CONTRIBUTION TO THE HISTORICAL DEVELOPMENT OF MACROMOLECULAR CHEMISTRY – EXEMPLIFIED ON CELLULOSE

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Dedicated to Professor Elfriede Husemann,
on the occasion of her 100th birthday in December 2008.
She was an admirable and internationally highly recognized scientist
and the first director of the Institute of Macromolecular Chemistry
(Hermann-Staudinger-Haus) of the Albert-Ludwigs-Universität Freiburg;
the foundation of the institute owing to the eminent scientific success
and recognition of the work of Hermann Staudinger,
leading to the Nobel Prize in the field of macromolecular chemistry.

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The development of the structure determination for cellulose and its derivatives as macromolecules is described from the beginning of the 20th century to the 1940s. The first correct presentation of the constitution of cellulose as a linear chain macromolecule of 1-4 linked β-D-anhydroglucopyranose, with the help of organic chemistry, dates from 1928. The size and shape of cellulose molecules still remained a controversial topic for some time. On the one hand, there were proposals of micelles i.e. aggregates of cyclic mono- or oligoanhydroglucose or micelles of small macromolecules of 30-50 glucose units. On the other hand, cellulose was seen as large macromolecules with more than 3000 glucose units for structures considered in solution as well as in fibres. The final clarification of the cellulose structure as a semi-flexible macromolecule of high molecular weight was extremely hindered by the inadequate interpretation of experimental results. Later, additional experimental and theoretical methods led to a consistent picture of the cellulose structure with high precision.

Keywords: cellulose constitution, structure, molecular weight; primary valence bonds of cellulose and polyoxymethylene as model

INTRODUCTION

For thousands of years, cellulose served humans’ needs, in various forms, such as fibrous materials (cotton, ramie, hemp, etc.) or composite materials, e.g. wood, even though it was much later that humans acquired knowledge of its chemical constitution, configuration or molecular conformation. This was also true of the cellulose derivatives, when they became available in the 19th century. It was only at the beginning of the 20th century that new and improved methods for evaluating materials were discovered and applied to cellulose with the goal of improving its physical properties and satisfying scientific curiosity. As a biopolymer and the main constituent of organic renewable materials, cellulose played a major role in the development of macromolecular chemistry.

Cellulose is defined as a linear macromolecule, a non-branched chain of variable length of 1-4 linked β-D-anhydroglucopyranose (Fig. 1). Cotton comes very close to this ideal of cellulose,
since it contains, beside cellulose, only ca. 5% impurities. Ramie is often chosen as a model cellulosic fibre, despite its ca. 25% impurities, because of its better oriented crystalline fibrils.

Figure 1: Representation of a cellulose molecule fragment as 1-4 linked β-D-anhydroglucopyranose and labelling of the C-atoms. The atoms linked to C, i.e. O and H, are assigned the same numbers. A dimer is observed at repeat distance (fibre repeat) in the crystalline state of native cellulose.

Today’s knowledge of the cellulose structure results from a great number of investigations carried out by many scientists. The clarification and development of the cellulose structure has been for a long time marked with controversial opinions and ideas. The influence and progress of ingenuous ideas and their scientific recognition can be studied here in various ways.

It is difficult to judge and assess knowledge within a certain field in a certain period of time, since we have to rely on the information available at that time, but we actually judge it according to our today’s knowledge. We all recognize and appreciate certain conceptions, which in the end may converge to an accepted representation of disputed ideas, structures or models, however, it is impossible to predict such a development in a field at the time when those conceptions were introduced.

The importance of some scientific discoveries, such as the discovery of X-rays or neutrons, is indisputable. However, there have been discoveries that led to Nobel Prize awarding and were still disputed when the prize was granted. Michelson’s work established the constant velocity of light in vacuum with and against the rotation of the earth, leading to the exclusion of an ether. This was the basic experiment for the special theory of relativity, but its author was honoured “for his optical precision instruments and the spectroscopic and metrological investigations carried out with their aid”. Einstein won the Nobel Prize “for his services to theoretical physics, and especially for his discovery of the law of the photoelectric effect”. Planck, Nernst and others rejected this law in an endorsement address supporting Einstein’s membership to the Prussian Academy of Sciences (c.f. Appendix). Einstein’s theory of relativity was regarded by many scientists as more important and Einstein himself chose the topic “Grundgedanken und Probleme der Relativitätstheorie (Fundamental Ideas and Problems of the Theory of Relativity)” for his Nobel Lecture.

