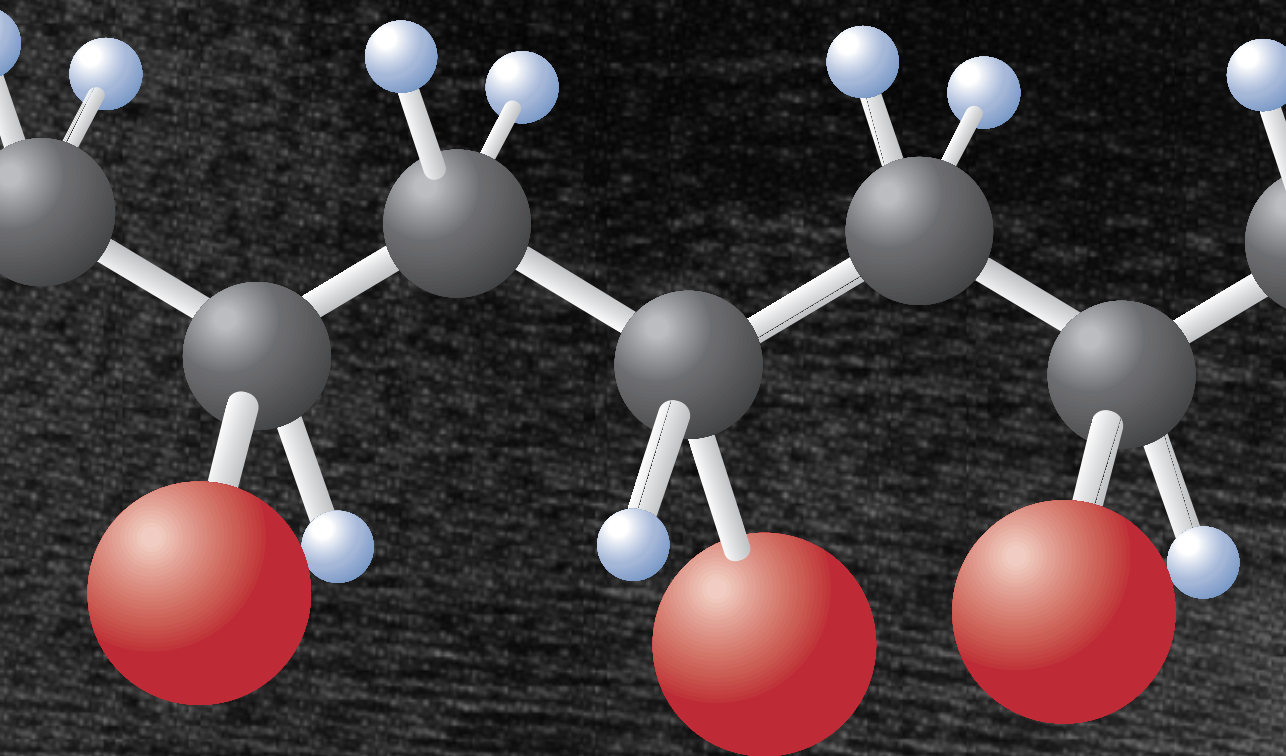# From polymers
to plastics

A.K. van der Vegt

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Preface

The two words in the title of this book, "polymers" and "plastics", could be considered as referring to two different worlds.

In the world of polymers, the properties of chain molecules are in the focus of attention, and are subject of thorough theoretical studies.

In the world of plastics, the end-use performance of the technically used materials counts, as well as their behaviour in the various processing operations in which they are transformed into finished articles.

Nevertheless, these two worlds are closely related to each other. The typical behaviour of plastics materials, strongly deviating from other materials, can only be understood on the basis of the chain properties.

In this book an attempt has been made to give a survey of polymer properties, and of the way these are, on the one hand, governed by their molecular structure, and are, on the other hand, responsible for the technological behaviour of plastics materials.

As a result of this intention, cross-references are given throughout the whole book: every aspect of polymer science and of plastics technology is closely related to practically every other aspect!

This book originates from several series of lectures at the Delft University of Technology during the years 1978 - 1988, later on integrated into a number of post-graduate and other courses. Since only a first introduction is given, more detailed treatment and more scientific depth have been sacrificed to the striving for survey and integration.

Delft, May 2001
A.K. van der Vegt

Note from the publisher

Just before he died in April 2002, Professor Em. Anne van de Vegt made a translation of his successful Dutch textbook on polymer science and technology "Polymeren, van keten tot kunststof". Initially we published this translation only on the internet, but decided that it would be worthwile to publish it in print as so many students and professionals took the trouble to let us know that an affordable edition on paper would be most welcome. So, we are very pleased to be able to publish Anne's much acclaimed text. We included the - initially separate - collection of problems as well, inserted at the end of each chapter.

J.S.
January 2006

Contents

Solutions to the problems can be downloaded from http://www.vssd.nl/hlf/m028.htm

1
Introduction

1.1. Origin of plastics / polymers

The main characteristic of polymers is, that they are composed of extremely large molecules; their molecular mass ranges from 10.000 to more than 1.000.000 g/mol, in contradiction to "normal" low-molecular substances, which in general are in the order of 100 g/mol (water 18, sugar 342). Polymer molecules are often long, *thread-like chains*, which are sometimes branched, sometimes chemically cross-linked with each other so that they form a network.

Polymers are abundantly present in nature, in vegetable and animal tissues (mainly as cellulose and proteins). Several technically used polymers have a natural origin; they are being used as technical materials as they are harvested from natural materials ("*natural polymers*").

Other polymers are partly from a natural origin; the chain molecule has grown in a living tissue, but has been chemically modified into a "*half-synthetic polymer*".

A growing number of polymers is wholly *synthetic*; the chain molecule or the network is being built up from small molecules (monomers) in a chemical process.

Some examples of these categories are given below:

Natural polymers:
– vegetable: timber, cotton, jute, sisal, hemp, cork, etc.
– animal : wool, silk, fur, etc.

Half-synthetic polymers:
– from wood: celluloid, cellophane, viscose-rayon, cellulose plastics,
– from milk: casein, from which casein plastics,
– from hides, via a tanning process: leather,
– from rubber latex, via i.a. vulcanization: technical rubber.

Synthetic polymers:
These are synthesized from low-molecular components, mostly organic monomers. Most of the monomers are prepared from fossil fuels; here we can distinguish between two main categories:
– *carbochemistry* (from coal)
– *petrochemistry* (from petroleum or natural gas).

Carbochemistry
–   Coal can be pyrolysed above 800 °C into coke, tar and a series of hydrocarbons.
–   Gasification of coal with steam and air results in, a.o., a series of hydrocarbons.

Petrochemistry
From distillation of crude oil a number of fuels are obtained (kerosine, petrol, gasoline, etc.) and a residue. The latter can be transformed into a series of lighter components by vacuum distillation and thermal cracking. Also lighter fuels ("naphtha") can be converted to a series of various hydrocarbons by thermal cracking and fractionation. Natural gas can supply a range of other components by steam conversion or partial oxidation. It is important that thermal cracking of saturated hydrocarbons results in unsaturated ones, containing one of more double bonds between the C-atoms. This renders these molecules very suitable to be used as *monomers* in polymerisation reactions. A long saturated chain is, for instance, split up into a number of shorter molecules which are *unsaturated* due to a shortage of H-atoms; they contain, therefore, one ore more double bonds:

$$C–C–C–C–C–C–C–C–C–C–C–C–C–C–C–C–C$$
$$\downarrow$$
$$C{=}C \quad C–C{=}C \quad C{=}C–C{=}C \quad C{=}C–C–C \quad C{=}C–C{=}C–C$$
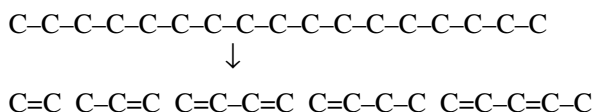
Some of these molecules, such as the first and the second (ethylene and propylene) can be used to build saturated chains (PE and PP). Other ones, such as the third one (butadiene) form unsaturated chains, which can react with sulphur to form vulcanized rubbers. (See Qu. 1.3, 1.4 and 1.5).

Polymer synthesis
From the monomers obtained from carbochemical or petrochemical sources polymers can be built up. As mentioned above, *double bonds* can thereby play an important role. Some simple examples:

$$
\begin{array}{llll}
\text{H} \;\; \text{H} & & \text{H H H H} & \\
\text{C=C} & \text{ethylene} \rightarrow & \text{--C--C--C--C--} & \text{polyethylene, PE} \\
\text{H} \;\; \text{H} & & \text{H H H H} &
\end{array}
$$

$$
\begin{array}{llll}
\text{H H H H} & & \text{H H H H} & \\
\text{C=C--C=C} & \text{butadiene} \rightarrow & \text{--- C--C=C--C---} & \text{polybutadiene} \\
\text{H} \quad\quad \text{H} & & \text{H} \quad\quad \text{H} &
\end{array}
$$
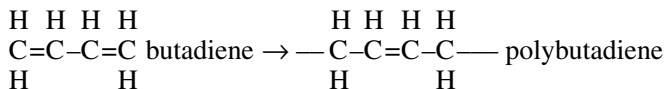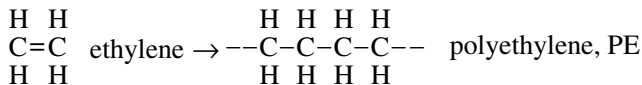
Polymers can also be synthesized from saturated monomers, e.g. by *condensation* of an organic acid with an alcohol into an ester with the formation of water. Simple alcoholes and fatty acids, such as ethyl alcohol (C_2H_5OH) and acetic acid (C_2H_5COOH) result in a low-molecular ester, ethyl acetate, but when bifunctional molecules are used, a polymer chain (a *polyester*) is formed:

$$HOOC–R_1–COOH + HO–R_2–OH \rightarrow \ —CO–R_1–CO–O–R_2–O— + H_2O$$
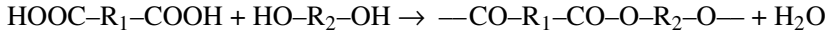
When the alcohol is trifunctional (a triol), the result is a *network*:.
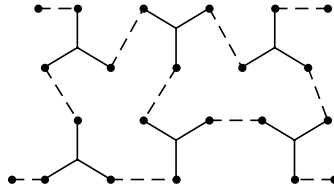
Figure 1.1.

Plastics

Plastics as technical materials are based on polymers (or macromolecular substances), but in most cases they contain a number of added components. Such an added material may be another polymer; in this case we have a polymer *blend*. Moreover, there is a large variety of *additives* and *fillers*, compounded into the polymer for various purposes, which are roughly categorized below:

– in behalf of *processing*:
  – lubricants for the transportation in the processing machine,
  – antioxydants for protection of the polymer against oxydative degradation during processing,
  – sulphur, for the vulcanization of rubbers,
  – accelerators, for speeding up the network forming reaction with rubbers and thermosets,
  – blowing agents, for producing foams,
  – etc.
– in behalf of *mechanical properties:*
  – plasticizers, e.g. in PVC, to obtain flexibility,
  – quartz powder, mica, talcum etc. to improve the stiffness.
  – short glass fibres, to improve stiffness and strength,
  – rubber particles, to improve impact strength,
  – etc.
– in behalf of *other properties:*
  – ultraviolet stabilizers, to protect the polymer against degradation in sunlight,
  – antioxydants, for protection against degradation during use at elevated temperatures,
  – antistatic agents, to reduce electrostatic charging,
  – pigments,
  – cheap fillers such as wood flour, for price reduction,
  – flame retarding additives, etc

1.2. Main categories

Taking the chain structure as a criterion, polymers can be subdivided into two main categories, viz. single chains and networks.

Single chains are linear macromolecules, though the chains may be branched. An average scale model for such a polymer chain is a human hair with a length of a metre. Normally, chains are not present in this extended shape, but rather as *diluted coils*, which may, in the scale model, have a diameter of a few cm.

The coils are mutually *entangled*; this fact is largely responsible for the special behaviour of polymers! Between chain segments relatively *weak interaction* forces are present; chain segments can move with respect to each other under the influence of relatively small external stresses. Consequently, the *stiffness* of polymers is rather low.

Flow, on the contrary, is strongly hindered by the entanglements between the coils; this is why fluid polymers show excessively *high viscosities*, which necessitate the use of heavy processing machines.

In *networks* the molecular chains are connected by strong primary chemical links; in fact a network is a single gigantic molecule. Networks can be formed in two different ways:

a. by forming *bridges* between single chains; this is the case with the vulcanization of rubbers, mostly by sulphur bridges. But also curing of unsaturated polyester resins is a matter of forming bridges between chains, in this case with the aid of (poly)styrene.

b. by reacting *bivalent* with *tri-(or more)-valent* molecules, e.g. in synthesizing formaldehyde resins.

In networks chain entanglements and local movements of chain segments with respect to each other also occur, but flow is not possible.

From the foregoing we can divide the field of macromolecular materials into three main categories:

Thermoplastics are non-crosslinked systems, which flow at elevated temperatures and which, upon cooling, return to the solid state.

Synthetic elastomers are analogous to thermoplastics, but they are in a softened condition. As such they show flow, but after the formation of a network (by cross-linking) they are no longer fluid but retain their shape.

Thermosets owe their name to the fact that the formation of a network, the curing reaction, in many (but not in all) cases occurs at elevated temperature. The network is considerably tighter than in vulcanized rubbers. A formed thermoset does not increase in hardness or stiffness upon temperature increase, but, on the contrary, shows softening, but no flow.

