instruments that measure rheology of liquids. Viscometers are most suitable for measuring shear viscosity of Newtonian liquids, whereas rheometers are most suitable for profiling the flow behavior of non-Newtonian fluids. Viscometers can be placed into three broad classes: (1) those that permit quite

accurate viscosity determinations, (2) those that permit determination of reasonable approximations of viscosity, and (3) those that provide flow data marginally related to viscosity. We restrict our discussion to major examples of each class. The general references at the end of this chapter are good sources of further information.

### 3.3.1 Capillary Viscometers

Figure 3.6 shows an example of a *capillary viscometer* (Schoff, 1991). The time required for a known amount of liquid to flow through a capillary tube is measured (Poiseuille, 1840). While viscosities can be calculated based on the diameter of the capillary, usually each instrument is standardized with liquids of known viscosity; then, calculation is simply based on instrument constants and time.

Since capillary flow is driven by gravity, kinematic viscosity (Section 3.1) is measured. Simple shear viscosity can be calculated by correcting for density. Capillary viscometers with a range of diameters permit the determination of viscosities from  $10^{-7}$  to  $10^{-1} \text{ m}^2 \text{ s}^{-1}$ . For liquids with a density of 1, these values correspond to a range of  $1 \text{ mPa}\cdot\text{s}$ – $1000 \text{ Pa}\cdot\text{s}$ .

Historically, capillary viscometers have been the instruments of choice for research work because of their accuracy. They are applicable only to Newtonian fluids and

are not appropriate for routine work, because determinations are relatively time consuming, especially when temperature dependence of viscosity data is desired. Temperature equilibration is slow because of the relatively large sample sizes and the low rate of heat transfer by glass. Careful cleaning is essential. Capillary viscometers are particularly appropriate for use in determining the viscosity of volatile liquids or solutions containing volatile solvents, since they are essentially closed systems.

Modified capillary viscometers are available that overcome limitations of the standard types. Vacuum viscometers suck up the sample into the capillary tube, and the time to pass from the lower marker to the upper one is measured. Since the flow is not driven by gravity, density does not affect the time, and viscosity is measured in  $\text{Pa}\cdot\text{s}$ , avoiding the need to determine density. Similar viscometers can be used for opaque liquids since the passage of liquid from the lower mark to the upper mark can easily be seen.

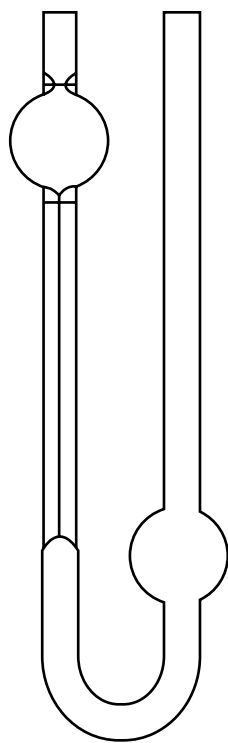
### 3.3.2 Rheometers

For non-Newtonian liquids, including pigmented liquids, the highest accuracy over a wide range of shear rates is obtained with rotational rheometers, exemplified by *cone and plate rheometers*. A schematic diagram is shown in Figure 3.7. The sample is placed on the plate that is then raised to a level with small clearance from the cone. The cone can be rotated at any desired number of revolutions per minute (rpm), and the torque is measured. The shallow angle of the cone is designed to make the shear rate constant throughout the sample in the gap. Shear rate is proportional to the rpm; and shear stress is related to the torque. Temperature is controlled by passing temperature-controlled water through the plate; temperature control problems are minimized by the small sample size.