The structure of the hydrogen atom, as it was proposed by Bohr, certainly represents an ingenuous idea for his times and explains the optical line spectrum of the hydrogen atom. However, the model cannot be transferred to helium nor explain chemical bonds. John von Neumann, who has influenced a great deal the basics of physics and computers, expressed his concept of models as follows: „The Sciences do not try to explain, they hardly even try to interpret, they mainly make models. By a model is meant a mathematical construct which, with the addition of some verbal interpretation, describes observed phenomena. The justification of such a construct is solely and precisely that it is expected to work.”

The development of models of cellulose in solid state or in solution shows that scientific knowledge and scientific progress rely on dispute. After overcoming the controversial conceptions and difficulties that were mainly related to the lack of exact methods at the beginning of the development of macromolecular chemistry, the 1953 Nobel Prize in chemistry was awarded to Hermann Staudinger, in recognition of “his discoveries in the field of macromolecular chemistry”. Herein, we will try to follow the path of the development of macromolecular
chemistry in elucidating the study of cellulose.

**Constitution**

The chemical constitution of a low or high molecular weight organic compound can be determined in the following steps. Elemental analysis leads to a quantitative composition formula for the substance. The materials must be pure and uniform. Purity is easy to confirm for low molecular weight compounds, since the materials will possess the same definite physical properties after fractional distillation or crystallisation. As a further step, the mass or respectively, the molecular weight of the kinetic active particles in solution or vapour should be determined. The size of a particle (molecule) provides information about how many atoms are linked by primary valences. Care has to be taken, because primary valence (covalently linked) molecules could be associated by secondary interactions, such as van der Waals forces or hydrogen bonding. Such association should be ruled out by changing the solvent, the temperature or by the influence of chemical reactions. The emerging materials may be characterized by analysis, e.g. by the melting point. Today, materials are easily analysed by spectroscopic methods – among others, NMR. Notably, crystalline materials can be precisely described by single crystal X-ray analysis, their composition may be detected and, in addition, both their conformation and absolute configuration may be rendered, if sufficient intensity data are collected.

For high molecular weight compounds, the analysis of configuration is more complex because of the distribution of molecular weights and imperfect crystallisation. Their structural analysis requires knowledge on the basic units (monomers) of the molecules, which can be obtained by a mild degradation and evaluated by subsequent examination of the products by chemical or spectroscopic methods.

**Chemical constitution of cellulose (before 1920)**

**Constitution of the monomer unit**

The structural chemistry of cellulose experienced little noticeable progress until 1920 because, except for chemical analysis, the methods needed for evaluating the structures were not developed yet or did not possess the necessary precision. In 1919, when Emil Fischer, the senior champion of organic chemistry, as he was called by Haworth,\(^1\) passed away, the bases for the structural knowledge on simple crystalline and soluble sugars were developed. Cellulose and its derivatives however were mostly considered insoluble, representing fibrous materials with no sharp melting point. Attempts to determine the molecular weight led to negative or indefinite results. The required criteria of homogeneity and purity of cellulose were not fulfilled, but investigations were carried out and the results obtained led to contradictory interpretations due to inadequate evidence. The composition of mixtures could vary, depending on their individual preparation, which led to confusion, also caused by divergent formulation of the data obtained with essentially the same methods. Thus, confusion spread instead of the expected clarification of the structural chemistry of cellulose. However, one basic idea was clear to many scientists – the physical properties of cellulose and its derivatives in the solid state or in solution required a molecular weight that was considerably larger than the monomeric unit.

This review will also present some results on sugars that were known before 1920 and that are necessary for the further discussion of the basic units of cellulose. Emil Fischer synthesised glucose i.e. the basic monomeric unit of cellulose. The anomeric α- and β-glucosidic series had been investigated by chemical reaction and optical rotation as well as the D- and L-structures without establishing absolute configurative relations. The configuration of cellobiose belonged to the β-series according to Fischer and Zemplén.\(^2\) The proposed pentagonal geometry of a glucose molecule originated from Böeseken\(^3\) as shown in Figure 2. That was the accepted configuration until 1925 when Haworth\(^4,5\) introduced a hexose in pyranose form (c.f. Fig. 1), i.e. a six-membered ring.