Within each of these three categories a large number of main types exists, each characterized by a a specific structure of the macromolecule. Within each main type several variations occur, e.g. concerning chain length, chain regularity, copolymerisation (presence of more than one monomer in the chain), etc.

In the assortment of technically used materials we also meet a broad variability of additives and fillers, added by the manufacturer.

In the next section an (incomplete) survey is given of a number of polymers, as a first orientation in the field of plastics materials.

1.3. The most important plastics

(See Qu. 1.14 – 1.20).

1.3.1. Thermoplastics

Polyethylene (*PE*) is a rather soft and tough, crystalline polymer, which is being manufactured in three main types: *LDPE* (low-density PE ≈ 0.92 g/cm^3), *HDPE* (high-density PE ≈ 0.95 g/cm^3), and, more recently, *LLDPE* (linear-low-density PE, ≈ 0.92 – 0.95 g/cm^3). The stiffness of PE increases strongly with increasing density. All types gradually lose their properties upon temperature increase, and they melt at 105 to 130 °C, respectively. Principal applications are: packaging film, bags, pipes, crates, pails, bottles, etc. Special grades are made in smaller quantities, such as *UHMPE* (ultra-high-molecular), which is extremely tough and abrasion resistant, and which is, moreover, used for making super-strong PE-fibres. A new development is a series of PE with very low density (.86 to .90 g/cm^3), a series which extends into the region of rubbers.

Polypropylene (PP) resembles PE, but is somewhat harder and stiffer than HDPE. It is crystalline as well, and melts at ≈ 165 °C. Its impact strength at lower temperatures is quite poor; therefore PP is often modified with a certain amount of rubber (mostly built-in as a copolymer). Main applications are: film for packaging, fibres, crates, pipes, automotive parts (often with reinforcing fillers). A special feature of PP is its ability to form integral hinges with a practically unlimited resistance against repeated bending.

Polyvinylchloride (PVC) is a hard, amorphous polymer which softens at about 85 °C. Also in PVC rubbers are sometimes added in order to improve the impact strength. The main applications of PVC are: pipes, gutters, front panels of buildings, cables, bottles, floor tiles. A much softer and more flexible material is obtained by blending with plasticizers: soft or plasticized PVC is being used in artificial leather, tubes and hoses, footwear, films, etc.

Polystyrene (PS) is an amorphous, very brittle, hard polymer with a softening temperature of about 90 °C. Improvement of its impact strength is again obtained by

blending with rubber (in most cases butadiene rubber), which goes at the cost of stiffness. Unmodified PS is being largely applied as foam for packaging and thermal insulation. High-impact PS (TPS or HIPS) is used for coffee cups, household ware etc.

Styrene-Acrylonitrile (SAN) is somewhat stiffer than TPS, and has a better resistance against impact and temperature. It is mainly used in parts of household- and electrical appliances, battery houses etc.

Acrylonitrile-Butadiene-Styrene (ABS) is sometimes a terpolymer of three mono- mers, but in most cases a blend of two copolymers. ABS has an excellent impact strength and a relatively high softening temperature (about 110 °C). Its stiffness is only marginally lower than that of PS. It finds large-scale applications in the automotive industry, in toys, telephones, TV-housings, etc.

Polymethylmethacrylate (PMMA), carrying trade names such as Perspex and Plexiglass, is an amorphous, relatively hard and transparent polymer. Its stiffness is retained until near its softening temperature (110 °C). Most applications are based on its superior optical qualities: safety glass, decoration material, traffic signs, etc.

Polyamide (PA) is generally known as "nylon". This is a collection of polymers, which differ in chain structure, and which are, according to the numbers of consecutive C-atoms in the chain, designated as (a.o.) PA-6, PA-6,6, PA-11, PA-4,6 and PA-12. Initially PA's were only used as fibre materials, but later on they found a position under the engineering plastics. Polyamides are crystalline polymers with relatively high melting points (between about 200 and 300 °C). They possess a good impact strength, due to the fact that they absorb several percents of water from the atmosphere. Moreover, a good abrasion resistance and a low friction make them suitable for technical use, such as in bearings and gear wheels. Quite often polyamides are reinforced with short glass fibres to improve their stiffness.

Polyoxymethylene (POM) is, again, a crystalline polymer, with a melting point of about 180 °C. Its mechanical properties enable it to gradually replace metals in a number of applications. Many technical parts are being made from POM, such as gear wheels, bars, automotive accessories, parts of several apparatuses and machines. The polymer is used as such (e.g. "Delrin"), but also as a copolymer with a small amount of ethylene oxide (e.g. "Celcon" and "Hostaform").

Polycarbonate (PC) is, up to about 140 °C, an amorphous glassy transparent polymer with excellent mechanical properties, in particular as regards its impact strength. This renders it very suitable for substitution of glass, but also for a series of technical applications in which it replaces metals. For the latter, reinforcement with short glass fibres opens further possibilities. A weak point of PC is its poor resistance against environmental stress cracking in contact with a number of organic liquids.

Polyethylene terephtalate (PETP) is a (saturated) polyester and is, like nylon, known for its large-scale use as a textile fibre. Moreover it is being applied at an increasing scale as a plastic, viz. in films, bottles (the "PET-bottle") and injection-mouldings. Though its stiffness decreases significantly above 70 °C, it remains a solid up to its melting point (255 °C).

Polybutylene terephtalate (PBTP) differs in its chemical structure only slightly from PETP; its melting point is somewhat lower and its processability is better. The applications in injection moulded articles are similar to those for PETP.

Polyphenylene oxide (PPO) or *Polyphenylene ether* (PPE) is an amorphous polymer with a softening temperature of about 210 °C. To improve its processability it is mostly blended with PS (modified PPE, e.g."Noryl"), which is at the cost of its heat distortion temperature. The properties are excellent; the applications are mainly in fine-mechanical construction, in automotive parts, in household equipment etc.

Polysulphone (PSU) is a high-performance polymer with superior mechanical, electrical and thermal properties in a temperature region from –100 up to 180 °C. It is mainly used in exacting mechanical and electrical applications.

Polyphenylene sulphide (PPS) (e.g."Ryton") is a highly crystalline polymer with a melting point of 290 °C. It combines good mechanical properties with very high thermal and chemical resistance; it is, moreover, self-extinguishing. It is, i.a., used as protective coating on metal surfaces.

Polyimide (PI) caps all other polymers in its temperature range of use (–200 to 260 °C in air; short-time even up to 500 °C). Because of its high price, it is used in special cases only, such as space vehicles, nuclear reactors and some electronic parts. Newer developments, related to polyimide, are the polyether imides (e.g. "Ultem"), polyester imides and polyamide imides (e.g. "Torlon"), all with very good mechanical, thermal and electrical properties and self-extinguishing.

Polytetrafluoroethylene (PTFE), mostly known as "Teflon", has as special properties its high melting point (327 °C), its very good resistance against chemicals and its extremely low friction. though the polymer is mechanically weak and shows a strong tendency to creep, though processing is very difficult (only possible via a sintering process) and though it is very expensive, it is being used in a number of applications such as bearings, pipes, sealing rings, electrical insulation and coatings on kitchen pans. Often the polymer is reinforced with fillers.

Tetrafluoroethylene-perfluoropropylene (FEP) resembles PTFE in its properties, but can be processed as a thermoplastic polymer.

Polyvinylidene fluoride (PVDF) and *Ethylene tetrafluoroethylene copolymer* (ETFE) can be considered as "diluted" PTFE's, which in their structure and their properties

are in between PTFE and the polyolefins PE and PP. They are processable with the normal techniques and find similar applications as PTFE.

Cellulose acetate (CA) and *Cellulose acetate butyrate* (CAB) are, contrary to the polymers mentioned so far, not fully synthetic, but derivates of vegetable cellulose. They are strong, tough and well processable materials, used in many household- and technical applications, such as hammer heads, magnetic tape, toys etc. CAB has a higher form stability than CA, and is used in automotive accessories and in pipes.

Polybutylene (PB) belongs to the family of polyolefins (PE and PP), but is much less used because of its higher price. Though it does not differ very much from PE in stiffness and melting point, it has a better resistance against creep and environmental stress cracking than PE and PP and a higher toughness and tear resistance. Its applications are mainly in film for heavy-duty bags and in hot water transport pipes.

Polymethylene pentylene (PMP) is, again, a polyolefin, but with a much higher melting point than the other ones (240 °C). Despite its crystalline nature PMP can be well transparent. It is used a.o. in laboratory bottles. One of its trade names is "TPX".

Polyether ether ketone (PEEK) and *Polyether sulphone* (PES) belong to the most recent developments in the field of technical high-performance polymers. Both possess very good thermal and mechanical properties, which can be further improved by reinforcing fibres. Their application is mainly in aircraft and space vehicles.

Polyketone (PK) ("CARILON") is a new polymer with an attractive combination of properties (very tough, high abrasion resistance, high temperature resistance, easy to process, good chemical resistance and barrier properties). It is trying to find its way in various potential applications.

1.3.2. Thermosets

Phenol-formaldehyde (PF) was the first fully synthetic macromolecular material ("Bakelite", 1907). In a slightly precured condition and provided with fillers, it is, as a moulding powder, available for processing into end-use articles such as bulb fittings, switch housings, coils, laminated wood and foam for thermal insulation.

Ureum-formaldehyde (UF) is comparable to PF, but is somewhat stiffer and has, because of its colourlessness and gloss, a more attractive appearance. The applications are in the same fields as PF.

Melamine-formaldehyde (MF) is qualitatively better than UF. It is, therefore, used in more demanding applications such as crockery, various electrotechnical articles and decorative panels.

Unsaturated polyesters (UP) can, with a second component, e.g. styrene, and with

initiators and accelerators be cured into a network structure. The reaction can take place at room temperature. UP is, in most cases, used in combination with glass fibres, and finds its applications in pipes, vessels, boat building etc.

Epoxy resin (EP) has to be mixed with a second component, the curing agent, to undergo the curing reaction, which, as with UP, can take place at ambient temperatures. Epoxy/fibre composites (with glass, carbon or aramid fibres) find similar applications as UP/glass, but are being applied more selectively because of their higher price and better properties. Besides, epoxies are used in lacquers and adhesives and as casting resins in electrotechnical applications.

Polyurethanes (PU). The thermosetting type of this large family of polymers is mainly used as foam. A mixture of two components with a foaming agent forms a light, hard foam, which is a superior thermal insulator.

1.3.3. Synthetic elastomers

Styrene butadiene rubber (SBR) is, quantitatively, the most important synthetic rubber. It is a copolymer of styrene and butadiene in such a ratio that its rubbery nature predominates. vulcanization is carried out with sulphur, reinforcement with carbon black. It is used at a very large scale in tyres for passenger cars, thanks to its excellent combination of abrasion resistance and friction on the road. In large tyres it can not replace natural rubber because of its heat development (hysteresis losses).

Butadiene rubber (BR) or Polybutadiene has an excellent abrasion resistance and a very low damping, but is, undiluted, too "jumpy" for use in tyres. In blends with SBR or natural rubber a good compromise of properties can be obtained.

Isoprene rubber (IR) or Polyisoprene is a synthetic copy of natural rubber (NR) and approaches NR in its properties. Besides for tyres, IR is, because of its good flow properties, suitable for injection moulding.

Butyl rubber (IIR) is derived from polyisobutylene, a polymer which is not further mentioned in this chapter, which has a rubbery nature, but which can not be vulcanised in the conventional way with sulphur. This objection is taken away by copolymerisation with a small amount of isoprene. Butyl rubber has a very low resilience, but outrivals all other rubbers in resistance to gas permeation; for that reason it is generally used for tyre inner tubes.

Chloroprene rubber (CR) is a synthetic rubber with very high chemical resistance, and is, therefore, applied in cable protection, oil transport tubes etc.

Nitrile rubber (NBR), a copolymer of butadiene and acrylonitrile, is characterized by its high resistance against light and oxygen, thus against ageing. Moreover it is not attacked by oil and several organic solvents. For these reasons, it finds its place in demanding applications.

Ethylene-propylene rubber (EPR or EPDM) is, basically, a copolymer of ethylene and propylene. Because of the random arrangement of the monomers in the chain, crystallization does not occur, and the material behaves as a rubber. Just as with polyisobutylene, vulcanization with sulphur is impossible (the chain is saturated). Also here, a small amount of another monomer is incorporated, which enables the vulcanization and thus the use as a technical elastomer. EPR has a high resistance against ageing and chemical attack, and is, compared with other "specialty" rubbers, relatively cheap.

Silicone rubbers have, contrary to all other polymers, no carbon atoms in their main chain, but silicium and oxygen atoms only. They can be used up to very high temperatures (250 °C) and are highly resistant against ageing, so that, despite of their high price, they are frequently used in demanding applications.

Thermoplastic elastomers (TPE's) are characterized by the exceptional property that, without vulcanization, they behave as cross-linked rubbers. They are block-copolymers, in which blocks of the same nature assemble in hard domains, acting as cross-links between the rubbery parts of the chain. These hard domains lose their function when they reach their softening temperature, so that the material can then be processed as a thermoplast. One of the oldest member of the family of TPE's is SBS (styrene-butadiene-styrene block copolymer), but several other TPE's have been developed, i.a. on the basis of polyesters, polyurethanes and polyolefins. In their properties these polymers cover a broad range between conventional rubbers and soft thermoplastics.

Polyurethane rubber (PUR). Not only in the thermosets (and the thermoplastics), but also in the field of synthetic elastomers polyurethanes have found a position, namely as a softer type. It is, again, formed from two components and is, with a blowing agent, processed into a foam. Polyether mattresses belong to this category, but also microcellular structural foams, used in bumpers, head- and arm-rests in motorcars, etc.