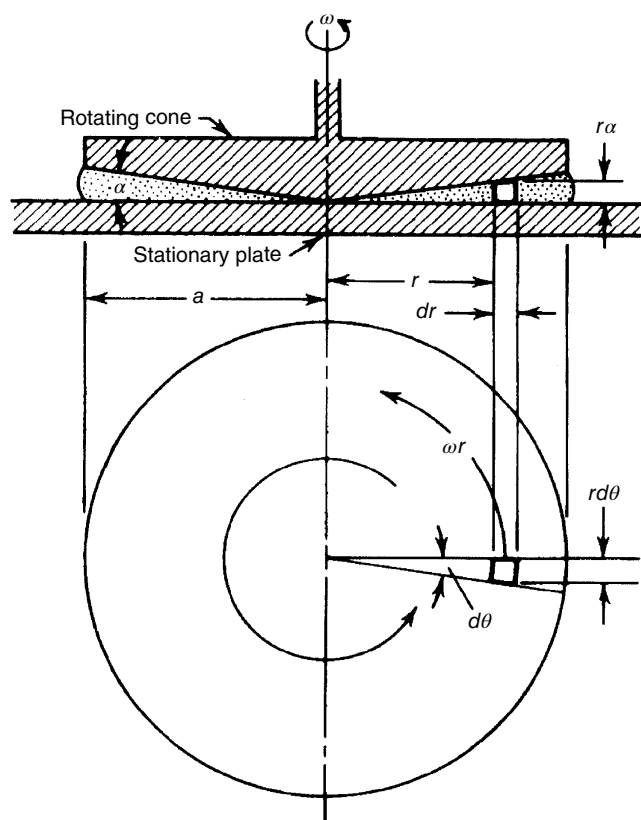
Rheometers vary in the range of shear rates that can be used and the time required to increase or decrease shear rate. (See general references and Schoff (1988 and 1991) for further discussion.) The least expensive instruments are sufficiently rugged, simple to use, and sufficiently fast for quality control applications. The most versatile ones are sensitive scientific instruments that require skill in use and are most appropriate for research applications. For solutions containing volatile solvents, the cone and plate unit is shrouded in an atmosphere saturated with solvent vapor to prevent evaporation.

Rheometers are available that control strain or stress. The latter type offers advantages for coatings, as it is generally superior for measurements at very low shear rates. Hybrid rheometers that operate in both modes are also available.

The viscosity of highly viscous materials can be determined at high rates of shear by the use of *mixing*



**Figure 3.6** Ostwald capillary viscometer. Source: Schoff (1991). Reproduced with permission of John Wiley & Sons.

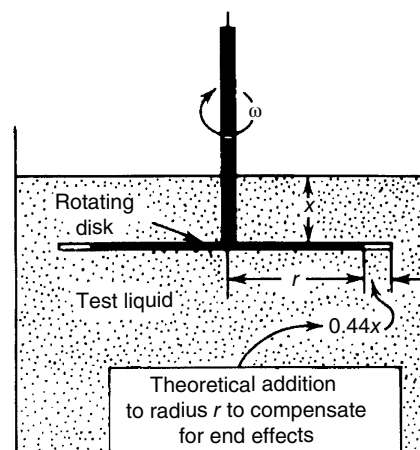


**Figure 3.7** Schematic representation of cone and plate viscometer geometry. Source: Schoff (1991). Reproduced with permission of John Wiley & Sons.

*rheometers* that are small, heavy-duty mixers. The test sample is confined to a relatively small space and subjected to intense mixing by dual rotors in the form of sigma-shaped blades. A dynamometer measures the work input. The speed is set by a tachometer. The newer instruments are computerized. These instruments were originally designed for studying the molding of plastics but are also used in studying the effect of pigments on viscosity. Heat buildup can be substantial with high viscosity fluids. A micro-twin-screw rheometer is available in which the rpm of the screws can be varied over a wide range, thereby permitting measurement of shear stress as a function of rpm.

### 3.3.3 Rotating Disk Viscometers

*Rotating disk viscometers* have a motor that rotates a disk immersed in a liquid over a range of rpm, and the resulting torque is measured. A schematic diagram is shown in Figure 3.8. The instruments must be calibrated with standards. Measurements of the sample and standards should be made in containers having the same dimensions, since the response can be affected by the distance of the disk below the surface of the liquid, above the bottom of the container,



**Figure 3.8** Schematic drawing of a disk viscometer. Source: Patton (1979). Reproduced with permission of John Wiley & Sons.

and from the side walls. In reporting results, the rpm setting should always be specified. The instruments are sturdy and relatively inexpensive, although they must be recalibrated periodically. Newer models have touch screen controls and computer interfaces. When properly used, rotating disk viscometers provide relatively accurate viscosity measurements for Newtonian liquids. For non-Newtonian liquids, the viscosity reading represents an average response corresponding to the viscosities resulting from a span of shear stresses.