Cellulose \[\left[\text{C}_6\text{H}_{10}\text{O}_5\right]_n\] by elemental analysis) degrades mostly if not completely...
to glucose (Ost and Wilkening⁶), which was confirmed by several other researchers with improved experimental techniques. The crystalline parts of cellulosic materials were identified by orientation birefringence (Ambroûn⁷) and X-ray investigations (Nishikawa and Ono⁸, Scherrer,⁹ Herzog and Jancke¹⁰) and the resemblance of crystalline cellulosic materials in various plants and wood pulp was recognised by Herzog and Jancke.¹¹ Surprisingly, in 1919 biosan (cellobiose) and triosan (cellotriose) were described as polysaccharides.

The treatment of cotton with sulphuric acid and acetic anhydride degrades cellulose and leads to remarkable amounts of cellobiose octaacetate, first isolated by Franchimont¹² and recognized as a disaccharide by Skraup and König.¹³ Haworth and Hirst¹⁴ showed that this compound consisted of two glucose units, which should be linked by a 1-5 or 1-4 glycosidic bridge, and proposed a similar linkage between the monomer units of cellulose. In 1927, the 1-5 linkage was excluded and a 1-4 linkage was established for cellobiose (Haworth et al.¹⁵, Zemplén¹⁶, Fig. 3).

Valence chain

The conceptions of Tollens¹⁷ on cellulose, represented in Figure 4, propose a high number of linked glucose residues (he discusses 4 as well as 20), Nastukoff¹⁸ and Böeseken proposed at least 40 – the ends were joined to form large rings.

Cellulose forms derivatives with nitric and acetic acid, i.e. a trinitrate and triacetate, as well as a trimethylether. Octaacetylcellobiose is obtained if cellulose is treated with a mixture of sulphuric acid and acetic acid anhydrate (so-called acetolysis, Franchimont¹²). These investigations provided no information on whether other sugars are present, on the steric or constitutional aspects of the type of linkage or the degree of branching.

Constitution and shape of cellulose (after 1920)

Primary valence chain

The first attempts made at clarifying the constitution of cellulose were based on limited methods of investigations. Progress in the methods of organic chemistry and especially of the physical investigations, in solid state as well as in solution, led to partly new controversial ideas about the structure of cellulose: is cellulose composed of long
linear chains of glucose residues connected by covalent bonds, or does it consist of a cluster of anhydroglucosidic rings held together by strong secondary valences?

Freudenberg\textsuperscript{19} (1921) improved the reaction by acetolysis and the yield of octaacetylecellobiose of Franchimont,\textsuperscript{12} Ost\textsuperscript{20} and Madson,\textsuperscript{21} who actually achieved the highest yield. Freudenberg came to the following experimentally supported conclusions: depending on the reaction time, about 40\% of the theoretical value of octaacetylecellobiose was isolated; during the reaction, about 20\% of the already formed octaacetate was degraded, which meant that about 60\% of the glucose units, but not much more, were initially obtained in the state of octaacetylecellobiose. This observation led Freudenberg to the following proposal relying on the experimental result that cellulose consists of 100\% glucose units: if all glucose units in a chain are connected by alike bonds and are split with equal probability, about 67\% of biose molecules should result according to the rules of probability. Freudenberg found 40\% which, considering the loss, led to 60\% – close to the expected 67\% – that is, considerably below 100\%. Freudenberg concluded from these results that these findings cannot be taken as a proof for a continuous cellulose chain, although nothing speaks against. In his cellulose model, each glucose unit is linked to the next one by a linkage that is structurally and configurationally identical to the linkages in cellobiose. On the other hand, Polanyi\textsuperscript{22} determined the content of the X-ray unit cell to four glucose units. Therefore, cellulose could consist of either continuous linked cellobiose anhydrides to form chains – two chains running through the unit cell - or of two rings of cellobiose anhydride. The rings of cellobiose anhydride should lead to 100\% cellobiose, in contradiction to the observed value of 67\%, and a chain structure can be concluded (Freudenberg\textsuperscript{23}). No experimental evidence about the length of the cellulose chains was accessible.

**Association of low molecular weight compounds**

Karrer,\textsuperscript{25} who shared the 1937 Nobel Prize with Haworth, opposed the projected continuous chain structure of Freudenberg observing that starch, the composition of which is comparable with cellulose, can be completely degraded by enzymes to maltose (the 1,4-linked dimer of \(\alpha\)-glucose). The acetolysis of cellulose, which resulted in 50\% cellobiose in his experiments, should not be over-emphasised. Later it was proposed that the degradation of starch by enzymes started from the end of the molecule and, therefore, did not fulfil the statistical degradation that had been assumed by Freudenberg.