1.3.4. Composite plastics

Blends of polymers are manufactured and applied at an increasing scale. Only in exceptional cases are polymers soluble in each other and can form a homogeneous blend (an example: PPE + PS, a blend known as "Noryl"). In most cases blends are, therefore, dispersions. Rubber particles are dispersed in brittle polymers to improve their impact strength (toughened PS and PP, ABS etc.), but also hard polymers are combined to reach a favourable compromise between properties (and price).

Reinforcement with particles such as chalk, quartz, mica and glass spheres, is frequently carried out with thermoplastics and thermosets to obtain a higher stiffness (and sometimes a higher strength). There is a gradual transition from high-quality to

cheap fillers, the latter being mainly used as price reducing agents, but also for. e.g. reducing shrinkage in processing. Rubber vulcanisates gain considerably in strength and abrasion resistance by the incorporation of carbon black (up to 40 weight %)

Reinforcement with short fibres is important for thermoplasts and thermosets. With the former, very short fibres (glass or other) are blended into the polymer; the latter allow the use of longer fibres. The effect is a 3- to 5-fold increase of the stiffness and a 1.5 to 3-fold increase in strength.

Foams can be made from thermoplastics, thermosets and rubbers. Densities can be obtained from nearly solid down to 200 times diluted. Structural (or integral) foams have a solid skin. The best known foam materials are polystyrene foam, polyurethane foam and polyether foam.

Reinforcement with continuous fibres. In this case the fibres, as strands or cloth, are largely responsible for the mechanical properties. Traditionally, thermosetting resins are used in this case, because of the ease of impregnating fibre bundles or cloth with the low-viscosity uncured resin. Recently however, techniques have been developed to also reinforce thermoplastics with long fibres. Conventional combinations are polyester/glass (GF-UP) and epoxy/glass (GF-EP), but also high-quality fibres as carbon and aramide, and thermoplastic matrices such as PEEK are being used for special applications.

1.4. Problems

1.1. Give twenty high molecular materials from a natural (both from vegetable and animal) origin, that are used as technical materials

1.2. Give ten technically used materials based on 'half synthetic' polymers and explain the addition 'half' to it.

1.3. Why are hydrocarbons, obtained from a cracking process, very suitable for the production of synthetic polymers?

1.4. Why are polymers, built up from dienes, very suitable for application as technical rubbers?

1.5. Which kind of chainstructures can be formed in the polymerisation of butadiene (CH_2=CH–CH=CH_2)?

1.6. Why is it not possible to vulcanise ethylene-propylene copolymers and polyisobutylene in the usual way. In what way are these polymers modified in order to make vulcanisation possible anyway?

1.7. In what way can polymers be formed from saturated monomers?

1.8. In which two manners can a three dimensional network be formed?

1.9. What is the meaning of the name 'thermosets'? Why can this name lead to misunderstanding?

1.10. What is the difference between thermoplastics on the one side and thermosets and rubbers on the other side?

1.11. What is the difference between thermosets and technical rubbers?

1.12. What is the difference between thermoplastic rubbers and ordinary rubbers?

1.13. What is the difference between thermoplastic rubbers and thermoplastics?

1.14. Give the most important thermoplastics, thermosets and synthetic rubbers.

1.15. Give the three maintypes of PE. What are the differences between these types.

1.16. Give a number of polymers (thermoplastics, thermosets and rubbers) in which styrene plays a role.

1.17. Which polymer cannot be manufactured to an end product in a normal production process? In what way is this polymer being processed? Which similar polymers are more suitable for production processes?

1.18. Give a polymer with an extremely high temperature resistance and some members of the same family.

1.19. Give a number of composite plastics

1.20. When and for what purpose are the following materials added to a polymer?
a. fine carbon black	*b.* chalk	*c.* glassfibres
d. plasticizer	*e.* mica	*f.* accelerators
g. lubricants	*h.* sulphur	*i.* pentane
j. wood flour	*k.* anti-oxidants	*l.* silicium carbide
m. UV-stabilisers	*n.* antistatic agents	*o.* rubber particles.

2
Molecular composition

2.1. Chain structure

A linear chain consists of a "backbone", the main chain, at which side groups are attached. In this section a simple classification of the various types of main chain will be given, followed by a survey of frequently occurring side groups.

2.1.1. Main chain (Qu. 2.1 and 2.2)

Carbon atoms only:
– saturated:

$$—C–C–C–C–C–C—$$
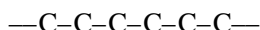
example: polyethylene (PE)

$$—\left[-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\right]_n—$$
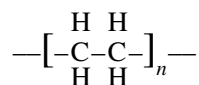
also PP, PS, PVC, PB, PMMA, PTFE, etc. (see § 2.1.2)
– unsaturated:

$$—C–C=C–C–C–C=C–C—$$
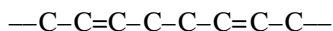
example: polybutadiene

$$—\left[-\underset{H}{\overset{H}{C}}-\underset{H}{C}=\underset{H}{C}-\underset{H}{\overset{H}{C}}-\right]_n—$$
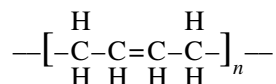
also IR, CR, etc. (see § 2.1.2)
– more unsaturated:

$$—C=C–C=C–C=C—$$
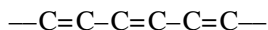
example: polyacetylene.

$$—\left[-\underset{H}{C}=\underset{H}{C}-\right]_n—$$
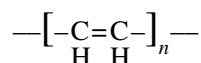
Carbon and oxygen atoms:

$$—C–O–C–O–C–O–C–O—$$
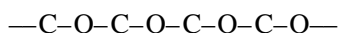
example: polyoxymethylene (POM) :

$$-\left[-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-O-\right]_n-$$
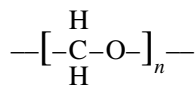
also

$$-C-C-O-C-C-O-C-C-O-$$
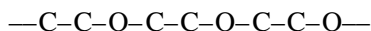
example polyethyleneoxyde (PEO)

$$-\left[-\overset{\overset{\displaystyle H\ \ H}{|\ \ \ |}}{\underset{\underset{\displaystyle H\ \ H}{|\ \ \ |}}{C-C}}-O\right]_n-$$
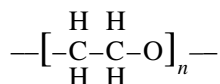
Carbon and nitrogen atoms:

$$-C-C-C-N-C-C-$$
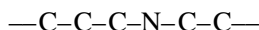
example: various types of PA (nylon):

$$-\left[-\overset{\overset{\displaystyle O}{\|}}{C}-(CH_2)_p-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle H}{|}}{N}-(CH_2)_q-\overset{\overset{\displaystyle H}{|}}{N}-\right]_n-$$
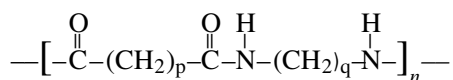
Carbon, oxygen and nitrogen atoms:

$$-C-C-\!\!-\!\!-\!\!-N-C-O-C-C-$$

example: various types of polyurethanes:

$$-\left[-(CH_2)_p-O-\overset{\overset{\displaystyle O}{\|}}{C}-\overset{\overset{\displaystyle H}{|}}{N}-(CH_2)_q-\overset{\overset{\displaystyle H}{|}}{N}-\overset{\overset{\displaystyle O}{\|}}{C}-O-\right]_n-$$
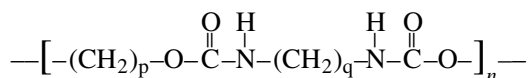
Carbon rings:

—⬡—

example: polycarbonate (PC):

$$-\left[-O-⬡-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-⬡-O-\overset{\overset{\displaystyle O}{\|}}{C}-\right]_n-$$
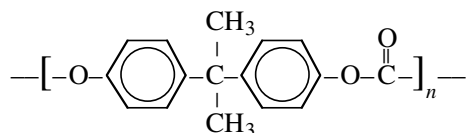
other example: polyethylene terephtalate (PETP):

$$-\left[-\overset{\overset{\displaystyle O}{\|}}{C}-⬡-\overset{\overset{\displaystyle O}{\|}}{C}-O-CH_2-CH_2-O-\right]_n-$$
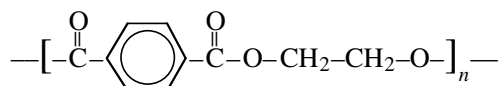
also PBTP, with four instead of two CH_2 groups,

$$—[-\overset{\overset{O}{\|}}{C}-\langle\bigcirc\rangle-\overset{\overset{O}{\|}}{C}-O-(CH_2)_4-O-]_n—$$

polyetherether ketone, PEEK:

$$—[-O-\langle\bigcirc\rangle-O-\langle\bigcirc\rangle-\overset{\overset{O}{\|}}{C}-\langle\bigcirc\rangle-]_n—$$
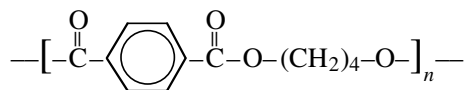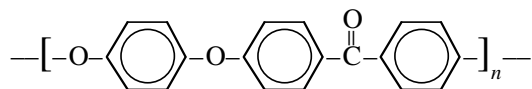
polyphenylene ether, PPE:

$$—[-\langle\overset{CH_3}{\underset{CH_3}{\bigcirc}}\rangle-O-]_n—$$
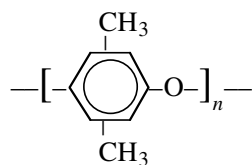
Combination with sulphur atoms:

examples:

polyphenylene sulphide (PPS):

$$—[-\langle\bigcirc\rangle-S-]_n—$$

polysulphone (PSU

$$—[-\langle\bigcirc\rangle-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{\|}}{C}}-\langle\bigcirc\rangle-O-\langle\bigcirc\rangle-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-\langle\bigcirc\rangle-O-]_n—$$

polyether sulphone, PES:

$$—[-O-\langle\bigcirc\rangle-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-\langle\bigcirc\rangle-]_n—$$
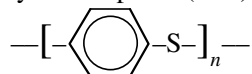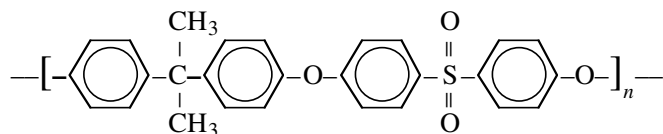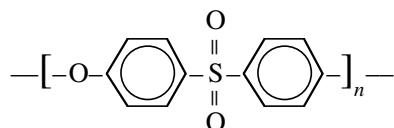
Silicium and oxygen atoms only:

example: polydimethylsiloxane (silicone rubber):

$$—[-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{Si}}-O-]_n—$$
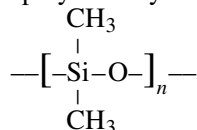
Multiple rings:

example: polyimide (PI):

$$—[-N{\overset{\text{CO}}{\underset{\text{CO}}{<}}}\hexagon{\overset{\text{CO}}{\underset{\text{CO}}{>}}}N-\hexagon-O-\hexagon-]_n—$$
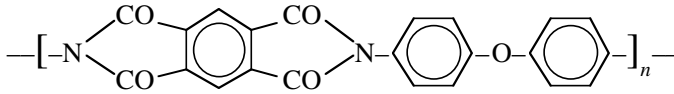
2.1.2. Side groups

– The most frequently occurring side group is the hydrogen atom; it is the only one
   with polyethylene, polybutadiene and polyoxymethylene.

– Other arrangements often met are:

– vinyl polymers

$$—[-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{R}{|}}{\overset{\overset{H}{|}}{C}}-]—$$
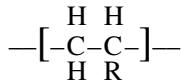
with: R = CH$_3$ polypropylpene (PP)
         R = Cl   polyvinylchloride (PVC)
         R = C$_6$H$_5$ = –◯   polystyrene (PS)
         R = CH$_2$–CH$_3$ polybutylene (PB)
         R = CN   polyacrylonitrile (PAN)

– vinylidene polymers

$$—[-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{R}{|}}{\overset{\overset{R}{|}}{C}}-]—$$
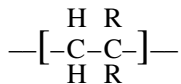
with: R = Cl   polyvinylidenechloride (PVDC)
         R = F   polyvinylidenefluoride (PVDF)
         R = CH$_3$ polyisobutene (PIB)

– polytetrafluorethylene (PTFE)

$$—[-\underset{\underset{R}{|}}{\overset{\overset{R}{|}}{C}}-\underset{\underset{R}{|}}{\overset{\overset{R}{|}}{C}}-]—$$
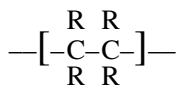
with: R = F

– polymethylmethacrylate (PMMA)

$$—[-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{R_2}{|}}{\overset{\overset{R_1}{|}}{C}}-]—$$
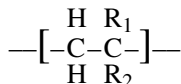
with: R$_1$ = CH$_3$ and R$_2$ = COOCH$_3$

– polydienes

$$—[-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\overset{\overset{H}{|}}{C}=\overset{\overset{R}{|}}{C}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-]—$$
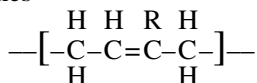
with: (R = H   polybutadiene (BR)

R = CH$_3$ polyisoprene (IR)
R = Cl   polychloroprene (CR)

– etc. etc.

2.1.3. Copolymers

Copolymer chains are built up from more than one type of monomeric units. Some examples::

ethylene + propylene: EPR
styrene + butadiene: SBR or SBS (see § 2.3)
styrene + acrylonitrile: SAN
isobutylene + isoprene: IIR (butyl rubber)
etc.