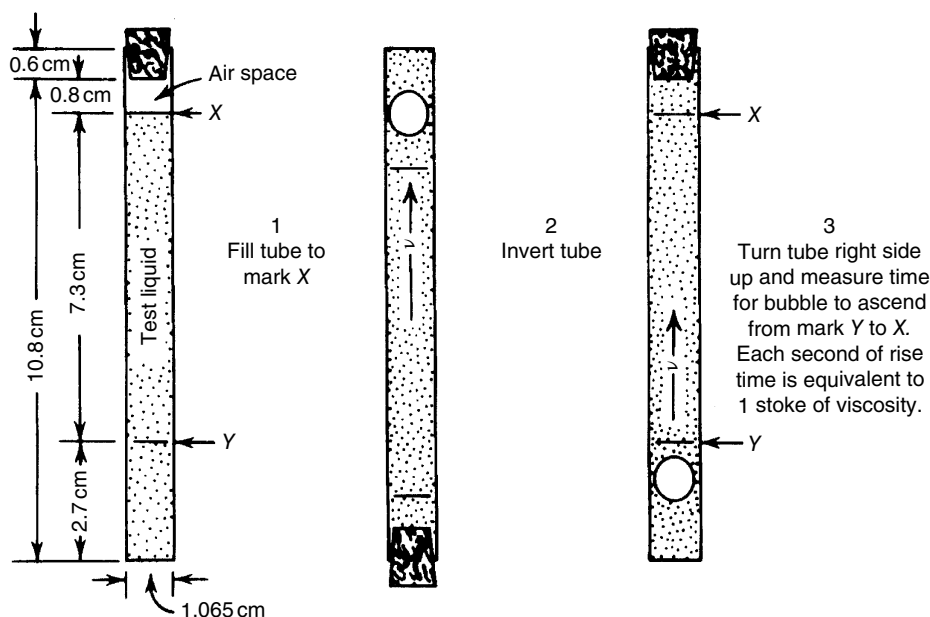
Rotating disk viscometers can detect whether a liquid is shear thinning or shear thickening by measurements carried out at different rpm settings. They can detect thixotropy by a change in response over time at the same rpm setting. Useful comparisons of thixotropic properties can be obtained by applying a high shear rate, then suddenly reducing the rate of shear to a lower value, and measuring the time required for the viscosity to reach equilibrium at that lower rate.

Several types of viscometers are designed for production use; in some circumstances viscosity can be monitored continuously.

### 3.3.4 Bubble Viscometers

Bubble viscometers are widely used in quality control to approximate the viscosity of solutions of resins (Section 15.5.2). The measurement is based on the rate of rise of an air bubble in a tube of liquid; the higher the viscosity, the slower the bubble rises. A glass tube is filled with a liquid to a graduation mark and stoppered so that a definite amount of air is enclosed at the top as shown in Figure 3.9. The tube is placed in a thermostatic bath and kept there long enough for the temperature to equilibrate. Equilibration is slow but is essential if meaningful measurements are to be made. The tube is then inverted, and the



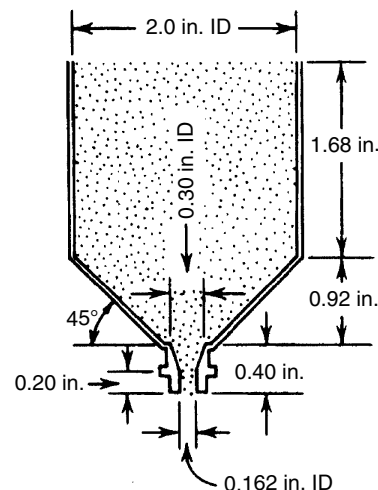


**Figure 3.9** Determination of viscosity with a bubble tube. Source: Patton (1979). Reproduced with permission of John Wiley & Sons.

time required for the air bubble to travel between two calibration marks on the tube is measured. Provided the length of the bubble is greater than its diameter, the rate of rise is independent of the bubble size. Density of the liquid affects the rate of rise of the bubble, so kinematic viscosity is measured. Sets of standard tubes are designated as A, B, C, and so on; after Z, tubes are designated as  $Z_1$ ,  $Z_2$ , and so on. Kinematic viscosities range from about  $10^{-5}$  to  $0.1 \text{ m}^2 \text{ s}^{-1}$ . Bubble viscometers are only appropriate for Newtonian transparent fluids. They are low in cost and simple to use. If the bubble has a tail, the resin is approaching gelation.

