

EUROPEAN COATINGS TECH FILES



Brock | Groteklaes | Mischke

# European Coatings Handbook



# eBook

Vincentz Network GmbH & Co KG

Thomas Brock  
Michael Groteklaes  
Peter Mischke

# **European Coatings Handbook**

2<sup>nd</sup> revised edition

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**Thomas Brock, Michael Groteklaes, Peter Mischke**

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Please ask for our book catalogue

Vincentz Network, Plathnerstr. 4c, 30175 Hannover, Germany

Tel. +49 511 9910-033, Fax +49 511 9910-029

E-mail: [books@european-coatings.com](mailto:books@european-coatings.com), [www.european-coatings.com](http://www.european-coatings.com)

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## Foreword

Anyone working in the coatings sector, whether in manufacturing or processing, knows – or will soon observe if they are new to the business – that an extremely broad knowledge base is a prerequisite for mastering this unique protective and finishing material. Coating chemistry in its widest sense, and especially polymer science, is of central importance. However, today's coatings specialist also requires a knowledge of process engineering in relation to the use of production or application equipment, an understanding of materials science in regard to substrate materials and more generally in terms of the quality of the paint system, and finally a familiarity with environmental and safety aspects.

Very few teaching institutions are able to offer a training programme that is specially designed to cover such an extensive field of knowledge. The Niederrhein University of Applied Sciences in Krefeld, Germany, is one of these – an institution with a long tradition and good reputation, whose name comes up repeatedly in discussions with leading figures in the coatings sector. A good many of them proudly and gratefully acknowledge that the framework for their career was built in Krefeld.

For this reason the publishers and editors are extremely grateful to the current teaching faculty, represented here by Peter Mischke, Michael Groteklaes and Thomas Brock, for deciding to make a large part of the Krefeld curriculum available to practitioners in the field. The authors have produced a contemporary handbook of coating technology. Each was responsible for around a third of the content, based on his own specialist subject areas and written in roughly the above sequence. The work merits the title of handbook for two reasons: firstly because of its solid theoretical basis, augmented by “in-depth” explanations (shown on a grey background) where necessary, and secondly because of its consistently relevant use of practical references to exemplify its themes. These features are underpinned by a constant awareness of emerging developments in the coatings sector, which remains as dynamic as ever.

The book covers the principles of raw materials, manufacture, application and testing of coatings; as a handbook, however, its principal aim is to illustrate and to create connections. Naturally only the essential themes could be addressed within the stated limits of the book. It does not wish or claim to be complete; the authors felt that it was more important to explain the foundations and principles as clearly as possible. For this reason also, the book does not contain all of the material taught to budding coating engineers at Krefeld; this would far exceed the scope of a single-volume handbook.

This work is intended to fill a gap in the current specialist literature: as an accompanying handbook it is intended on the one hand to provide a trainee or student with the basic knowledge to form a solid foundation for a closer study of coating technology; on the other hand it is designed to help people from other disciplines – scientists, engineers, business people – to find out more about this subject which, in its fascinating diversity, is difficult to assimilate. Experienced coating specialists may use it to refresh or to extend their knowledge. It may also enable them to take a glance over the “garden fence” into neighbouring disciplines, into the raw materials used every day or into the application and usage of coating materials.

The authors hope that also the second edition of the book will meet the expectations of the reader and stimulate him (or her) to take it out of the shelves very often.

No book is ever perfect. – There will certainly be specialists amongst our readers who can offer changes or improvements to particular topics; the authors will be grateful for any constructive suggestions!

Krefeld, August 2009

Peter Mischke, Michael Groteklaes and Thomas Brock



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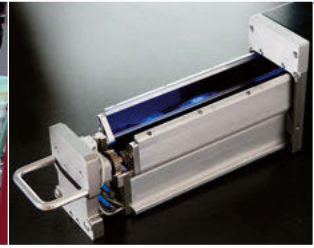
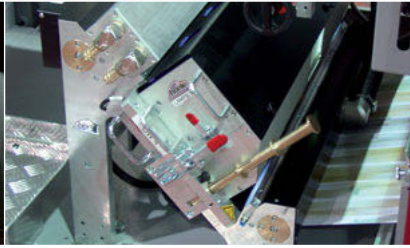
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**Organisation**

NürnbergMesse GmbH  
Messezentrum  
90471 Nuremberg  
Germany  
Tel +49 (0) 911.86 06-84 52  
Fax +49 (0) 911.86 06-82 87  
[ecs@nuernbergmesse.de](mailto:ecs@nuernbergmesse.de)



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# 1 Introduction

## 1.1 Historical perspective

The earliest known use of paint dates back around 30,000 years. People used mixtures of coloured earth, soot, grease and other natural substances to ornament their bodies and to decorate their homes and places of worship, one such example being the cave paintings discovered in southern France and northern Spain.

### *In ancient times...*

The advanced civilisations of the Egyptians (from 4000 years BC), Greeks and Romans used sophisticated painting techniques to decorate or to identify vessels, statues, tools and buildings. Raw materials included vegetable gums, starches, hide glue, milk (products), beeswax, charcoal and various minerals. Natural dyes such as indigo, purple and madder were used to dye textiles, fibres, wood, paper and leather.