Also terpolymers (with three monomers) are made:

ethylene + propylene + a diene: EPDM
acrylonitrile + styrene + acrylic ester: ASA
ethylene + CO + propylene: PK, poly ketone ("Carilon").
(see further § 2.3)

2.2. Chain length and distribution

2.2.1. Averages

The chain length can be expressed as degree of polymerisation P (number of monomeric units in the chain), or, in most cases, as molar mass (or molecular weight) in g/mol. Sometimes the "better" unit, kg/mol is used; the difference is a factor of 1000. In this book the older unit, g/mol, will mostly be used.

An example: PE with a degree of polymerisation P of 5000 has a molar mass:

$$M = 5{,}000 \cdot (2C + 4H) = 5{,}000 \cdot (24 + 4) = 140{,}000$$

Of most polymers various types exist, which differ in molecular mass. The strongest example is PE, which is made at more than 10 different levels of M, the extremes differing by a factor of 20. But also within each type the chains may largely differ in length, namely by a factor of 100 or even 1000. Therefore every statement about a molar mass indicates an *average*.

Averages can be defined in several ways, for example after number or after weight. A simple example:

1 chain with mass 100 and
1 chain with mass 10

then the *number average* is:

$$\frac{1}{2} \cdot 100 + \frac{1}{2} \cdot 10 = 55$$

since the numbers are equal, and the number fractions n_1 and n_2 are both $\frac{1}{2}$.
Now consider a system with:

<div align="center">
1 chain with mass 100 (total mass 100) and
10 chains with mass 10 (total mass 100)
</div>

then the *weight average* is:

$$\frac{1}{2} \cdot 100 + \frac{1}{2} \cdot 10 = 55$$

because now the weight fractions are equal (w_1 en w_2 both $\frac{1}{2}$).

Expressed in a formula:

$$\text{number average } \overline{M}_n = \sum n_i \cdot M_i$$

in which n_i is the number fraction of the chains with mass M_i, and $\sum n_i = 1$.
The weight fraction is $W_i = n_i \cdot M_i$; now however, $\sum W_i$ is not equal to 1; the fractions W_i must, consequently, be reduced (*normalized*) to w_i, so that $\sum w_i = 1$:

$$w_i = \frac{n_i \cdot M_i}{\sum n_i \cdot M_i} = \frac{W_i}{\sum W_i}$$

The weight average is now:

$$\overline{M}_w = \sum w_i \cdot M_i$$

Also valid is:

$$\overline{M}_w = \frac{\sum n_i \cdot M_i^2}{\sum n_i \cdot M_i} = \frac{\sum n_i \cdot M_i^2}{\overline{M}_n}$$

In most cases it is necessary to work backward from the weight fractions w_i:

$$N_i = \frac{w_i}{M_i}$$

but

$$\sum N_i \neq 1$$

so N_i has to be normalized to n_i with:

$$n_i = \frac{N_i}{\sum N_i} = \frac{w_i/M_i}{\sum (w_i/M_i)}$$

Now $\sum n_i = 1$, and $\overline{M}_n$ follows from $\overline{M}_n = \sum n_i \cdot M_i$.

The calculation of $\overline{M}_n$ is easier with:

$$\overline{M}_n = \sum n_i \cdot M_i = \frac{\sum w_i}{\sum (w_i/M_i)} = \frac{1}{\sum (w_i/M_i)}$$

Also "higher" averages are used:

$$\overline{M}_z = \sum z_i \cdot M_i$$

in which

$$z_i = \frac{w_i \cdot M_i}{\sum w_i \cdot M_i} \quad \text{(normalized)}$$

so

$$\overline{M}_z = \frac{\sum w_i \cdot M_i^2}{\sum w_i \cdot M_i} = \frac{\sum n_i \cdot M_i^3}{\sum n_i \cdot M_i^2}$$

This is the so-called *z-average*. A further step in the same direction gives the (z+1)-average:

$$\overline{M}_{z+1} = \frac{\sum n_i \cdot M_i^4}{\sum n_i \cdot M_i^3}$$

We apply the formulae for $\overline{M}_n$. $\overline{M}_w$ and $\overline{M}_z$ to the simple example given above:

A   <u>100</u>   <u>10</u> $(100 + 10)$
B   <u>100</u>   <u>10</u> __ __ __ __ __ __ __ __ $(100 + 10 \times 10)$

		A	B
M_1	= mass chain 1	100	100
M_2	= mass chain2	10	10
n_1	= number fraction 1	1/2	1/11
n_2	= number fraction 2	1/2	10/11
$\overline{M}_n$	$= \sum n_i \cdot M_i$	55	18.2
w_1	= weight fraction 1 = $n_1 \cdot M_1 / \sum n_i \cdot M_i$	10/11	1/2
w_2	= weight fraction 2 = $n_2 \cdot M_2 / \sum n_i \cdot M_i$	1/11	1/2
$\overline{M}_w$	$= \sum w_i \cdot M_i$	91.8	55
z_1	= z-fraction 1 = $w_1 \cdot M_1 / \sum w_i \cdot M_i$	100/101	10/11
z_2	= z-fraction 2 = $w_2 \cdot M_2 / \sum w_i \cdot M_i$	1/101	1/11
$\overline{M}_z$	$= \sum z_i \cdot M_i$	99.1	91.8

Another, more realistic example: A blend is made of three monodisperse fractions (i.e. in each fraction all chains have the same length), with masses of 20, 50 and 30 grammes and molar masses of 20,000, 100,000 and 300,000 g/mol, respectively. The mass fractions are now:

$$w_1 = \frac{20}{100} = 0.2$$

$$w_2 = \frac{50}{100} = 0.5$$

$$w_3 = \frac{30}{100} = 0.3 \quad (\Sigma\, w_i = 1)$$

This leads to:

$$\overline{M}_w = 0.2 \cdot 20000 + 0.5 \cdot 100000 + 0.3 \cdot 300000 = 144000$$

$\overline{M}_n$ can be calculated with:

$$N_1 = \frac{0.2}{20\,000}, \quad N_2 = \frac{0.5}{100\,000}, \quad N_3 = \frac{0.3}{300\,000}, \quad \Sigma\, N_i = \frac{4.8}{300\,000}$$

After normalization we find: $n_1 = 10/16$, $n_2 = 5/16$, $n_3 = 1/16$.

$$\overline{M}_n = (10/16) \cdot 20000 + (5/16) \cdot 100000 + (1/16) \cdot 300000 = 62.500$$

(The calculation is simpler with $\overline{M}_n = 1/\Sigma(w_i/M_i)$).

The *z*-fractions are, unnormalized:

$$Z_1 = 0.2 \cdot 20000 \qquad Z_2 = 0.5 \cdot 100000 \qquad Z_3 = 0.3 \cdot 300000$$

and normalized:

$$z_1 = \frac{4}{144} \qquad\qquad z_2 = \frac{50}{144} \qquad\qquad z_3 = \frac{90}{144}$$

It simply follows now that:

$$\overline{M}_z = 222{,}778$$

The examples show clearly that in $\overline{M}_n$, $\overline{M}_w$ and $\overline{M}_z$ in this order of sequence, the longer chains play an increasingly dominant part.

In most cases $\overline{M}_w$ is used for general characterization of the molar mass besides $D = \overline{M}_w/\overline{M}_n$, the heterogeneity index, is of importance as a simple measure for the spread in chain length. In the first example $D = 1.67$ for A and 3.03 for B. In the second example $D = 2.3$. For technical polymers D can have values from 1.1 up to 30.

An even more realistic question is, how the averages change when two polydisperse polymers of the same type are being blended. Suppose two batches, A and B, are available with weight average molar masses $(\overline{M}_w)_A$ and $(\overline{M}_w)_B$ and a blend is made of a weight fraction φ of A with a weight fraction $(1 - \varphi)$ of B. For the blend C the weight average is now:

$$(\overline{M}_w)_C = \varphi \cdot (\overline{M}_w)_A + (1 - \varphi) \cdot (\overline{M}_w)_B.$$

The number of chains in 1 gramme of polymer is $N\overline{M}_n$ (N is the Avogadro number). In 1 gramme of the blend C, φ grammes of A and $1 - \varphi$ grammes of B are present,

so).

or:

$$N/(\overline{M}_n)_C = \varphi \cdot N/(\overline{M}_n)_A + (1 - \varphi) \cdot N/(\overline{M}_n)_B,$$

$$\varphi/(\overline{M}_n)_C = 1/(\overline{M}_n)_A + (1 - \varphi)/(\overline{M}_n)_B$$

How broad is now the distribution of the blend C? We find D_C by multiplying the expressions for $(\overline{M}_w)_C$ and $1/(\overline{M}_n)_C$. A much simpler expression is found when we consider a special case, viz. two components with the same degree of dispersion D, in which $(\overline{M}_w)_A = \alpha \cdot (\overline{M}_w)_B$ (and, therefore, $(\overline{M}_n)_A = \alpha \cdot (\overline{M}_n)_B$). Some calculation leads to

$$D_C = \frac{(\overline{M}_w)_C}{(\overline{M}_n)_C} = D[\varphi \cdot (1 - \varphi) \cdot \frac{(\alpha - 1)^2}{\alpha} + 1].$$

An example: $\alpha = 4$, $\overline{M}_w$ of A (e.g. 60,000) is four times greater than $\overline{M}_w$ of B (15,000). We choose $\varphi = \frac{1}{2}$, so we blend equal masses, and the blend has an $\overline{M}_w$ of 37.500. When now, for instance, $D = 6$, so that the $\overline{M}_n$'s of both components are six times smaller than the $\overline{M}_w$'s (10,000 en 2,500, respectively), then

$$D_C = 6 \cdot [\frac{1}{2} \cdot \frac{1}{2} \cdot \frac{9}{4} + 1] = 6 \cdot \frac{25}{16} = 9.375 ;$$

the distribution width is increased by more than a factor 1.5. $\overline{M}_n$ of the blend is now 37,500 / 9.375 = 4,000.

This simple rule, though based on the assumption that the molar mass distributions are similar, has practical significance because polymers made in one and the same process, do in general not differ much in their heterogeneity index.

So far, we have considered the magnitudes of several types of average molar masses. The question may arise what the use is of these different averages; the attention paid to them might look a bit artificial. Well, it is easy to understand that various polymer properties are influenced by the molar mass. Moreover, it appears that different physical properties of polymers are controlled by different types of average molar mass. A few examples:

– The *number average*, $\overline{M}_n$, is proportional to the mass of one gramme of the polymer divided by the number of chains. It is, therefore, a function of the number of chains, and thus of the number of *chain ends* (apart from branching). Now suppose that a crack with a sharp tip propagates through a piece of the polymer, then this propagation is easier as less chains have to be broken, and it meets more chain ends on its way. This means that all properties in which crack propagation plays a role, such as impact strength, tear strength and environmental stress cracking are governed by $\overline{M}_n$.

- The *weight average,* $\overline{M}_w$, is the most practical one. If you blend, for instance,

equal quantities (in kg) of two batches with molar masse M_1 and M_2, then you would expect the average $(M_1 + M_2) / 2$. And this is, of course, a weight average, for nobody would consider to blend equal nunbers of chains with each others! In addition, $\overline{M}_w$ is specially responsible for the *viscosity* of the polymer in molten condition, and, therefore, for the processability. This holds, however, only as a first approximation, as we will see later in § 5.3.

– As a third example we look at the *z-average*, $\overline{M}_z$. In the foregoing we have seen that $\overline{M}_z$ (and, in particular, $\overline{M}_{z+1}$), are governed by the longest cahains, while the sort chains have hardly any effect. A property in which the longest chains have a predominant effect, is the *melt elasticity.* This is a rather unexpected expression, because a fluid is, in general, not an elastic substance. Yes, but for polymers, it is! Let us consider a polymer, consisting for the larger part of short chains, with a single very long chain. When this polymer is deformed in a flow field, the long chain will, as a tracking-thread, keep the short chains together, and force them to return to the most probable conformation, so to return back. This is further treated in § 5.3.2. This "melt-elasticity" is of major importance for practical processing technology and for some other properties. It is clear that we cannot neglect higher averages, such as $\overline{M}_z$ and $\overline{M}_{z+1}$

2.2.2. Example of a chain length distribution

In a polymerization process the chain length distribution or molar mass distribution (MMD) is influenced by a large number of factors and conditions; the kinetics of the reaction plays a very important role. The calculation of the resulting MMD is thus very complicated. For one of the simplest cases, a step reaction with polycondensation, a first-order approach is given here. As an example we take a hydroxy acid HO–R–COOH, which, upon condensation, forms the chain –[–O–R–CO–]$_n$.

With each step a –COOH and an –OH group react with each other, forming an ester group and a water molecule. If we denote the numbers of –COOH and –OH groups both by U, then at the start of the reaction $U = U_0 =$ the total number of hydroxy acid molecules.

After some time t, $U = U(t)$; the number of –COOH and –OH groups disappeared is $(U_0 – U)$, which also is the number of ester groups formed. We define the *conversion grade p* as the fraction of the number of groups which have reacted:

$$p = \frac{U_0 - U}{U_0} \quad \text{or } U = (1 - p)U_0$$

Now there are U molecules, containing together U_0 basic units; the number of units per chain, the average *degree of polymerization* $\overline{P}$, is, therefore:

$$\overline{P} = \frac{U_0}{(1-p)\cdot U_0} = \frac{1}{1-p}$$

An example: With a conversion grade of 0,99 $\overline{P} = 100$. Evidently, this $\overline{P}$ is a number average degree of polymerization, $\overline{P}_n$.