### 3.3.5 Efflux Cups

The most widely used control device for measuring flow of industrial coatings, especially for spray application, is the *efflux cup*. A variety of efflux cups is available. Schoff (1988, 1991) compares about two dozen of them. A schematic diagram of one of the most common efflux cups, the Ford No. 4 cup, is shown in Figure 3.10. One holds a thumb over the hole in the bottom of the cup, fills the cup with coating, removes the thumb, and then determines the time at which there is a break in the stream of coating flowing through the hole. The result is expressed in seconds. The data should not be converted into kinematic viscosity numbers, since a significant amount of the force is converted into kinetic energy, especially with low viscosity coatings. The method is not appropriate for non-Newtonian liquids, although efflux cups are frequently used for coatings that exhibit a small degree of shear thinning. Despite their limitations, efflux cups are useful quality control devices. They



**Figure 3.10** Schematic diagram of a Ford No. 4 efflux cup. Source: Patton (1979). Reproduced with permission of John Wiley & Sons.

are low in cost, rugged in construction, and easily cleaned. Results are simply and quickly obtained, but reproducibility is poor, reportedly in the range of only 18–20% (Schoff, 1991).

The proper way to use an efflux cup to control viscosity for spraying, for example, is to adjust the viscosity of the coating by solvent addition until the coating sprays properly and then measure the time it takes to flow through the efflux cup (see aforementioned paragraph). This time can then be used as the standard for spraying that particular coating through that spray gun at that distance from the object being sprayed. Proper efflux cup flow times for

spraying vary with different coatings for a given application system and with different application systems for a given coating.

### 3.3.6 Paddle Viscometers

The *Stormer viscometer* has been widely used for architectural paint formulation. The instrument paddle is immersed in the paint and rotated at 200 rpm. The force required to maintain this rotation rate is measured by adding weights to a platform at the end of a cord over a pulley connected by a gear train to the paddle. A schematic diagram is shown in Figure 3.11. The weight loaded is converted into *Krebs units* (KU) by an arbitrary conversion scale. Originally, a KU value of 100 was considered to correspond to good brushing consistency. In current practice, paints are usually formulated with somewhat lower KU. The instrument is of little utility with Newtonian fluids; and the readings have no real meaning for non-Newtonian fluids, which include most architectural paints. Even when used only for quality control, the paddle viscometer is not satisfactory.

The proper way to establish the flow properties for a trade sales paint is to apply the paint with a brush or roller and adjust the viscosity until the best compromise of such properties as ease of brushing, leveling, sagging, settling, and so forth has been achieved. Having done this work, then a quality control test can be set up. Appropriate quality control instruments are cone and plate viscometers (some

of which are reasonable in cost) or, lacking that, rotating disk viscometers. Unfortunately, Stormer viscometers are widely used. The director of research of a large manufacturer of trade sales paints in the United States said some years ago that the Stormer viscometer was responsible for setting back the formulation of one-coat hiding latex paints by 20 years.