In contrast to the decorative or colour-giving use of paints described so far, the art of lacquerwork was developed in China from around 2000 years before Christ, to produce smooth and glossy surfaces. The lacquers were based on the sap of the Chinese rhus tree and, in addition to their decorative effect, they also had a protective function. Raw materials such as balsams and resins, vermilion and ultramarine, came predominantly from India. The word “lacquer” itself stems from the term “Laksha”, from the pre-Christian, sacred Indian language Sanskrit, and originally referred to shellac, a resin produced by special insects (“lac insects”) from the sap of an Indian fig tree.

Seafaring brought with it another important area of application for coatings. The fourth century before Christ saw a wave of migration spreading from Asia Minor as far as England and Scandinavia – some of it by land and some by sea. The wooden ships that carried the migrants were made watertight with mixtures of non-drying (non-curing) oils and tree resins or rock asphalt.

Leaping further forward in time, around the year AD 1100 the German goldsmith and monk *Roger von Helmarshausen (Theophilus)* described the manufacture of a coating by boiling linseed oil with molten amber. This process, known as paint boiling, continued to develop and by the 17<sup>th</sup> century there were numerous recipes for coatings made from a variety of natural resins, linseed oil and spirit.

### *In modern times ...*

In the 18<sup>th</sup> century the Industrial Revolution brought about a dramatic rise in the demand for paints and coatings. In particular, the increasing numbers of goods and buildings produced from rust-prone iron needed to be treated to protect them against weathering. Furthermore, countries with a strong seafaring economy required large quantities of marine paints. The first paint factories, which appeared in England in 1790, grew out of the larger paint workshops. They were followed by factories in Holland and later in Germany and other countries.

With the exception of a few synthetic pigments already produced on an industrial scale (Berlin blue, cobalt blue, mineral green, chromium yellow), the raw materials for coatings were all of natural origin even in the 19<sup>th</sup> century. A distinction was made between “volatile paints”, “varnishes” and “long-oil paints”. This last group were manufactured by boiling resins with drying oils in “brewing kettles”, adding pigments if required. The addition of pigments became increasingly mechanised – first using cone mills then, from the early 20<sup>th</sup> century, cylinder mills. One weak point of these products was their extended drying time; it could take several weeks to paint an entire coach or car.

### ***In the 20<sup>th</sup> century...***

Huge innovations took place after the turn of the century. In terms of coating technology, the following advances were particularly important:

- the development of synthetic polymer chemistry
- the invention of the production line by *Henry Ford* (1913) and the mass production of cars arising from it.

In response to the demand for faster coating technologies, the spraying of coatings based on cellulose nitrate (nitrocellulose) was introduced.

In 1907 the first entirely synthetic resins, phenol-formaldehyde condensates (“Bakelite”) were launched on the market. These were followed in rapid succession by vinyl resins, urea resins and, from the 1930s onwards, alkyd resins, acrylic resins, polyurethanes and melamine resins. Epoxy resins were introduced in the late 1940s. Titanium dioxide established itself as the leading white pigment when it went into mass production in 1919.

These developments in *coating chemistry* were paralleled (finally) by advances in *coating technology*. The various methods of brush application and spraying were supplemented by electrodeposition, electrostatic coating and powder coating techniques. Ambient air drying was joined by infrared and radiation drying methods (UV, electron beam), and the automation of coating processes continued to advance. It is also worth mentioning environmental technologies for the control of air and water pollution and for waste reduction.

Measuring techniques for coatings can be regarded as the pillar supporting modern coating technology. The reproducible quantifiability of flow properties, optical characteristics, drying behaviour, adhesion, anti-corrosion action and many other properties of coating materials and/or coatings is the precondition for selective product development and the practical usage of products. Many companies now sell instruments for performing the various measuring techniques – most of them governed by standards – for coatings and related products.

At the start of the 21<sup>st</sup> century, there do not appear to have been any clear-cut revolutionary innovations in the coatings sector, but rather a great many individual developments have been aimed at improving and attaining highly specific functional properties and effects. The primary development goal of the last two decades, namely enhanced environmental compatibility of products, now seems to be taking a backseat (see section 1.2), aside from a general tendency to substitute renewable materials for mineral-oil-based products, wherever possible, in the long term.

To recap and to summarise, we can see that:

*The production and use of paints and coatings has developed from a prehistoric art form via an empirical craft into the multi-disciplinary, highly complex coating technology of today.*

## ***1.2 The economic importance of paints and coatings***

The coatings industry is a medium-sized sector, albeit with a growing tendency towards internationalisation. In 2005 some 250 paint factories in Germany employed around 20,500 people. In 2007 they produced over 2.4 million tonnes of coatings, paints and thinners, with an overall worth of approximately 5 thousand million euro. In terms of value this equates to about 1 % of Germany’s commodities production. The tonnage produced is the equivalent of 4000 fully laden trains.

The economic benefit of these products only becomes clear if we look at their applications. The overwhelming majority of coatings and paints have, in addition to their optical or aesthetic function, a protective and hence value-retaining function. 2.0 million tonnes of paint could cover and therefore protect against corrosion, weathering and/or mechanical damage an area of around 3,000 km<sup>2</sup> (roughly the size of Oxfordshire) with a 200 µm thick (dry) coat.