Karrer\textsuperscript{26,27} investigated amylose and natural starch and reached the conclusion that after derivatisation and comparison with identical derivatives of maltose, these two materials (amylose and starch) consisted of maltose anhydride in colloidal form. The molecular weight determination of a soluble but dissociated product, obtained by alkaline methylation of starch, the reaction of which proceeded without degradation in his opinion, led to an upper limit of molecular particle weight – from 900 to 1200. Karrer concluded that these particles were identical with the starch molecules and consisted of 4 to 6 glucose units, some still in aggregated form. He also proposed maltose anhydride aggregates for amylose due to the high value of the heat of combustion. Exactly the same value for the heat of combustion was observed for cellulose and, therefore, Karrer excluded a long chain for the cellulose molecule and proposed, in analogy to starch, cellobiose anhydride as the basic unit of cellulose. The content and symmetry of the X-ray unit cell, established by Herzog and Jancke\textsuperscript{28} (2 cellobiose anhydride units), supported his idea that cellulose fibrils consisted of aggregated cellobiose anhydride.

Similar ideas were developed by Herzog,\textsuperscript{29} as well as by Bergmann\textsuperscript{30} and Hess,\textsuperscript{31} who even proposed glucose anhydride as the structural unit. On the other hand, Bergmann refused to apply the term “molecule” for insoluble or only colloidal dispersed organic materials. In solution, these proposed small compounds form aggregates or so-called micelles (c.f. Appendix) arranged similarly to micelles in a soap solution. This proposal of a micellar
concept of cellulose dominated the scientific literature for almost a decade. Especially biologists were attracted to it, since the idea followed the thoughts of C. v. Nägeli,24 (Fig. 5), who showed by microscopy that cotton crystallises in domains, and the so-called micelles formed would also necessitate a colloidal character in solution. This idea was confirmed by diffusion experiments carried out on cellulose nitrate by Herzog.29 He found the same size for the micelles (crystallites) in the solid state and those in colloidal solution, the interpretation being that the micelles of the crystalline structure transfer without changes into solutions. Hess et al.32 concluded from these data that the properties of cellulose are not based on the size of the molecules, but rather on a skin that surrounds the cellulose micelle. Therefore, cellulose degradation depends to a large extent on the slow destruction of these skin systems.

Meyer and Mark33 expressed similar thoughts, interpreting the domains determined by the Scherrer X-ray method in crystalline fibres as the size of micelles (crystallites). They proposed a micelle model for cellulose fibres – shown in Figure 6 – consisting of bundles of parallel primary valence chains of cellulose (c.f. the discussion on the cellulose structure). The micelles are held together by special micellar forces and are still present in the solution. This concept of K. H. Meyer34 was well-accepted among chemists. By inter-micellar swelling, these micelles would be loosened and finally dissolved as colloidal particles in solution. Osmotic measurements provide micellar weights and not molecular weights. This interpretation appeared quite plausible, since the solutions of many macromolecular materials behave like colloidal soap solutions. Therefore, McBain,35 who worked primarily in the field of soaps, stated that cellulose and similar materials show a micellar form.

In a survey on the constitution of carbohydrates, Haworth1 expressed the opinion that Hermann Staudinger most effectively opposed the association theory. By synthesis as well as by investigations of high molecular weight materials, Staudinger had supported the classical principles of the formation of biopolymers as very large chains of monomer units linked by primary valences.

In an interdisciplinary research project, chemists and physicists in Freiburg showed that the basic units of polyoxymethylene are connected by chemical valences – advanced by Kekulé – to give long chains of single molecules that surpass the longest dimension of the X-ray unit cell. For cellulose in solution, the concept of micelles was contradicted by the results of Stamm,36 who detected molecular disperse particles (single molecules) by studies with an ultracentrifuge. He complained that the diffusion measurements by Herzog and Krüger (1926)37 showed particle weights that were too high because they were carried out at insufficient low concentrations to actually obtain free diffusion. Also, their evaluation did not take into account the fact that the particles were not spherical.
Molecular disperse solutions of cellulosics were later detected by many authors.