## 3.4 SHEAR VISCOSITY OF RESIN SOLUTIONS

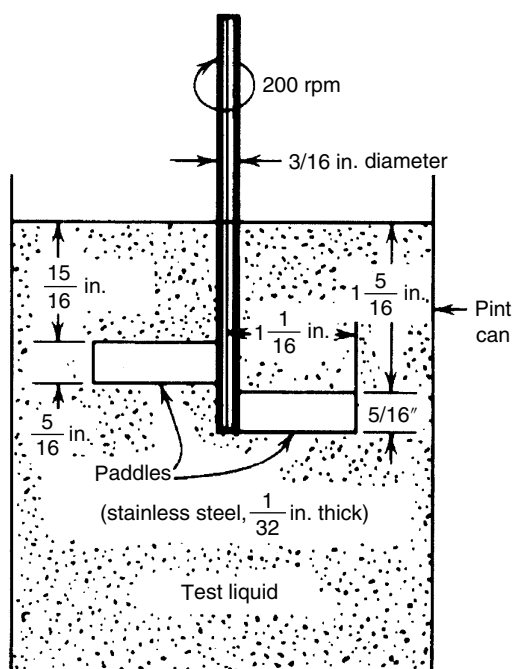
The viscosity of liquids depends on free volume availability. To put it somewhat simplistically, there are free volume holes rapidly opening and closing in a liquid; molecules move randomly through these free volume holes. When a stress is applied, movements in the direction that relieves the stress are favored, and the liquid flows. Therefore, factors that control viscosity of resin solutions are those that control the availability of free volume. Many coatings are based on solutions of polymers or oligomers. The variables affecting the flow behavior of these concentrated solutions are not fully understood. The variables that govern the flow of very dilute polymer solutions have been extensively studied and are better understood. Factors affecting the flow of dilute solutions are discussed in Section 3.4.2, and factors affecting the flow of more concentrated solutions are discussed in Section 3.4.3.

### 3.4.1 Temperature Dependence of Viscosity

Temperature dependence of viscosity for a range of low molecular weight (MW) resins and their solutions has been shown to fit a Williams–Landel–Ferry (WLF) equation (Section 2.3) (Wicks et al., 1985; Toussaint and Szigetvari, 1987; Jones, 1996; Haseebuddin et al., 1997). In Eq. 3.2,  $T_r$ , the reference temperature, is the lowest temperature for which experimental data are available, and  $\eta_r$  is the viscosity at the reference temperature,  $T_r$ . Except for very dilute solutions, data fit Eq. 3.2 when  $\eta_r$  is assumed to be  $10^{12}$  Pa·s (Wicks et al., 1985):

$$\ln \eta = \ln \eta_r - \frac{c_1(T - T_r)}{c_2 + (T - T_r)} \cong 27.6 - \frac{A(T - T_g)}{B + (T - T_g)} \quad (3.2)$$

For higher MW polymers at temperatures above  $T_g + 100^\circ$ , the temperature dependence of viscosity approximately fits an Arrhenius equation, shown in Eq. 3.3, where  $E_v$  is the activation energy for viscous flow. (Note that the Arrhenius  $A$  value in Eq. 3.3 is not the same as constant  $A$  in Eq. 3.2.)



**Figure 3.11** Schematic diagram of a paddle viscometer. Source: Patton (1979). Reproduced with permission of John Wiley & Sons.

$$\ln \eta = K + B/T = \ln A + \frac{E_v}{RT} \quad (3.3)$$

Using the data available for low MW resins and their solutions, Arrhenius plots of  $\ln \eta$  as a function of  $1/T$  have been found to be curved and not linear (Wicks et al., 1985; Jones, 1996). On the other hand, the data do fit a WLF equation. From a practical viewpoint, the differences in the models are small if the temperature range is small. However, over a wide range of temperatures, the differences are relatively large.

A major factor controlling viscosity of resin solutions is  $(T - T_g)$ , but it is not the only factor. When the differences between  $T_g$ s are small, differences in WLF constants  $A$  and  $B$  may overshadow the small difference in  $(T - T_g)$ . Constant  $A$  depends on the difference in thermal expansion coefficients above and below  $T_g$ , but no studies have been reported on the structural factors that control these coefficients. Constant  $B$  is the value of  $(T_g - T)$  at which viscosity goes to infinity. The so-called universal value of this constant is 51.6°C, but the “constant” varies considerably with composition. No studies have been reported on the relationship between structure and the value of constant  $B$ .

Generally, in designing resins, it is reasonable to predict that a lower  $T_g$  will lead to a lower viscosity of the resin and its solutions. (See Section 2.1.2 for discussion of the factors controlling the  $T_g$  of polymers.) Linear poly(dimethylsiloxanes) have low  $T_g$ s and low viscosities. Linear polyethylene glycols have almost as low  $T_g$ s and viscosities. Poly(methyl methacrylate) resin solutions have higher  $T_g$  values and viscosities than comparable poly(methyl acrylate) resin solutions. BPA epoxy resins have higher  $T_g$  values and viscosities than corresponding hydrogenated derivatives. Exceptions to this generalization on the effect of  $T_g$  have been reported for some high solids acrylic resins (Section 8.2.1). Acrylic resins made with a comonomer that has a bulky group, such as 3,3,5-trimethylcyclohexyl methacrylate (Kruithof and van den Haak, 1990) or isobornyl methacrylate (Wright, 1996), are reported to have low viscosities at high solids even though their homopolymers have high  $T_g$  values; no explanation of this effect has been advanced.