The overall quantity of coatings produced covers a vast range of product types:

- emulsion paints and renderings: approx. 45 %
- solvent-based coatings: approx. 21 %
- powder coatings: approx. 3 %
- electrodeposition coatings and water-thinnable industrial coatings approx. 2 %
- other miscellaneous coatings: approx. 29 %

In the breakdown above, the proportion of powder coatings seems too low, since one part by weight of powder coating is equivalent to two to three parts of wet paint.

We will end with a look at the three environmentally friendly coating classes: water-based coatings, powder coatings and high solid coatings (see Figure 1.1). Annual production of high solid coatings and especially powder coatings increased steadily during the 1990s, whereas water-based volumes stagnated. The current overall trend is negative, with production of water-based coatings seemingly having collapsed altogether. In view of manufacturers' efforts to be able to supply water-based products, this observation comes somewhat as a surprise. It would

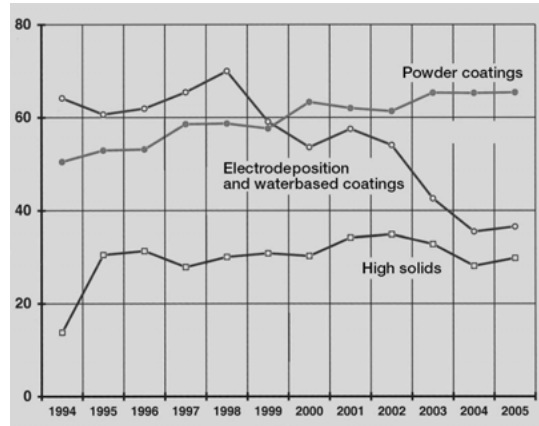


Figure 1.1: Evolution in production of environmentally friendly coatings 1995-2006 in Germany. (source "besser lackieren!" Jahrbuch 2008, Vincentz Network 2007)

also appear that more and more attention has been paid since 2000 to coating properties, such as new optical and haptic effects, enhanced scratch resistance and easy-to-clean properties, all grouped together under the fashionable term "performance", frequently in combination with the buzzword "nanotechnology". For the sake of completeness we should add that there are other low-solvent or solvent-free products, e.g. radiation-curing coatings, solvent-free two-component systems and paint-like emulsion coatings.

### 1.3 Classification and material structure of coatings

The title of EN ISO 4618 is "Paints and varnishes - Terms and definitions". In Germany, this standard has been supplemented by DIN 55945 (2007-03) "Paints and varnishes - Additional terms and definitions to EN ISO 4618".

A **paint** is defined in the standard as a product in liquid or paste form that is applied primarily by brushing, rolling or spraying.

A product based on organic binders (modified natural substances, synthetic resins), which when applied to a substrate produces a cohesive, virtually water-impermeable (non-absorbent), protective and possibly decorative film, is called a **coating material**. The coating itself is properly termed a **coating system**; it comprises the **coating film**.

Products not covered by this definition include (polymer) emulsion paints, silicon emulsion paints and distempers. Printing inks are naturally also excluded.

A **coating powder** is a powder coating which produces a film after it has been applied to and fused onto the substrate. (Since coating powders are not in liquid or paste form, they do not by definition belong to the category of paints). The term "paint" in the trade sense refers to a pigmented coating ("paint") or alternatively to a pigmented varnish ("gloss paint").

Coating material	
non-volatile matter	volatile matter
pigments fillers film-formers non-volatile additives	solvents or dispersants volatile additives (any elimination products from stoving)

Other materials covered by the standard include fillers, synthetic resin renderings and floor coating compounds.

All coating materials are based on the structure shown in the table below. Not every coating material necessarily contains all the components listed. (A clear varnish does not contain any pigments or fillers, whilst a powder coating contains no solvents).

**Pigments**

Very finely dispersed colouring and/or corrosion-inhibiting powder that is practically insoluble in the application medium.

Examples include titanium dioxide, carbon black, pearlescent pigments, zinc phosphate.

**Fillers**

Powders that are practically insoluble in the application medium and which impart or improve particular technological properties and give the coating material greater volume (body).

Examples include chalk, talcum, cellulose fibres.

**Film formers**

Macromolecular or macromolecule-forming substances responsible for film formation.

Examples include chlorine rubber, alkyd resin, polyester/polyisocyanate blends (two-component systems), polyester acrylate (radiation-curable).

**Additives**

Substances that are generally added in small quantities and which have particular chemical or technological effects.

Examples include hardening accelerators (catalysts), thickeners, dispersants, flow control agents, flattening agents, preservatives.

**Solvents**

Liquids or blends of liquids that are able to dissolve the film former(s).

Examples include butyl acetate, butyl glycol, white spirit, water.

Also known as *thinning agents* or *thinners* when used to adjust processing characteristics (viscosity).

**Dispersants**

Liquids that do not dissolve the film former(s) but instead hold them in a fine, microheterogeneous dispersion (or emulsion).

Examples include water and, in non-aqueous dispersions, hydrocarbons.

One further term, which is frequently used incorrectly, is “binder”. According to the standards, the **binder** is the non-volatile part of the coating material, excluding pigments and fillers but including non-volatile additives such as plasticisers and driers. In common usage, however, binder is frequently used to mean film former.

## 1.4 *Technology of paints and coatings* (“Coating technology”)

In broad terms the whole teaching of coatings (and paints) – as is the case in this book – can be regarded as “coating technology”. In more precise terms, however, coating technology – as opposed to coating chemistry – refers to the process technology of the manufacture and processing of coatings and paints, where processing can be subdivided into the processes of application (spraying, dipping, brushing, etc.) and of drying or curing (air drying, stoving, radiation curing).