The question is now, how the distribution of P (and thus of M) looks like. We consider, during the reaction, when the conversion grade is p, a single –COOH group. The chance that the –OH group of this monomer has reacted with another –COOH group, is p; the chance that it has not reacted, is $(1-p)$.

The chance of HOOC–R–OH thus is $(1-p)$
The chance of HOOC–R–OOCR is p
The chance of HOOC–R–OOCR–OH is $p(1-p)$
The chance of HOOC–R–OOC-R–OOCR is p^2
etc.

The chance of $(i-1)$ times addition is p^{i-1}
the chance of not reacting with the ith monomer is $(1-p)$
the chance of both events, so the chance of the occurrence of a chain of i units, is the product $p^{i-1}(1-p)$. This is, therefore the number fraction, n_i.

$$\frac{N_i}{N} = n_i = p^{i-1}(1-p)$$

It follows easily that:

$$\sum_1^\infty n_i = 1$$

With this formula the value of the number average, found before, can be checked:

$$\overline{P}_n = \overline{i} = \frac{\sum n_i \cdot i}{\sum n_i} = \frac{1-p}{1-p} \cdot \frac{1 + 2p + 3p^2 + \dots}{1 + p + p^2 + \dots} = \frac{1}{1-p}$$

The weight average degree of polymerization is:

$$\overline{P}_w = \frac{\sum W_i \cdot i}{\sum W_i} = \frac{\sum n_i \cdot i^2}{\sum n_i \cdot i} = \frac{\sum p^{i-1}(1-p)i^2}{\sum p^{i-1}(1-p)i} = \frac{1 + 4p + 9p^2 + 16p^3 + \dots}{1 + 2p + 3p^2 + 4p^3 + \dots}$$

$$= \frac{\dfrac{1+p}{(1-p)^3}}{\dfrac{1}{(1-p)^2}} = \frac{1+p}{1-p}$$

The ratio $D = \overline{P}_w/\overline{P}_n$, *the heterogeneity index,* is $D = (1+p)$. For the usually high conversion rates (e.g. $p = .995$), $D \approx 2$.

The chain length distribution can be represented graphically in several ways, e.g. as number fractions or as weight fractions. In Figure 2.1 both cases are given (together with the *z*-fractions) for a *p*-value of 0.99. From the graph of number fractions it appears that the monomer has, numerically, the highest fraction! The distribution of the weight fractions w_i has its maximum at the number average degree of polymerization, $\overline{P}_n = 100$, while $\overline{P}_w = 199$. Further calculation gives: $\overline{P}_z = 299$.
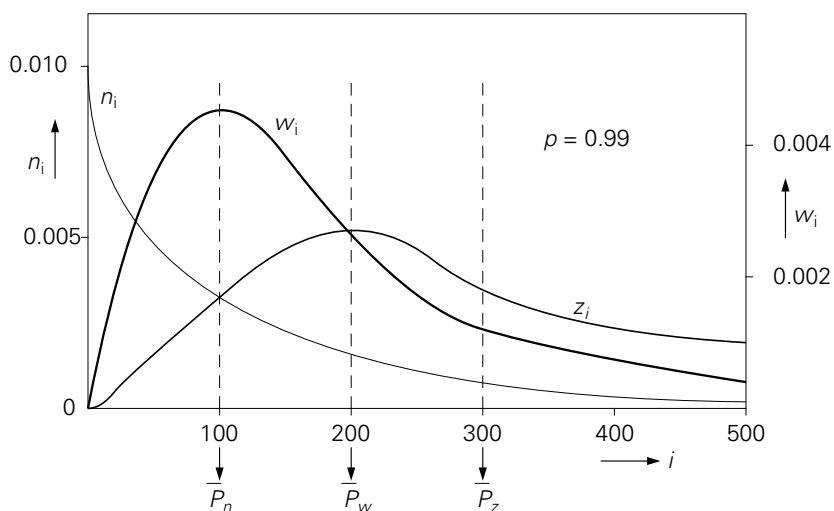
Figure 2.1. Chain length distribution of a polycondensate.

2.2.3. Measuring methods

The *number average* $\overline{M}_n$ can, in principle, be determined by counting the molecules in a gramme of polymer. This is possible by measuring colligative properties of the polymer in solution; these are properties which are strictly dependent on the *number* of molecules per unit volume of the solution, and independent of their nature or size. Colligative properties are:

- vapour pressure reduction,
- freezing point reduction,
- boiling point increase,
- osmotic pressure

For polymers with normal, high molar masses the osmotic pressure is the only possibility; the other methods give a too small effect because of the relatively small number of molecules.

The *osmotic pressure*, Π, is the pressure difference between solution and pure solvent when these are separated by a semipermeable membrane (see Figure 2.2). For very dilute solutions the osmotic pressure is given by (see Qu. 2.35 and 2.36):

$$\Pi = kT \frac{N}{V}$$

in which N is the number of molecules in a volume V, k is Boltzmann's constant and T the absolute temperature. N can, via the molar fraction and the weight fraction, be expressed in the concentration c (g/dl) and the molar mass M; the formula then reads:

$$\Pi = RT \frac{c}{\overline{M}_n}$$

However, Π/c does not automatically lead to the correct value of $\overline{M}_n$, since Π/c is still slightly dependent on c. Measurements are, therefore, carried out at a number of different concentrations and a plot of Π/c against c is extrapolated to $c = 0$.

solution   solvent
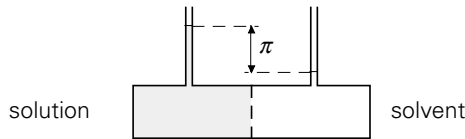
Figure 2.2. Principle of osmometry.

For the determination of the *weight average*, $\overline{M}_w$, about *light scattering* is the standard method. This is based on the fact that a density fluctuation in a solution, brought away by the presence of a coil molecule, causes a deviation of a ray of light. The amplitude of the scattered waves is proportional to the mass of the particle; the intensity is proportional to the square of the amplitude and thus to the square of the mass. From this simple reasoning it can be intuitively understood (though not proven), that the total amount of scattered light from all molecules present is related to the weight average molar mass.
A strict condition is, that the scattered waves do not interfere with each other so that the concentration must be very low. Light scattering is a very laborious and difficult method; minor contaminations are disastrous for the result. It is only used when absolute determinations of $\overline{M}_w$ are necessary.

Higher averages can be obtained by measuring the rate of sedimentation in solvents with the aid of an ultracentrifuge. This is based on the fact that the rate of sedimentation depends on the molar mass. The measurements supply $\overline{M}_w$ and $\overline{M}_z$,, sometimes $\overline{M}_{z+1}$.

The *viscosity average*, $\overline{M}_v$, does not belong to the series $\overline{M}_n$, $\overline{M}_w$, $\overline{M}_z$ etc. The measurement does not supply an absolute value of the molar mass, but can, by

contrast with the other methods mentioned so far, be carried out in an easy way. Its principle is, that a polymer, even at very low concentrations, brings about a significant viscosity increase of the solvent. This increase is not only dependent on the concentration but also on the molar mass. The measurement is carried out as follows (see also Qu. 2.14 - 2.18 and 2.31 - 2.34):

In a capillary viscometer the time is determined in which the liquid has dropped from the initial level h_1 to h_2 (see Figure 2.3); this time is proportional to the viscosity of the liquid. When we denote the viscosity of the solvent by η_0 and that of the solution by η, then the *specific viscosity* is defined as:

$$\eta_{sp} = \frac{\eta - \eta_0}{\eta_0}$$

This is the relative increase in viscosity, which, in a first approximation, appears to be proportional to the concentration c. A better measure is, therefore :

$$\frac{\eta_{sp}}{c} = \frac{\eta - \eta_0}{\eta_0 \cdot c} = \eta_{red},$$

the *reduced viscosity.*

This η_{red} is still somewhat dependent on the concentration. It is, therefore, measured at a number of (low) concentrations; the values found are extrapolated to $c = 0$, where the *intrinsic viscosity* is read off, which is denoted by $[\eta]$:

$$[\eta] = \lim_{c \to 0} \eta_{red} = \lim_{c \to 0} \frac{\eta - \eta_0}{\eta_0 \cdot c}$$

$[\eta]$ does *not* have the dimension of a viscosity, but of c^{-1}; in most cases it is given in dl/g.

A strongly schematized example: For a certain polymer in a certain solvent, times of flow through the capillary at several concentrations are found as indicated in the table. The specific viscosities $(\eta - \eta_0)/\eta_0$ can now be calculated as $(t - t_0)/t_0$; from
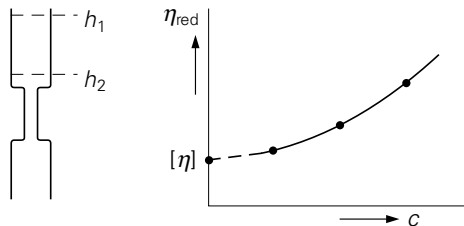

Figure 2.3. Principles of measuring intrinsic viscosity

these values the reduced viscosities follow, and extrapolation to $c = 0$ (in this case very simple, because the relation is linear) leads to:

$[\eta] = 1.525$ dl/g

c (g/dl)	t (sec)	η_{sp} (–)	η_{red} (dl/g)
0	10		
0.2	13.3	0.33	1.65
0.4	17.1	0.71	1.775
0.6	21.4	1.14	1.90

The intrinsic viscosity appears to depend on the molar mass according to the *Mark-Houwink relation*:

$[\eta] = k \cdot M^a$

in which k en a are constants for a given combination of polymer, solvent and temperature. k is in the order of magnitude of 10^{-3} when $[\eta]$ is expressed in dl/g; a is mostly in between 0.5 and 1. The measurement of the molar mass is not an absolute one; for each combination k and a have to be determined in an empirical way with the help of absolute characterization methods such as light scattering. Values of k and a are amply being supplied in handbooks.

The question is now, what kind of average molar mass is found from the intrinsic viscosity and the Mark-Houwink equation. To answer this question, we imagine the polymer to be split-up into a number of monodisperse fractions. Each of this fractions brings about a viscosity increase, which for the ith fraction amounts to:

$\eta_{sp,i} = (\eta_i - \eta_0)/\eta_0.$

We assume that the total increase in viscosity is, simply, the sum of the contribution of all fractions, while the concentration of the ith fraction is c_i. Then

$$\eta_{red} = \frac{\Sigma\, \eta_{sp,i}}{\Sigma\, c_i} = \frac{\Sigma\, (\eta_{red,i} \cdot c_i)}{\Sigma\, c_i}$$

When the limit to $c \rightarrow 0$ is taken, this becomes:

$$[\eta] = \frac{\Sigma\, [\eta]_i \cdot c_i}{\Sigma\, c_i} = \Sigma\left\{ [\eta]_i \cdot \frac{c_i}{\Sigma\, c_i} \right\} = \Sigma\, w_i \cdot [\eta]_i$$

since

$$\frac{c_i}{\Sigma\, c_i} = w_i$$

$$[\eta] = \Sigma\, (w_i \cdot k \cdot M_i{}^a) = k \cdot \Sigma\, (w_i \cdot M_i{}^a) \equiv k \cdot \overline{M}_v)^a$$

In this way the average $\overline{M}_v$ is defined as

$$\overline{M}_v = [\sum w_i \cdot M_i^a]^{1/a}$$

So, for $a = 1, \overline{M}_v = \overline{M}_w$; for usual values of a, such as 0.8, $\overline{M}_v$ is situated between $\overline{M}_n$ and $\overline{M}_w$, but more closely to $\overline{M}_w$. In practice the full procedure of measuring at different concentrations and extrapolation to zero concentration, is often replaced by a simpler standard method; for a given polymer in a given solvent, only one concentration is taken. Optionally, a correction factor can be applied to obtain from η_{red} the best estimate of $[\eta]$.

Sometimes, from such a *single-point measurement* of the solution viscosity, an arbitrary measure has been defined, which for a given polymer supplies a useful measure for comparing levels of the molar mass. An example is the so-called k-value for PVC; k values of 55, 60, 65 and 70 denote grades of increasing M. (see Qu. 2.40 and 2.41).

The *melt index m.i.* (or melt flow index m.f.i.) is a rough empirical measure of the molar mass of some polymers. It is, again, based on a viscosity measurement, but now not of a solution, but of the molten polymer. Through a standard capillary the polymer moves under a standard pressure at a standard temperature. The number of grammes transported in 10 minutes is defined as the melt index (in dg/min). The method is frequently applied to e.g. PE and PP, and results in some measure for the molar mass. The m.i. values range from 0.1 (high M) to 80 (low M) dg/min. In fact a reciprocal melt viscosity is determined. In a first approximation this depends on $\overline{M}_w$, viz according to $\eta (:) \overline{M}_w^{3,4}$ (see § 5.3). In a certain sense this characterization of the molar mass is functional, since the processability is one of the most important criteria for the selection from a number of grades of the same type of polymer (see § 5.4).

Molar mass distribution MMD
The oldest method to determine the whole molar mass distribution is *fractionation*. This method is based on the fact that in some solvents the short chains are better soluble than the long ones. The polymer is precipitated onto a column, e.g. on small glass spheres, over which a mixture of solvent and non-solvent is passed while the concentration of the solvent increases with time. First the smaller molecules are taken away from the column, later on the bigger ones. The fractions are collected and characterized as to their concentration and molar mass (e.g. by a viscosity measurement). From this procedure the MMD can be derived in a number (e.g. 20) of different fractions. This Baker-Williams method is very time-consuming: fractionation and characterization of a sample takes, in total, about a week.
A more modern method to determine the MMD is *GPC, gel permeation chromato-graphy,* also named size-exclusion chromatography, *SEC*. A polymer solution is

passed over a column with a porous structure. The residence time of the chains on the column depends on the diameter of the coiled chain: smaller chains can migrate through more pores (they can also enter into the smaller ones), and it takes a longer time for them to pass along the column. The bigger ones cannot enter into any of the side-pores and pass in the shortest time.