### 3.4.2 Dilute Polymer Solution Viscosity

Measurement of viscosities of very dilute solutions of polymers played an important part in the early development of polymer science, since they were the earliest method of estimating MW. However, this method is obsolete in coatings technology, so the rather complex subject is not covered here. It is described in previous editions and in polymer chemistry textbooks, such as Allcock and Lampe (1990).

### 3.4.3 Concentrated Polymer Solution Viscosity

Concentrated solutions of polymers behave quite differently than dilute solutions. The binders of solventborne coatings are usually concentrated solutions of polymers, and their viscosity affects application behavior. Viscosity of such solutions is influenced by many factors—a partial list:

- Concentration
- MW of the polymer and its MW distribution
- Polymer structure—linear versus branched
- Viscoelastic effects
- Viscosity of the solvent(s)—surprisingly an important variable
- Hydrogen bonding between polymer molecules and with solvent
- Temperature
- Changes in solvent composition during and after application
- Effects of pigments
- Effects of additives such as thixotropes

It is no wonder that there have been relatively few fundamental studies of the factors controlling viscosity of more concentrated solutions of polymers and resins, such as those used in the coatings field. Several empirical relationships have been proposed, such as the concentration dependence of *relative viscosity*, shown in Eq. 3.4, in which  $w_r$  is the weight fraction of resin and  $k$ 's are the constants:

$$\ln \eta_r = \frac{w_r}{k_1 - k_2 w_r + k_3 w_r^2} \quad (3.4)$$

Relative viscosity is a unitless number that expresses the ratio of solution viscosity to solvent viscosity. By studying relative viscosity, researchers can eliminate the important variable of solvent viscosity (see succeeding text) and gain some insight into the behavior of more concentrated solutions. Nonlinear regression analysis of the limited number of sets of data available in the literature in 1985 fit Eq. 3.4 over a wide range of concentrations (Wicks et al., 1985). Even with this many constants, there is some systematic deviation from the model at very low concentrations. Constant  $k_1$  is the reciprocal of *weight intrinsic viscosity*,  $[\eta]_w$ , which, although formally unitless, is based on the number of grams of solution containing a gram of resin. Weight intrinsic viscosity can be converted into the more familiar volume intrinsic viscosity  $[\eta]$  by dividing the density of the solution at the concentration  $w_r = k_1$ . No physical significance of the other two constants,  $k_2$  and  $k_3$ , has been elucidated; they are presumably related to further solvent–resin interactions and to free volume availability.

Over narrower ranges of concentration, the experimental data reasonably fit the simpler Eq. 3.5. The even simpler Eq. 3.6 has been extensively used to calculate approximate relative viscosities over a range of concentrations in which viscosities range from around 0.01 to 10 Pa·s:

$$\ln \eta_r = \frac{w_r}{k_1 - k_2 w_r} \quad (3.5)$$

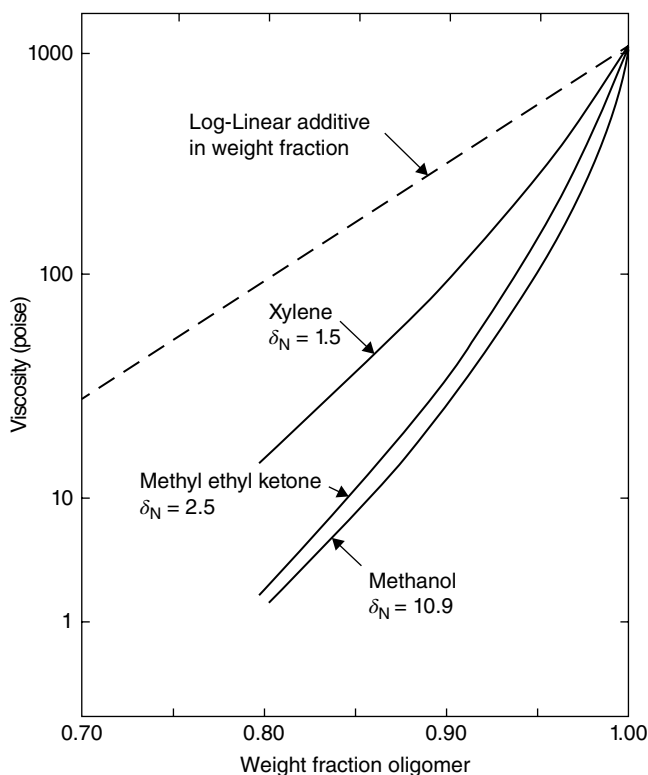
$$\ln \eta_r = \frac{w_r}{k_1} = [\eta]_w w_r \quad (3.6)$$