A typical problem in coating technology, which is representative of many others, is the balance in a coating between spreading and dripping. After a coating has been applied it should normally form a uniform surface. In order to achieve this, any irregularities arising from its application, such as brush strokes, build-up of droplets from spraying or roller marks, should even out naturally if the coating is still sufficiently flowable, i.e. not too dry. On the other hand, however, the flowable coating must not drip when applied to vertical surfaces, since this would lead to “running”, “sagging” and other unattractive forms of curtaining. We can see that two conflicting properties are expected of the coating, and these can only be balanced by means of skilful formulation and adjustment of application conditions.

The following parameters are specifically involved in this problem:

- roughness of the substrate
- form and degree of the initial unevenness of the wet film
- evaporation behaviour of the solvent or solvent blend
- change in viscosity during evaporation
- rheological behaviour (Newtonian, pseudoplastic, thixotropic)
- surface tension (size and uniformity)
- slope of the surface in question.

This example not only illustrates the complexity of coating technology but also shows that the development of coatings and paints requires the properties of the material to be precisely adjusted to the particular technological conditions existing in individual coating workshops.

### Sources and references for Chapter 1

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## 2 *Raw materials for coatings*

### 2.1 *Film formers*

Film formers, which are frequently also referred to imprecisely as binders ( $\rightarrow$ 1.3), are polymers or oligomers (prepolymers) that are generally organo-chemical in nature and which polymerise as the coating cures. The role of the film former is to form a cohesive coating or paint film on a given substrate and – where relevant – to hold together or to embed the other non-volatile components of the coating, particularly the pigments and fillers. The film former thus constitutes the basis for the coating material in question.

Depending on their origin, film formers can be categorised into

- natural substances
- modified natural substances
- synthetic substances.

The importance of the product types increases through the above sequence. Unmodified natural substances are used in very few coatings now and never as the sole film former. With the exception of “bio-coatings” or “natural coatings”, natural film formers are now used primarily in certain printing inks. Before exploring the chemistry and properties of individual film formers, it is important to establish a grounding in polymer science, which is covered in the section below.

#### 2.1.1 *General polymer science*

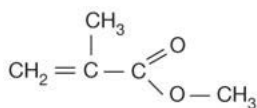
##### 2.1.1.1 *Basic concepts*

The following section introduces the basic concepts of polymer chemistry that are relevant to the field of coating film formers.

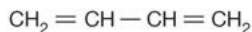
##### A **monomer**

is a substance consisting of small, reactive molecules that can be converted to a polymer through what is known as a polymerisation reaction (see below).

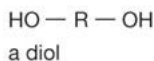
Examples:



methyl methacrylate  
(methacrylic acid methyl ester)

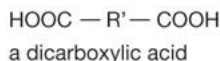


1,3-butadiene

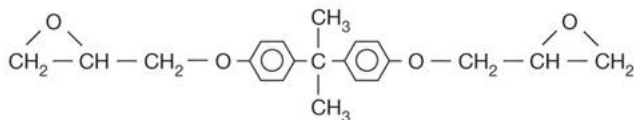


a diol

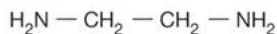
(R, R' = molecule skeleton, not otherwise specified)



a dicarboxylic acid



bisphenol-A-diglycidyl ether (BADGE)

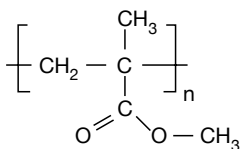


ethylene diamine

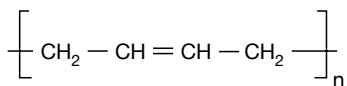
A **polymer** (macromolecular substance)

is a substance consisting of (very) long molecules (polymer or macromolecules) or extended molecule networks. Individual polymer molecules may have a molecular weight ranging from a few thousand to several million g/mol.

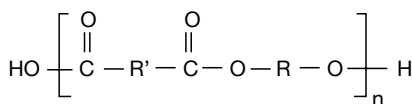
Examples:



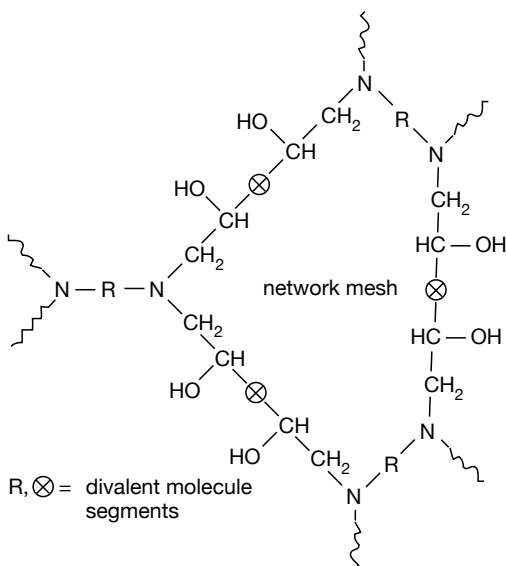
polymethyl methacrylate



1,4-polybutadiene



linear polyester



amine-cured epoxy resin  
(section from three-dimensional network)

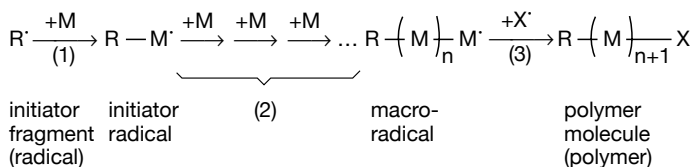
A relatively low-molecular polymer, up to a molecular weight of around 2000 g/mol, is classed as an **oligomer**.