The concentration of the eluted solution is continuously measured as a function of time (or of eluted volume), e.g. via its refractive index, in comparison to that of the pure solvent.

This procedure results in a concentration - volume curve, from which, after previous calibration, the molar mass distribution can be derived. Calibration can be carried out with known monodisperse polymers, and is needed only once for a certain type of polymer on a certain column. The measurement takes only a few hours. From the measured MMD the various averages can be computed easily. It is also possible to characterise the eluted polymer solution not only on concentration, but also on molar mass, e.g. by laser light scattering. In this way the calibration can be avoided.

2.3. Chain regularity

Polymer chains are, in general, regularly built-up, but a few variations are possible. We shall, successively, consider: arrangement of monomers, situation of side groups, arrangement round a double bond, branching, and copolymer structure.

– *monomer arrangement* is, in principle, possible as "head-tail" or as a "head-head" (or "tail-tail") i.e. for a vinyl polymer $-CH_2-CHR-$:

$$-CH_2-CHR-CH_2-CHR-CH_2-CHR-$$

or:
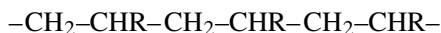
$$-CH_2-CHR-CHR-CH_2-CH_2-CHR-$$

Practically always the head-tail connection is formed. One of the exceptions is polyvinylalcohol, in which between 1.5 and 2 % head-to-head sequences occur.

– *situation of side groups*; the chain $- CH_2- CHR-$ can be regular or irregular:

```
   H  H  H  H  H  H  H  H
 –C–C–C–C–C–C–C–C–
   H  R  H  R  H  R  H  R
```
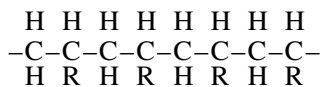
regular; all R's are at one side: *isotactic*.

```
   H  H  H  R  H  H  H  R
 –C–C–C–C–C–C–C–C–
   H  R  H  H  H  R  H  H
```
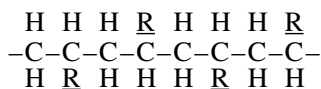
regular; the position of the R's is alternating: *syndiotactic*.

irregular: *atactic*.
This can, more clearly, be seen in a three-dimensional representation, in view of
the actual valency angles (tetraedic, 109°); the –C–C– main chain is situated in
the plane of drawing (Figure 2.4), while the side groups protrude at the front side
or the backside. (syndiotactic configuration)

Figure 2.4. Syndiotactic chain.

With conventional polymerization processes, atactic chains are predominantly
formed; for the formation of isotactic and syndiotactic chains a special catalyst
system is required, e.g. Ziegler-Natta catalysts. Such a process is called:
stereospecific polymerization. It enables the manufacture of, i.a., technically
usable PP and also unbranched PE (see § 4.1). The newest development is the
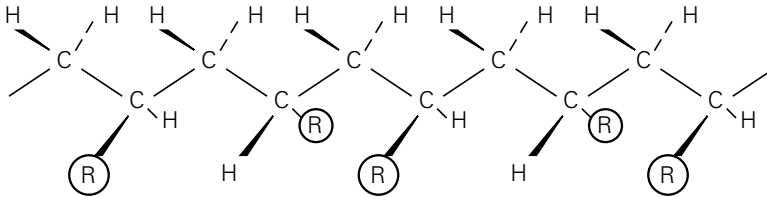metallocene katalyst; it enables the building-up of "chains-to-measure" with very
high degrees of chain regularity; also the manufacture of syndiotactic polystyrene
is technically possible in this way (see Qu. 2.47).

– Round a *double bond* the main chain can show two different configurations,
  e.g. with polybutadiene and polyisoprene (Figure 2.5):
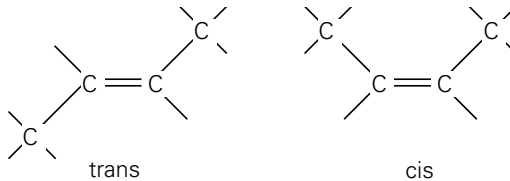
Figure 2.5. Cis- and trans-configuration. E.g. polybutadiene and polyisoprene

Cis-1,4 polyisoprene (natural rubber or synthetic isoprene rubber) and trans-1,4
polyisoprene (balata or guttah-percha) show strongly different properties.
Within a single chain cis- and trans configuration can also both occur in a random
sequence; the chain is than irregular (some kinds of polybutadiene). This has
consequences for the occurrence of strain-induced crystallization (see Chapter 4).

– *Branching* disturbs the chain regularity if the branches are situated at random
  positions   along the chain. In particular with PE a number of branching types
  are present (see Figure 2.6):

a. *strongly branched* with irregular branches: low-density PE LDPE)

b.*little branched*: high-density PE, (HDPE)

c. *strongly branched*, but more regularly: linear-low-density PE (LLDPE)

The names reflect the effect of the branches on the crystallinity and thus on the density and the stiffness.

Figuur 2.6. Three types of branching for PE.

– With *copolymerization* irregular chains are formed when the sequence of the monomers is random::

–A–A–B–A–B–B–B–A–B–A–A–A–B–B–A–

This is called a *random-copolymer*. An example is styrene - butadiene rubber, SBR.

A more regular chain structure is the *block copolymer*:
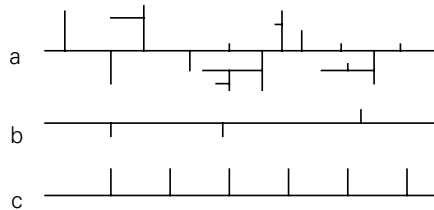
–(A–A——A–A)–(B–B——B–B)–(A–A——A–A)–(B–B——B–B)—
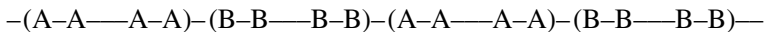
examples are the thermoplastic elastomer SBS (see § 9.1.4) and the *graft copolymer*:

```
–A–A–A–A——A–A–A–A——A–A–A–A——A–A–A–A–A–
     B              B           B             B
     B              B           B             B
     B              B           B             B
```
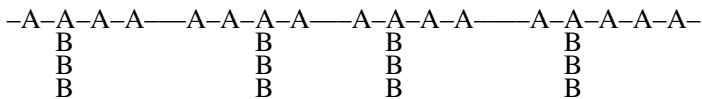
and, in particular, the *alternating copolymer*:

–A–B–A–B–A–B–A–B–A–B–A–B–A–B–
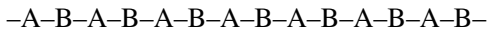
Strictly speaking, condensation polymers such as polyesters could be considered to belong to this category. Also polyketone ("Carilon") would be a strictly alternating copolymer, if the regularity would not have been disturbed by a third comonomer, propylene.

2.4. Chain conformations

Polymer chains are hardly ever met in a totally stretched condition, but are, because of their mobility and flexibility, present as coils. The coil can show all kinds of

shape, as dictated by chance; as a first approximation we may assume a spherical shape. The diameter of this sphere is hard to define; the density in the coil decreases from the centre to the outer boundary. The easiest criterion is the *end-to-end distance,* r_0; this is a strongly fluctuating statistical quantity, of which we must, therefore, try to define some kind of average. This average has some relation with the effective coil diameter.

In order to estimate the end-to-end distance r_0 we assume, as a first approximation, that the chain segments can move freely with respect to each other in all directions. The chain contains *n* segments, each with a length b_0. The next simplification is, that we consider the chain in two dimensions. We now have a simple "random walk" ("drunk man's walk") problem. We situate one chain end in the origin of an *x-y* coordinate system and we build the chain step by step with randomly chosen angles φ (see Figure 2.7). The position of the other end is than given by

$$x = b_0 \cdot \cos \varphi_1 + b_0 \cdot \cos \varphi_2 + \ldots + b_0 \cdot \cos \varphi_n$$

$$y = b_0 \cdot \sin \varphi_1 + b_0 \cdot \sin \varphi_2 + \ldots + b_0 \cdot \sin \varphi_n$$

or:

$$x = b_0 \cdot \sum_{i=1}^{n} \cos \varphi_i; \quad y = b_0 \cdot \sum_{i=1}^{n} \sin \varphi_i$$
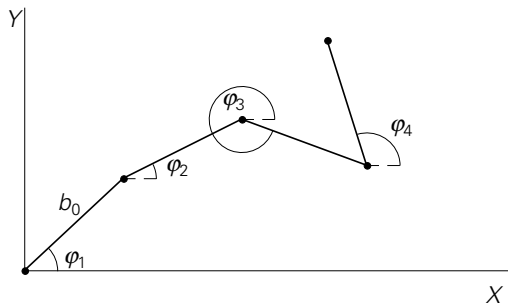
Figure 2.7. 'Random walk'.

The end-to-end distance is $r_0 = \sqrt{x^2 + y^2}$.

$$r_0^2 = x^2 + y^2 = b_0^2 \cdot (\Sigma \cos \varphi_i)^2 + b_0^2 \cdot (\Sigma \sin \varphi_i)^2$$

$$\frac{r_0^2}{b_0^2} = \Sigma^i \cos^2 \varphi_i + \Sigma^i \Sigma^j \cos \varphi_i \cdot \cos \varphi_j + \Sigma^i \sin^2 \varphi_i + \Sigma^i \Sigma^j \sin \varphi_i \sin \varphi_j =$$

$$= \sum_1^n{}^i (\cos^2 \varphi_i + \sin^2 \varphi_i) + \Sigma^i \Sigma^j \cos(\varphi_i - \varphi_j) =$$

$$= n{\cdot}1 + 0 = n$$

The second sum is 0 because $\varphi_i - \varphi_j$ is distributed at random.

The statistical value (the average) of the square of the end-to-end distance is given by:

$$\langle r_0{}^2 \rangle = n{\cdot}b_0{}^2 \quad \text{or} \quad \sqrt{\langle r_0{}^2 \rangle} = b_0 \sqrt{n}$$

Further calculation shows that for a three-dimensional random walk the same result is obtained.

In a second approximation we have to introduce a fixed value for the angle between two links of the chain; since, e.g., the angle between two valency bonds of the C-atom is always $\theta = 109.5°$. (Figure 2.8). For the time being, we suppose *free rotation* around this angle. The approach is similar to the previous case (of course now three-dimensional), and results in:

$$\langle r_0{}^2 \rangle = n{\cdot}b_0{}^2{\cdot}\frac{1 - \cos \theta}{1 + \cos \theta}$$
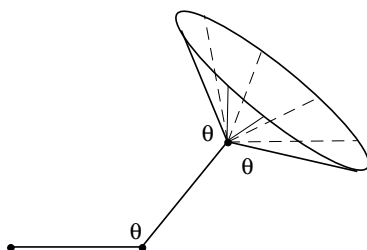
Figure 2.8. Free rotation with fixed valency angle.

This formula is not valid when θ is close to $0°$ or $180°$. It appears that the correction factor

$$= 1 \text{ for } \theta = 90°$$
$$< 1 \text{ for } \theta < 90°$$
$$> 1 \text{ for } \theta > 90°$$
$$= 2 \text{ for } \theta = 109{,}5°$$

In a third approximation we also limit the *freedom of rotation*. This can be illustrated with ethane CH_3–CH_3; when this molecule is rotated around the C–C bond, potential barriers have to be overcome as a result of the interaction between the H-atoms (see Figure 2.9). For PE a similar potential curve can be calculated; this has a more complicated shape as also indicated in Figure 2.9.
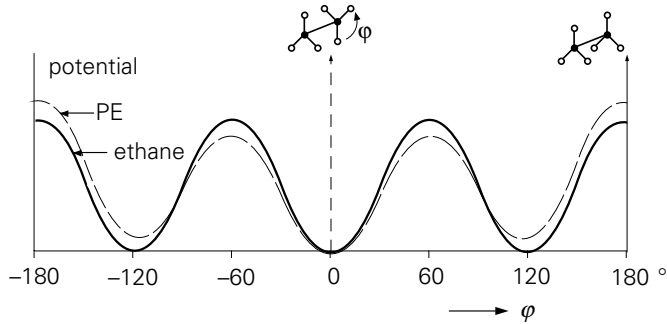
Figure 2.9. Potential curve for rotation

The hindering in rotation necessitates the introduction of an extra correction factor in the formula for $\langle r_0^2 \rangle$. This factor contains the quantity $\langle \cos \varphi \rangle$, which is the average cosine of the rotation angles. For free rotation $\langle \cos \varphi \rangle = 0$ (all values for φ are equally probable), but it differs from 0 when potential barriers are present. It can be calculated from the potential curves. The formula becomes now

$$\langle r_0^2 \rangle = n \cdot b_0^2 \frac{1 - \cos \theta}{1 + \cos \theta} \cdot \frac{1 + \langle \cos \varphi \rangle}{1 - \langle \cos \varphi \rangle}$$

A simplified formula is:

$$\langle r_0^2 \rangle = n \cdot b^2$$

in which b is the effective bond distance, i.e. the length of the fictitious link, which behaves without restrictions as a random walk. We maintain n as the number of primary links (sometimes n is taken as the number of fictitious links), and we define b/b_0 as the *characteristic chain stiffness*. This quantity is, therefore $= \sqrt{2}$ for a –C–C- chain with unrestricted rotation; $b/b_0 > \sqrt{2}$ with hindered rotation.