Relative viscosity of dilute solutions of polymeric resins increases as the solvent gets “better” in the sense of their solvency. However, in concentrated solutions, relative viscosity is often higher in poor solvents than it is in good solvents. In good solvents, there are stronger interactions between solvent molecules and resin molecules than in poor solvents. In very dilute solutions, this signifies that the chains become more extended and sweep out larger hydrodynamic volumes in good solvents than in poor solvents. However, in more concentrated solutions, flow of resin molecules is constrained by the hydrodynamic volumes swept out by neighboring resin molecules. In theory, when interaction between solvent and resin is stronger than resin–resin interactions, the molecules can flow readily through the hydrodynamic volumes of neighboring molecules (provided the free volume is adequate), and relative viscosity is lower. When, on the other hand, resin–resin interactions are stronger, transient polymer clusters form and relative viscosity increases. In solutions containing good solvents, flow is generally Newtonian. In many cases, more concentrated resin “solutions” flowing in poor solvents behave somewhat like dispersed systems; they are non-Newtonian because shear can break up or distort resin clusters.

Although the difference in the viscosity of resin solutions in good and poor solvents is reasonably well understood, there is little definitive work in the literature on comparisons between solutions in various good solvents in which some of the solvents are “better” than others. Erickson (1976) studied relative viscosities of solutions of several low MW resins in a range of solvents. He concluded that relative viscosities decrease as one changes from a very good solvent to a good solvent, pass through a minimum, and then increase rapidly in very poor solvents. Equations 3.4–3.6 relate relative viscosity to concentration, the hydrodynamic volume of the isolated resin molecule plus its associated solvent molecules. Hydrodynamic volume is a factor in determining the viscosity not just of very dilute solutions but also of more concentrated ones. In changing from a very good to a less good solvent, the equations predict that intrinsic viscosity and, hence, relative viscosity should decrease; this prediction conforms with

Erickson’s hypothesis. The range of error in Erickson’s work is not small enough to establish his conclusions beyond doubt.

Solvent effects on hydrogen bonding between resin molecules can be substantial (Schoff, 1999). Figure 3.12 shows the viscosities of solutions of an acrylated epoxidized linseed oil in three solvents chosen because of their similar viscosities but very different hydrogen-bonding characteristics (Hill and Wicks, 1982). The resin molecules have multiple hydroxyl groups. Note that the viscosities of the xylene solutions are highest. Xylene is a poor hydrogen-bond acceptor and hence promotes intermolecular hydrogen bonding between the resin molecules. Methyl ethyl ketone (MEK) is a good hydrogen-bond acceptor and reduces the viscosity more effectively than xylene by reducing intermolecular hydrogen bonding. Although methanol is a much stronger hydrogen-bonding solvent than MEK, it is only marginally better at reducing viscosity. Since methanol is both a hydrogen-bond donor and acceptor, methanol can possibly bridge resin molecules by functioning as a hydrogen-bond donor with one resin molecule and a hydrogen-bond acceptor with the other. Such bridging would counteract the effectiveness of viscosity reduction.



**Figure 3.12** Viscosity reduction of a hydroxy-functional UV-curable oligomer with xylene, MEK, and methyl alcohol compared with predicted viscosity if the viscosity reduction were a log-linear additive relationship by weight. Source: Hill and Wicks (1982). Reproduced with permission of Elsevier.