*Polymerisation* is a chemical reaction in which one or more (different) monomers are converted into a polymer.

There are three basic types of polymerisation reactions, as briefly described below.

### • Addition polymerisation as a chain reaction

A polymer molecule is produced after a starting reaction, typically within a maximum of a few seconds, through the chemical bonding of numerous monomer molecules with no separation of by-products. This process can be formulated as shown below in relation to a radical polymerisation:



(1) Initiation reaction      (2) Propagation (very rapid)

(3) Chain termination      M = monomer molecule      X<sup>·</sup> = terminating radical

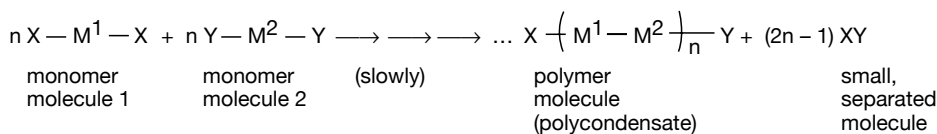
In chemical kinetics terms, this is a chain reaction in that one propagation step inexorably draws the next immediately after it.

Acrylic resins and polymer dispersions are examples of polymerisation products.

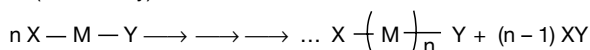
### • Condensation polymerisation

The monomer molecules react relatively slowly in discrete, mutually independent propagation steps to form the polymer, causing small molecules (mainly water) to be separated. The macromolecules are formed successively over a long period of time, generally several hours.

Schematic reaction equation (for bifunctional monomers):



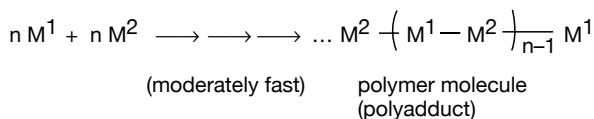
or (more rarely)



The synthesis of a polyester (see above) or a melamine resin proceeds as a condensation polymerisation with separation of water.

### • Addition polymerisation as a stepwise reaction

The reaction proceeds in approximately the same way as a condensation polymerisation, but with no separation of molecules. Schematic reaction equation (for bifunctional monomers):



M<sup>1</sup>, M<sup>2</sup> = bifunctional monomer molecules

The crosslinking of an epoxy resin with an amine (see above) and the formation of a polyurethane from a polyol and a polyisocyanate are examples of stepwise addition polymerisation reactions.

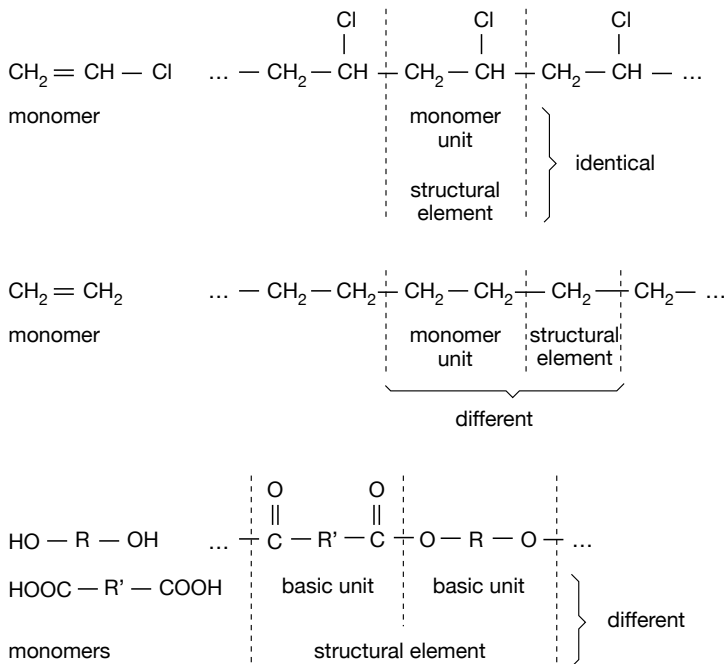


The products of polymerisation reactions are known as *polymers*, *polycondensates* or *polyadducts*, according to the reaction type.

*Monomer unit* or *basic unit* is the name given to a section of a polymer molecule produced from a monomer molecule. (The monomer changes on transition into the polymer).

The term *structural element* (*structural unit*, *constitutional repeating unit*) refers to the smallest possible chain section of a polymer molecule; when arranged in series – up to the end groups – these constitute the complete polymer molecule. Only simple polymer molecules with very regular structures, such as homopolymers (see below), contain a structural element. Most synthetic coating film formers are random copolymers (see below) and therefore by definition do not have any structural elements.

Examples:



### Linear, branched, crosslinked polymers

As Figure 2.1 illustrates, *linear polymers* consist exclusively of chain-like, unbranched molecules. *Branched polymers* consist of branched molecular chains; where possible, one should distinguish between the main chain and side chains. *Crosslinked polymers* consist of three-dimensional molecular networks. The average mesh width of the network can also be expressed by the term *crosslink density* ( $\rightarrow$  2.1.1.4).