Still further approximations are required to account for the "*excluded volume*": the chain parts cannot coincide. An important complication is met when the side groups are big enough to hinder each other during chain rotations (see § 2.5). In all cases the formula $\langle r_0^2 \rangle = n \cdot b^2$ remains valid, though b/b_0 increases as a result of these effects. Some estimated values:

	PE	PVC	PMMA	PVAc	PS
(b/b_0)	2.50	2.61	2.97	3.00	3.29

We can now ask the question: What is the magnitude of the *coil density*? How far is the statistical coil, which we have considered so far, diluted? How many monomer units are present in a unit volume? It is possible to calculate how the density, ρ, depends on the distance to the centre of gravity and on the number of links n. It appears that the volume fraction in the centre equals $f_0 = 1/\sqrt{n}$, i.e.:

for $n = 1,000$ $f_0 = 0.03$
for $n = 1,0000$ $f_0 = 0.01$

in other words: the coils are, even in their centre, *highly diluted!*

A rough estimate can also be made without much theory, namely from $\langle r_0{}^2 \rangle = n \cdot b^2$, for example for PE with $M = 140,000$. A chain contains 10,000 CH_2 links, so $n = 10,000$. The length of a link is $b_0 = 0.154$ nm, and we simply assume unrestricted rotation, so that $b = b_0 \cdot \sqrt{2} = 0.218$ nm. We then find:

$$\langle r_0{}^2 \rangle = 10,000 \cdot (0.218 \cdot 10^{-9})^2 \text{ m}^2$$

If we, loosely, think of a sphere with radius r_0, then the volume of this sphere is:

$$V = \tfrac{4}{3}\, \pi \cdot \langle r_0{}^2 \rangle^{3/2} = 0.433 \cdot 10^{-22} \text{ m}^3$$

The mass is $m = 140.000$ g $/ 6 \cdot 10^{23} = 2.3 \cdot 10^{-22}$ kg. The specific mass of the coil is:

$$\rho = m/V = 5.3 \text{ kg/m}^3$$

When we compare this value with the density of amorphous PE ($\rho = 855$ kg/m^3), then the polymer in the coil appears to be 160 times diluted. If we choose the value for b/b_0 as given above, then the result is a dilution factor of 890. Taking into account that the formula $f_0 = 1/\sqrt{n}$ holds for the tightest packed centre, then the results are in the same order of magnitude.

Coiled chains, are, therefore, strongly interwoven; in each volume element of the size of a coil, parts of hundreds of separate chains are present!

The reasoning followed so far is based on the assumption that chains, in finding their most probable coil dimensions, are not affected by their environment; in other words, that no special interactions, either attractive or repulsive, with neighbouring molecules are present. This holds, therefore, for an undiluted polymer, in which a chain does not undergo interactions from the surrounding chains other than those from parts of the chain under consideration itself.

If we now look at polymer solutions, then there are three possibilities (see also Qu. 2.20 –2.23):

– A very *good solvent*; this means that there is an extra interaction between parts of the chain and   the molecules of the solvent, so that the chain segments prefer to be surrounded by more solvent molecules. The coil will then become more expanded.

– A *poor solvent*; parts of the chain feel better in an environment consisting of similar chain segments; the coil will become more compact.

– In between these cases we can define a so-called *theta-solvent,* which, as far as interactions are concerned, behaves, at a certain temperature, like the polymer.

Our calculation of $\langle r_0^2 \rangle$ is therefore, for polymer solutions, only valid for theta conditions. We shall consider this case in somewhat more detail. We have seen that for the determination of the viscosity average molar mass, the Mark-Houwink equation is valid

$$[\eta] = k \cdot M^a$$

in which, in general, a is in between 0.5 and 1. Moreover, it is known that under theta conditions $a = 0.5$.

We have also seen that we have to extrapolate to concentration zero to obtain the intrinsic viscosity$[\eta] = \lim \eta_{\text{red}}$.
Considering the calculation of coil density, this is not surprising. A concentration of 1% in a solution seems small, but when the coil is more than 100 times diluted, considerable mutual penetrations of the coils can be expected, and, therefore, strong deviations from the behaviour of single, separate coils.
Only at very low concentrations can the coils be considered as separate spheres. In that case *Einstein's relation* for the viscosity of suspensions can be applied:

$$\eta = \eta_0 \cdot (1 + 2.5 \cdot \varphi) \ ,$$

in which φ is the volume concentration and η_0 the viscosity of the liquid. Then:

$$\eta_{\text{sp}} = \frac{\eta - \eta_0}{\eta_0} = 2.5 \cdot \varphi \quad \text{en} \quad \eta_{\text{red}} = 2.5 \cdot \varphi / c = 2.5 / \rho$$

in which ρ is the specific mass of the coil, or:

$$\rho = \frac{M}{V}$$

with M the molar mass and V the volume of the coil.
This, combined with the Mark-Houwink equation, yields:

$$[\eta] \ (:) \ M^a \ (:) \frac{V}{M}$$

or

$$V \ (:) \ M^{1+a}$$

If, as above, we express V as:

$$V \ (:) \ \langle r_0^2 \rangle^{3/2}$$

and

$$\langle r_0^2 \rangle \ (:) \ \text{number of links, so} \ (:) \ M$$

then:

$$V \text{ (:) } M^{3/2} \text{ (:) } M^{1+a}$$

so: $a = 0.5$.

This (too) simple derivation confirms that for theta conditions: $a = 0.5$!

When another type of solvent is chosen, a higher value for a can be found, e.g. $a = 1$; in this case:

$$\langle r_0^2 \rangle \text{ (:) } M^{4/3} \text{ instead of (:) } M$$

or a lower a, e.g. 0.35; then $\langle r_0^2 \rangle \text{ (:) } M^{0,9}$.

Deviations of $\langle r_0^2 \rangle$ (:) M can also be brought about by other causes, for example by chain *branching*; as an extreme case we can think of a highly complex branched structure in which the many branches are again branched, so that it can hardly be defined as a chain. The conformation statistics is then no longer applicable, and for such polymers a value of a near to 0 has even be found; this means that V (:) M, just as with small molecules. Viscosimetric determination of M is then no longer applicable, since $[\eta]$ is independent of M.

A deviation in the other direction occurs with super-stiff chains, in the extreme case with rigid rods. The end-to-end distance then equals the whole chain length, so:

$$\langle r_0^2 \rangle \text{ (:) } M^2$$

which means $a = 2$.

This value is, therefore, mentioned as the theoretical maximum of a; it remains an open question what the significance of V is in such a case, thinking of our spheres! For liquid-crystalline polymers values round $a = 1.5$ are indeed being found.

2.5. Chain flexibility
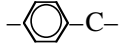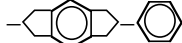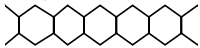
The flexibility of chains is governed by the freedom of rotation of the main chain, and also by the effect of side groups. First we consider the *main chain*. In the foregoing we have already seen that the possibilities for rotation of the main chain are restricted by potential barriers. Some examples for simple compounds are:

$CH_3–(CH_3)$	2.8 kcal/mol
$CH_3–(CH_2–CH_3)$	3.3
$CH_3–(CH.CH_3–CH_3)$	3.9
$CH_3–(OH)$	1.0
$CH_3–(O–CH_3)$	2.7
$CH_3–(COH)$	1.0
$CH_3–(C≡C)$	0.5

Double (C=C) and triple (C≡C) bonds cannot rotate; the ease of rotation of the neighbouring bonds is, however, increased.

The series shown below represents a number of types of main chains with decreasing flexibility:

–C–O–C–   e.g. POM, polyoxymethylene

–C–N–C–   e.g.PA, polyamide, nylon

–C=C–C–   e.g.BR, butadienerubber

–C–C–C–   e.g.PE, polyethene

–⬡–C–   e.g.PC, polycarbonate

–⬡⬡–⬡   PI, polyimide

⬡⬡⬡⬡⬡   ladderpolymers

Side groups mainly affect chain flexibility when the main chain is flexible. An example is *steric hindrance* with (see Figure 2.10)

Figuur 2.10. Steric hindrance.

$X =$ H: $R = 0.09$ nm,   little hindrance
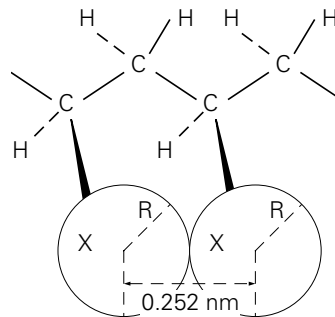$X =$ F: $R = 0.14$ nm,   some hindrance
$X =$ Cl: $R = 0.18$ nm,   considerable hindrance
$X =$ CH$_3$: $R = 0.20$ nm,   considerable hindrance

The situation sketched above is not quite exact, since the substitution of a side group also causes a slight change of θ.
When the sterical hindrance is considerable, no zig-zag conformation of the chain is possible; the number of conformations is then drastically reduced.
The effect of a restriction in rotation is an increase of b/b_0, and, therefore, of the effective coil diameter $\sqrt{\langle r_0^2 \rangle}$.
The chain flexibility has, a.o., a large influence on the glass-rubber transition temperature, and (if applicable) on the melting point.

2.6. Chain interactions

Between parts of the chains interaction forces are active, the *secondary binding forces*, which are much smaller than the primary chemical bonds by which the chains are held together. Several kinds of secondary binding forces exist:

– *dipole forces*; here the distribution of electrical charges within an atom or group of atoms is asymmetric with respect to the centre of gravity (see Figure 2.11). Polar groups form permanent dipoles, which align in the electric field of their neighbours; this results in an electrical attraction force. The interaction is proportional to $1/r^3$ (r = distance), and is slightly dependent on the temperature as a result of the thermal motion of the dipoles. A measure for the interaction force is the *dipole moment*, the value of which is, for a few groups, given in the table below.

permanent dipole   induced dipole
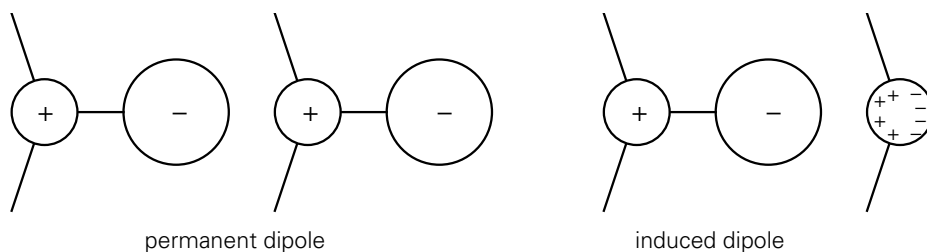
Figuur 2.11. Permanent and induced dipoles.

– *induced dipole*; this is formed when a neutral group is being polarized by induction from a neighbouring permanent dipole. The attraction force is proportional to $1/r^6$ and is slightly temperature dependent.

CH_3–CH_2–X

X	dipolemoment	X	dipolemoment
–CH_3	0	–COOH	1.73
–O–CH_3	1.2	–$COOCH_3$	1.76
–NH_2	1.2	–$COCH_3$	2.78
–OH	1.69	–NO_2	3.68
–Cl	2.05	–CN	4.0

– *dispersion forces* originate from random fluctuations in the charge distribution of an apolar group as a result of the revolution of electrons. A fluctuating dipole induces another one; the net result is an attraction force. Dispersion forces, also called London-Van der Waals forces, are independent of temperature and proportional to $1/r^6$ They form the most important class of interaction forces, as for instance in hydrocarbons.
– *hydrogen bridges* occur between chains in e.g. the following situations (Figure

2.12):
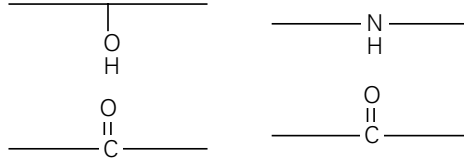
Figuur 2.12. Hydrogen bridges.

The H-valency is being shared with the neighbouring atom, e.g.:

    –N—H—O–
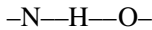
This leads to relatively strong bonds, as in nylon and cellulose. The hydrogen bonds are also responsible for the strong link between water molecules; that is why water, as a very small molecule, has a high boiling point!

Consequences of chain interactions for the behaviour of a polymer are, just as with chain flexibility, mainly the height of the *glass-rubber transition* and the *melting point*.

2.7. Cross-linking

The most important characteristic of a network is the tightness, the spacing between cross-links. Some quantities frequently used will be elucidated in a simple schematic example:

Suppose that we have two chains, each of 20 links, which are, at equal distances, connected by cross-links, as illustrated in Figure 2.13.
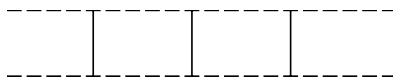
Figure 2.13. Cross-links.

The *cross-link density* is defined as:

$$\rho = \frac{\text{number of units connected}}{\text{total number of units}} = \frac{6}{40} = 0.15$$

The quantity ρ is between 0 and 1; ρ is low for vulcanized rubbers, namely 0.01 – 0.02, and much higher for thermosets.

We further define:

$$
\begin{aligned}
M_0 &= \text{molar mass of the monomer (here e.g. } M = 50) \\
M_c &= \text{molar mass between cross-links (here } 5 \times 50 = 250) \\
M &= \text{molar mass of the whole chain (here } 20 \times 50 = 1000) \\
v &= \text{a number of chain elements, separated by cross-links (here } v = 8)
\end{aligned}
$$

v_e =   effective number of chain parts, contributing to the coherence and the elasticity of the network (here $v_e = 4$).

v_e is related to v, M and M_c according to

$$v_e = v \cdot \left[1 - 2 \cdot \frac{M_c}{M}\right]$$

since the chain is divided into $n = M/M_c$ parts, two of which are always loose, so that the effective fraction is $(n - 2)/n = 1 - 2/n$.