According to these structures, polymers can be divided into the following three types:

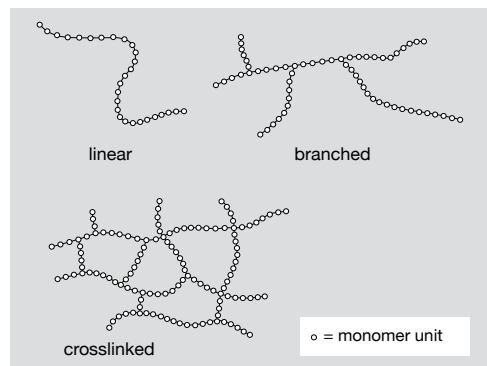


Figure 2.1: Linear, branched and crosslinked molecules/polymers

- *Thermoplasts*

These are linear or branched, soften at elevated temperatures, and are soluble in suitable solvents<sup>1)</sup>

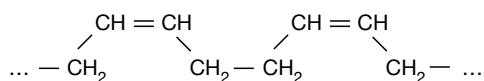
- *Elastomers*

Loosely crosslinked<sup>2)</sup>, rubbery-elastic (not plastic), insoluble in solvents, but readily swellable

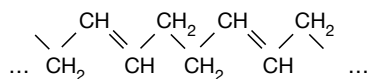
- *Thermosets*

These are closely crosslinked, scarcely softening at elevated temperatures, insoluble in solvents but slightly swellable

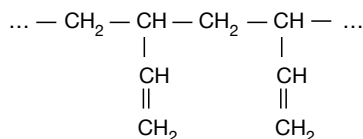
In the case of polymers of dienes, i.e. of molecules with two conjugated double bonds, a distinction must be made between *cis*- and *trans*-polymers and between 1,2- and 1,4-polymers as shown by way of example in the formulae below for 1,3-butadiene:



*cis*-1,4-polybutadiene



*trans*-1,4-polybutadiene



1,2-polybutadiene

## Homopolymers, copolymers

Polymerisation of a single monomer produces what is known as a *homopolymer*. When two or more monomers are involved, we refer to a *copolymer*. The term *terpolymer* is also used to refer to a polymer produced from three monomers. Depending on the sequence of the various monomer units in a copolymer, we can distinguish between a *random* copolymer, an *alternating* copolymer, a *block* copolymer and a *graft* copolymer:

A A A B A A B B B B A B A A A B B A

A, B = monomer units

random copolymer

A B A B A B A B A B A B A B A B A

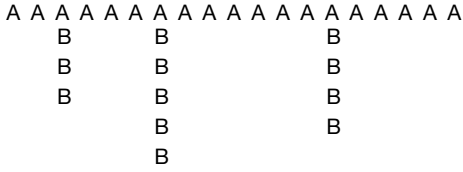
alternating copolymer

A A A A A B B B B B B A A A A B B B

block copolymer

<sup>1)</sup> Apart from extreme exceptions such as PTFE

<sup>2)</sup> Uncrosslinked thermoplastic elastomers are a relatively new type of polymer.



#### graft copolymer

The structural features of polymer molecules described so far are grouped together under the collective term of *primary structures*. *Secondary* and *aggregate structures* develop because molecules form in various ways in a space and then congregate below one another.

#### 2.1.1.2 Degree of polymerisation, molecular weight, molecular weight distribution

Only an average value can be given for the size of the molecules of an engineering polymer, since polymerisation reactions lead to a random distribution of molecule sizes. The following two dimensions are conventionally used:

- Average degree of polymerisation ( $\bar{P}$ ):

Average number of monomer units (basic units) per polymer molecule

- Average molecular weight ( $\bar{M}$ ):

Average molecular weight of a polymer molecule

These two quantities are linked by the molecular weight of the monomer unit (in the case of homopolymers) or the average molecular weight of a monomer unit  $M_{\text{mono}}$  (in the case of copolymers):

$$\bar{M} = \bar{P} \cdot M_{\text{mono}}$$

It is more usual to quote the average molecular weight than the average degree of polymerisation.

There are a number of differently defined average values for the molecular weight of a polymer. The two most important are explained below.

*Number average:*

$$\bar{M}_n = \sum \left( \frac{N_i}{\sum N_i} \right) \cdot M_i = \frac{\sum N_i M_i}{\sum N_i}$$

where  $N_i$  is the number of molecules having molecular weight  $M_i$  and  $\sum N_i$  is the total number of molecules in the quantity of polymer under consideration.

The number average – mathematically expressed – is the arithmetic mean of the molecular weight.

*Weight average:*

$$\bar{M}_w = \sum \left( \frac{N_i M_i}{\sum N_i M_i} \right) \cdot M_i = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$

Since weight average considers not the number but the mass of the molecules, large molecules have a greater influence on the calculation of the average value than do the same number of small molecules. As a consequence, the weight average works out higher than the number average.

The greater the relative difference between the number average and the weight average (known as *non-uniformity*,  $U$ ), the broader the molecular weight distribution.

$$U = \frac{\bar{M}_w - \bar{M}_n}{\bar{M}_n} = \frac{\bar{M}_w}{\bar{M}_n} - 1$$

(The quotient  $D = \bar{M}_w / \bar{M}_n$  (*polydispersity*) is frequently used in place of  $U$ .)