In our case $v_e = 8(1 - 2 \times 250/1000) = 4$.

In this example only one half of the chain parts are effectively contributing to the network properties; the remaining part, the loose ends, are not being deformed when the material is strained.

The various parameters can be determined from measurements of the modulus of elasticity (see § 5.1) and from swelling in solvents.
In most cases, cross-linking is effected by the formation of *chemical bonds* between the chains; the network is then stable, such as with:
– sulphur bridges with rubbers,
– polystyrene chains with unsaturated polyesters,
– bivalent with three- (or more-)valent reacting components,
– cross-linking by irradiation; via radical formation a chemical link between chains is formed.
– other cross-linking agents such as peroxides.

Also *physical cross-linking* occurs with:
– crystallization (see § 4.5 and § 7.2.1),
– domain formation in block copolymers, "self-vulcanizing rubber" or "thermo-plastic elastomer" (see § 9.1.4),
– temporary entanglements, causing rubbery behaviour in unvulcanized rubbers and in molten thermoplastics.

2.8. Problems

2.1. In what aspects can the mainchains of polymers differ?

2.2. *a*. Give the name of four polymers with sidegroups only consisting of hydrogen.
b. Give the name of some vinylpolymers of the type -CH$_2$-CHR-.
c. Give the name of some vinylidenepolymers, -CH$_2$-CR$_2$-.

2.3. Of three polymers, PE, PS and PA-12 the degree of polymerisation is 500.

– Calculate their molar masses.
– Calculate for each polymer the contour length.
– For which types of PE and PS the contour length calculation is valid?

2.4. If we lay a chain with molar mass of 80,000 kg/kmol next to a chain with molar mass of 120,000 kg/kmol, why is the average molar mass not 100,000 kg/kmol? What is the real meaning of the value 100,000 kg/kmol and what is the real value of $\overline{M}_w$?

2.5. Give a definition of n_i, w_i, z_i, and $\overline{M}_n$, $\overline{M}_w$ en $\overline{M}_z$. What is the value of $\sum n_i$, $\sum w_i$ and $\sum z_i$?

2.6. Show that $\overline{M}_n$ can be calculated from the weight fractions w_i through $1/\overline{M}_n = \sum(w_i/M_i)$.

2.7. Show that $\overline{M}_w \cdot \overline{M}_n = \sum n_i \cdot M_i^2$.

2.8. Show that $\overline{M}_w \cdot \overline{M}_z = \sum w_i \cdot M_i^2$.

2.9. *a*. Give a description of a monodisperse polymer.
b. Give the definition of the degree of polymerisation.

2.10. How will an originally very narrow molar mass distribution change if the polymer is being broken down gradually, for example under the influence of oxygen?

2.11. We mix two polydisperse polymers, A and B with average molar masses: A: $(\overline{M}_n)_A$, $(\overline{M}_w)_A$ and $(\overline{M}_z)_A$; B: $(\overline{M}_n)_B$, $(\overline{M}_w)_B$ and $(\overline{M}_z)_B$. The mass fractions of A and B are w_A and w_B. Give a formula from which the $\overline{M}_w$ can be calculated.

2.12. We have three batches, A, B and C of a polymer, each with a $\overline{M}_w$ of of 60,000 kg/kmol, while the heterogenity indices ($D = \overline{M}_w/\overline{M}_n$) are 6.3 and 2, respectively. 10 kg of A is mixed with 10 kg of B. How many kg of C must be added to this mixture to obtain a mixture with $D = 4$?

2.13. Equal weight quantities of two polydisperse polymers with $\overline{M}_n$ of 15,000 and 10,000 respectively, $\overline{M}_w$ of 50,000 and 60,000 respectively and $\overline{M}_z$ of 100,000 and 200,000 kg/kmol are mixed. Calculate the $\overline{M}_n$, $\overline{M}_w$ and $\overline{M}_z$ of the mixture.

2.14. Three monodisperse polystyrene fractions A, B and C have molar masses of 76,000 , 250,000 and 850,000 kg/kmol respectively. The intrinsic viscosities [η], as measured in toluene, are 0.382, 0.91 en 2.21 dl/g. Determine the values of the constants k and a in the Mark-Houwink equation from these data.

2.15. From the fractions in 2.14, 37 grammes of A, 18 grammes of B and 45 grammes of C are mixed. Calculate $\overline{M}_w$ and $\overline{M}_n$ of the mixture.

2.16. From the mixture of 2.15 solutions in toluene are being made with concentrations of 0, 0.1, 0.2, 0.3 and 0.4 g/dl. These fluids need 95.0, 107.7,

121.4, 136.3, and 152.8 seconds to run through an Ubbelohde viscosimeter. Determine the intrinsic viscosity of the mixture and from the intrinsic viscosity the the average molar mass. Compare the value with the values calculated in 2.15.

2.17. Calculate the $\overline{M}_v$ of the mixture, without the determination of the $[\eta]$.

2.18. Eight fractions of polystyrene with very narrow molar mass distributions are mixed

fraction nr	1	2	3	4	5	6	7	8
mass (g)	10	18	25	17	12	8	6	4
M (kg/mol)	15	27	39	56	78	104	120	153

a. To which particular fraction can the mixture be compared best with respect to melt-viscosity?

b. What is the difference between the injection moulding behaviour of this particular fraction in comparison with that of the mixture?

c. To which particular fraction can the mixture be best compared with respect to impact strength?

d. To which particular fraction can the mixture be compared best with respect to die-swell?

e. To which particular fraction can the mixture be compared best with respect to modulus of elasticity in the solid state?

2.19. 50 kg of a monodisperse polymer with $M = 60,000$ kg/kmol is mixed with a certain quantity of a comparable, also monodisperse polymer with $M = 600,000$ kg/kmol

a. How many kg of the latter polymer are needed to obtain a number average molar mass of 100,000?

b. What will then be the values of weight average and z-average molar masses.

2.20. For the end-to-end distance in a coil of a polystyrene with M = 1000,000 kg/kmol it can be determined that $(\langle r_0^2 \rangle)^{1/2} = 73{,}5$ nm. Calculate the coil density and compare this value with the density of polystyrene 1050 kg/m^3.

2.21. Calculate the "degree of dilution" for a polystyrene with M= 10,000 kg/kmol.

2.22. What are the consequences from the results found in 2.20 and 2.21 for the so-called dilute solution (a solution in which the coils do not penetrate into each other)?

2.23. In what way will this influence the measurement of the intrinsic viscosity?

2.24. Two batches of PE, A and B, with $\overline{M}_w = 200,000$ and 30,000 kg/kmol respectively are being mixed with the intention to obtain a mixture with $\overline{M}_w = 81,000$. Both batches have the same form of molar mass distribution, with D = $\overline{M}_w /\overline{M}_n = 5$, and $\overline{M}_z/\overline{M}_w = 3$.

Calculate how many kg of each component is needed to obtain 1000 kg of the desired mixture. Calculate the $\overline{M}_n$ and $\overline{M}_z$ of the mixture. To what extent will the

properties of this mixture differ from a directly produced batch with $\overline{M}_w = 81{,}000$ and the same distribution width as A and B?

2.25. The intrinsic viscosity is related to the molar mass by the Mark-Houwink equation: $[\eta] = k \cdot M^a$.
a. In what range can the value of a usually be found?
b. What is the relation of $\overline{M}_v$ of a polydisperse polymer, calculated from the Mark-Houwink equation, to $\overline{M}_n$ and $\overline{M}_w$?
c. In which case can $\overline{M}_v$ be higher than $\overline{M}_w$?

2.26. We have two white cubes. One cube is a polymer. The other one is a low molecular substance. Both cubes can be solved in the same solvent. Give some simple ways how to determine in the laboratory which of the two cubes is made of the polymer?

2.27. Explain why the heterogenity index $D = \overline{M}_w/\overline{M}_n$ is approximately 2 for an ideal polycondensation process.

2.28. Equal molar quantities of 1,2 ethanediole and benzene-1,4-dicarbonic acid are mixed in order to react to a polymer.
a. What is the mass ratio of the components?
b. Give the equation of reaction. What is the name of the polymer?
c. What is the meaning of the symbols in the formula $P = 1/(1 - p)$?
d. Which conversion is needed to reach a $\overline{M}_n$ of 40,000 kg/kmol? What will then be the value of $\overline{M}_w$?
e. Which circumstances can prevent that the desired conversion will be reached?

2.29. Which type of polymerisation process will result in a polymer with a D-value close to 1?

2.30. Which methods can be use for the measurement of $\overline{M}_n$, of $\overline{M}_w$ and $\overline{M}_z$ and give a description of the principles on which these methods are based.

2.31. For a polymer in solution the following data were found from a viscometer experiment:

run time solvent		100	sec
run time solution	0.05 g/dl	106.25	sec
	0.1 g/dl	115	sec
	0.15 g/dl	126.25	sec
	0.2 g/dl	140	sec

Calculate the intrinsic viscosity from these data.

2.32. If the value of $[\eta]$ for the same type of polymer with $M = 50{,}000$ and $M = 800{,}000$ is 0.5 and 2.0 dl/g respectively, what is the value of M of the sample under investigation?

2.33. Calculate the values of the constants in the Mark-Houwink equation for the polymer solvent combination from 2.31.

2.34. *a*. A monodisperse polymer with M = 20,000 is contaminated with 2% (w/w) polymer of M = 200. Calculate the values of $\overline{M}_n$, $\overline{M}_w$ and $\overline{M}_z$.
b. Now the monodisperse polymer contains 2% (w/w) chains with M = 2,000,000. Calculate also the values of $\overline{M}_n$, $\overline{M}_w$ and $\overline{M}_z$ for this contaminated polymer.

2.35. Osmotic pressures are measured at 25 °C from a dissolved polymer at various concentrations c and the following fluid heights were found:

c (g/dl)	h (mm)
0.12	6.50
0.18	9.94
0.25	14.05
0.33	18.8
0.45	26.6

Determine $\overline{M}_n$ from these data. The solvent density is 903 kg/m³, R = 8.314 J/mol.K and g = 9.81 m/s².

2.36. The two figures (Figure 2.14) give imaginary results of osmotic pressure measurements ($\prod/c$ versus c) and solution viscosity measurements (η_{red} versus c), each with two different solvents A and B. Explain why in the case of the osmotic pressure measurements extrapolation leads to the same value and in the case of the viscosity measurements extrapolation does not lead to the same value.
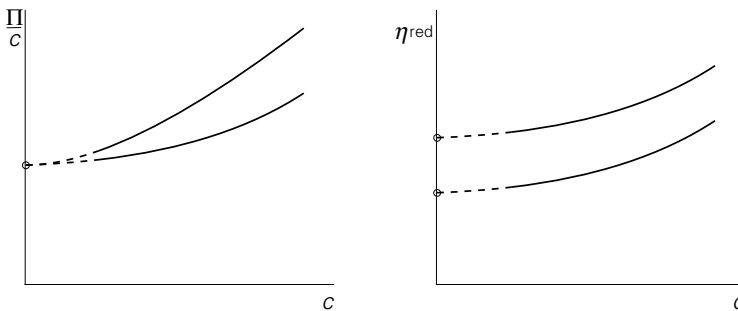

Figure 2.14. Figure for problem 2.36

2.37. Why does the sensitivity of the determination of the intrinsic viscosity increase with increasing molar mass but decrease with the determination of the osmotic pressure?

2.38. Nylon 6.6 is produced twice by an ideal polycondensation process from adipic acid, HOOC-(CH₂)₄-COOH, and hexamethylenediamine H₂N-(CH₂)₆-NH₂. In the first case (A) the conversion p = 0.99, in the second case (B) the conversion is 0.995. Calculate $\overline{M}_n$ and $\overline{M}_w$ for both cases.

2.39. 30% of A and 70% of B are mixed. Calculate $\overline{M}_n$ and $\overline{M}_w$ for this mixture.

2.40. How can, without measuring the viscosities of solutions at various concentrations, a simple comparative measure be found for the average molar mass?

2.41. For PVC k-values are used, like k = 55, k = 70. What is the meaning of these values both molecular and technological?

2.42. Why is the melt-index, as used for e.g. PE, PP and ABS a useful and functional measure for the molar mass?

2.43. A light scattering experiment applied to two types, A and B, of the same polymer results in the same value for M for both types. The value of the intrinsic viscosity of type A is however higher than that of type B. What can be said about the ratio of the osmotic pressures of A and B?

2.44. Which principle is the basis of GPC (Gel Permeation Chromatography or SEC, Size Exclusion Chromatography) How can the various average molar masses like $\overline{M}_n$, $\overline{M}_w$ and $\overline{M}_z$ be determined from the result of a GPC-measurement?

2.45. In what aspects can a polymer chain be built up irregularly? Give examples of each aspect.

2.46. Give schematically the difference in the structure of an isotactic, an atactic and a syndiotactic polymer formed from the monomer $CH_2=CHX$.

2.47. What are the consequences of the steric configuration of the chain for practical usability and for the properties if X is CH_3 or C_6H_5? (T_g of PP and PS are –15 °C and 95 °C respectively)

2.48. Give two factors which cause a high chain stiffness. Give an example of each factor.

2.49. Give two strong and one weak interaction force between chains and give examples of polymers in which these forces occur.

2.50. What is being understood by the expression cross-link density?   Give another measure to characterize the degree of crosslinking. How can these properties be determined?

2.51. What is the difference between chemical and physical cross-linking. Give examples of both types. In what way does the difference show up in the properties of the network?