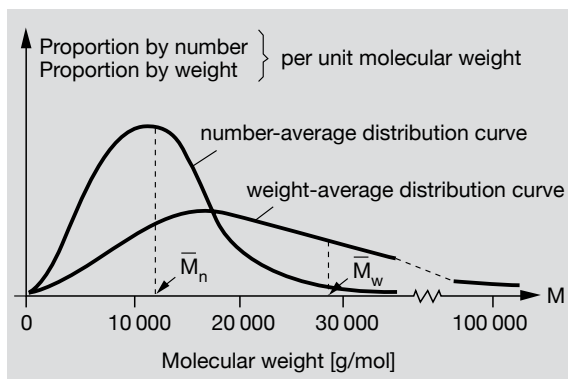


Figure 2.2: Molecular weight distribution curves for a coating resin (schematic view, curves smoothed)

In practice, molecular weight distribution curves are not symmetrical but distorted, as shown diagrammatically in Figure 2.2. In polymerisation reactions in particular, the molecular weight distribution can frequently be extremely irregular, which is due to the fact that there is no temporal or spatial consistency in the reaction conditions for typical industrial polymerisations. As a consequence of this, the overall distribution is the product of an overlay of many narrower individual distributions.

Three methods are conventionally used in industry to determine average molecular weight:

- **Viscometry**

Viscometry utilises the relation between the molecular weight of a polymer and the viscosity of the solution in a suitable solvent; the viscosity average of the molecular weight is obtained (or other quantities such as the K-value).

- **Vapour phase osmometry (vapour pressure osmometry)**

This is a thermodynamic (microcalorimetric) method; it determines the number average of the molecular weight.

- **Gel permeation chromatography (GPC)**

GPC has established itself as the standard method. A sample of the polymer in dissolved form is allowed to migrate through a columnar gel bed of a swollen, microporous substance. The larger the molecules, the less frequently or less deeply they enter the pores and hence the more quickly they pass through the column. Various evaluation methods enable one to calculate the number average, the weight average or the molecular weight distribution.

### 2.1.1.3 Secondary and aggregate structures of polymers

Uncrosslinked polymer molecules, both in the undissolved state and in solution, generally take the form of coils extended to a greater or lesser degree (see Figure 2.3). The reason for this is firstly that the many atoms of a polymer chain linked together through single bonds can be twisted in virtually any direction

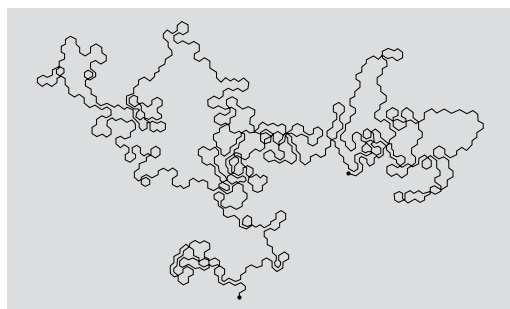


Figure 2.3: Random coil of a linear polymer molecule (macromolecule) according to<sup>[3]</sup>

in respect of one another, and secondly that the bonds are angled, i.e. they are not aligned with one another. In an extreme case a zigzag chain is theoretically possible, although the probability of all the bonds orienting themselves in the appropriate pattern by chance is virtually nil. (As a comparison, gas molecules likewise fill an available space uniformly and do not voluntarily arrange themselves into a chain.)

Where many such polymer coils occur together, they may either lie adjacent to one another whilst remaining largely separate (cell structure,

see Figure 2.4 (a)), or they may interpenetrate with one another, forming a kind of molecular felt (network structure, see Figure 2.4 (b)). For coating films the latter is preferable because of its superior mechanical properties.

In addition to these random conditions, the intra- and intermolecular forces of attraction<sup>1)</sup> (van der Waals' forces and hydrogen bridges) between polymer segments must be taken into account. A distinction is normally made between the following basic types of intermolecular interactions:

- **Dispersion forces:**

Weak; exist between all atoms and molecules (cause: temporary asymmetries in the charge distributions within the atoms or molecules).

- **Polar forces:**

Moderately strong; exist between polar bonds (permanent dipoles) or ions and polarisable bonds (induced dipoles).

- **Hydrogen bridges:**

Strong; form primarily between OH or NH bonds and free pairs of electrons of O or N atoms.

(The order of magnitude of normal chemical bonds (primary valency bonds) is ten times greater than that of hydrogen bridges).

The following general rule applies: the stronger the intermolecular forces of attraction, the stronger the mutual coherence between different polymer molecules through the layering of molecule segments. One of the mechanical effects of intermolecular interactions is increased tensile strength.

If in addition to their mutual attraction the molecules or segments are arranged in a regular structure, bundles or concentrations of molecule segments may be produced; the braid of molecules has something of the appearance of a heap of spaghetti (see Figure 2.4 (c)). These bundles can sometimes have a role to play in coating technology. They have a positive impact in polyurethane films, for example, where the stacked urethane groups are responsible for the material's good abrasion resistance. A negative example is the poor solubility of polyesters containing too high a proportion of very symmetrical basic units (e.g. terephthalic acid).

The most extreme example of molecular bundling is where many molecule segments of different molecules form crystallites (small crystals of around 10 nm in size). The crystallites in turn arrange themselves into what are known as superstructures (textures). Figure 2.4 (d) shows in diagrammatic form the structure of a partially crystalline polymer with "fold crystallites" – regular bundles of folded chain segments. The appearance of *partial crystallinity* requires a very regular polymer structure (e.g. tacticity). It plays a major role in the plastics sector and has a certain importance in adhesives technology. In coating film formers, however, partial crystallinity is undesirable since:

- partially crystalline polymers are poorly soluble in coating solvents;

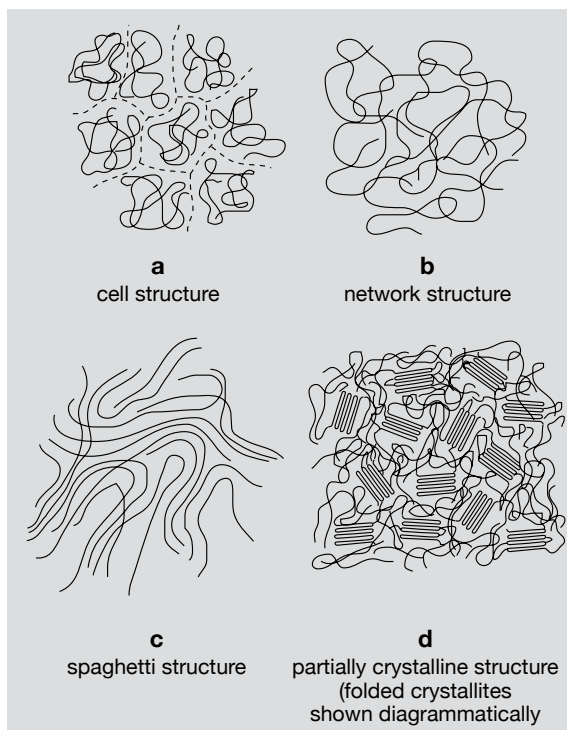


Figure 2.4: Aggregate structures of polymers

1) Intramolecular: within a molecule, Intermolecular: between different molecules

- partial crystallinity is accompanied by cloudiness (the crystallites have a different refractive index from the amorphous areas);
- the flow of coatings made from partially crystalline polymers would be impaired.

For these reasons we will not cover them in any further detail.

In the dissolved state, polymer molecules again occur as isolated or as varyingly interpenetrated coils. In this case, however, the molecular chains are surrounded by adhering solvent molecules, i.e. they are solvated.

#### 2.1.1.4 Crosslinked polymers

In liquid or powdered coating materials, film formers occur as uncrosslinked, discrete molecules; this means that they are soluble or fusible. In finished, cured coating films polymers normally need to be crosslinked, since this is the only way to achieve the best mechanical and chemical properties. Chemically crosslinked structures can be obtained – in molecular terms – by a number of different routes, as briefly described below.

- First route: The film former originates in the form of linear polymers. In the chemical curing reaction the chains are crosslinked either directly or using short bridges. One example is the curing of unsaturated polyesters with styrene as reactive diluent and peroxide as initiator.
- Second route: The film former consists of highly branched polymer molecules. Continuous crosslinking is initiated by the formation of relatively few intermolecular chemical bonds. Example: the oxidative drying of alkyd resins.
- Third route: The film former consists of two low-molecular (oligomeric) components, which form a macromolecular crosslinked substance on curing. Example: the formation of polyurethane from low-molecular polyester polyol and polyisocyanate surface coating resin.

The most important general characteristic of crosslinked polymers is the *crosslink density*  $v$ . This refers to the number of *network chain segments* – expressed in mol – per unit volume of the polymer, where a network chain segment is the chain unit stretching from one crosslink point to the next. Instead of crosslink density the average molecular weight  $\bar{M}_c$  of a network chain segment can also be quoted. Both quantities are connected via the density  $\rho$  of the polymer:

$$\bar{M}_c = \frac{m_c}{n_c} = \frac{m_c/V_c}{n_c/V_c} = \frac{m_p/V_p}{n_c/V_p} = \frac{\rho}{v}$$

$n_c$ : number of moles of network chain segments

$m_c = m_p$ : mass of the network chain segments or the polymer

$V_c = V_p$ : volume of the network chain segments or the polymer

The greater the crosslink density, the greater the hardness and the chemical (solvent) resistance of the polymer; its elasticity or flexibility is reduced, however.

Crosslink density should not be used when “degree of crosslinking” is meant. The latter is used variously to mean the gel content of the polymer, the degree of crosslinking conversion (curing conversion) and the crosslink density.

A crosslinked polymer can still contain molecules which are not bound to the network. This sol content ( $w_s$ ) can be extracted from the polymer sample with a suitable solvent. The non-soluble, bound fraction is called the gel content ( $w_g$ ). Naturally, both fractions must add up to 100%.

Crosslinking in the narrow sense always involves the chemical joining together of individual molecules to form three-dimensional networks. However, in the extended sense, crosslinking can also be the outcome of the interaction of weaker, physical secondary bonding forces, i.e. Van der Waals forces and hydrogen bonds, as well as steric effects, called entanglements. These network bonds can generally be broken by high shearing forces or rapid shearing and/or heating. They play a major role in organic rheological additives (thickeners etc).