Bergmann and Machemer corrected their own misconception as well as that of Herzog and that of Hess and Friese, according to which cellulose consisted of associated celllobiose anhydride or associated glucose anhydride. They investigated the degradation products of cellulose acetate by titration of the end-groups with iodine and found a mixture of oligosaccharides of 7-9 and 9-11 hexose residues, respectively, depending on preconditioning, and excluded celllobiose anhydride as the structure of cellulose. Haworth and Machemer hydrolysed trimethyl cellulose and isolated both the expected 2,3,6 trimethyl glucopyranose and 2,3,4,6 tetramethyl glucopyranose. They concluded that their cellulose material contained not less than 50 and not many more than 100 celllobiose units. This proof on trimethyl cellulose is of importance since the methyl group cannot be transferred during the reaction to other positions in the molecules. Further evidence against celllobiose anhydride as representing cellulose in the fibres came from the hydrolysis of cellulose performed by Willstätter and Zechmeister, who found cellobiose and -tetraose as degradation products.

Side groups and ring structure

Cotton derivatisation led to the conclusion that three hydroxyl groups are present in the monomer unit, which means that trinitrate and triacetate can be formed. The position of the hydroxyl groups was detected by Denham and Woodhouse by the methylation and hydrolysis of cotton. The product obtained was identified as 2,3,6 trimethyl glucose. Irvine and Hirst showed that complete methylation yielded only 2,3,6 trimethyl glucose, and proposed a ring-shaped trisaccharide as a model for cellulose. They favoured the structure shown in Figure 7, i.e. trianhydroglucose, which may be realised by various isomeric units, as the simplest form for a model of cellulose with a 1-5 linkage of monomers. The maximum theoretical yield of celllobiose amounts to 70%, with 37% of glucose. The researchers did not exclude larger odd-numbered rings of anhydroglucose residues, but were unable to make assumptions on the size of the cellulose molecule. They refused to accept the hypothesis that cellulose was based on a molecule containing an even number of hexose units. Their proposed model, plotted in Figure 7, is in disagreement with the X-ray results of Polanyi and with the dimeric models obtained by researchers later. Irvine and Hirst stressed that the fragments of cellulose consist of 1-5 linked anhydroglucose – this linkage is also present in celllobiose - and that all glucose units are identical in the cellulose molecule. The isolated 2,3,6 trimethyl glucose excludes a number of structural models for cellulose, e.g. the comb model of Hess, described in the paper of Irvine and Hirst. Their model is certainly strongly influenced by the discussion of the cellulose structure as aggregations of small ring-like molecules.

Figure 7: Preferred structure of cellulose, adapted from Irvine and Hirst

The model given in Figure 7 was not confirmed by later experiments of Zechmeister and Tóth, nor by their joint publication with Mark, who isolated cellobiose, tetrose and -hexose with glycosidic linkages from the hydrolysis mixture (c.f. also Willstätter and Zechmeister). However, the length of the original chain of cellulose remained undetermined and linkages, other than the β-glycosidic ones, were not excluded with certainty. In contrast, Freudenberg and co-
workers rejected the presence of non β-glycosidic bonds by iodine-controlled hydrolytic scission and confirmed a chain structure of cellulose.

Until 1925, chemists had accepted a five-membered ring for glucose, cellobiose and cellulose, as consistent with the experimental facts. The formulation of glucose as a six-membered ring by Haworth changed the situation completely, above all clarifying the representation of cellobiose as a 1-4 linked β-D-glucose (Haworth). The twisting of the second ring by ca. 180° is necessary to obtain a reasonable glycosidic bond angle (Fig. 1) and a linked sequence of cellobiose molecules leading to an extended cellulose chain, which would meet the observed 10.3 Å fiber repeat distance. The spatial shape of the glucose molecule was proposed by Reeves as a 4C₁ trans-Sachse chair conformation in today’s nomenclature, which was the energetically favoured structure confirmed by experimental observations (Fig. 8). This proposal was later confirmed by the X-ray single crystal analysis of β-D-glucose (Ferrer, Chu and Jeffrey) and of the 1-4 linked β-cellobiose (Jacobson et al., refined by Brown, and further by Chu and Jeffrey) or of methyl cellotrioside (Raymond et al.) and of cellotetraose (Gessler et al., Raymond et al.) as a fragment of cellulose. With sufficient precise data from X-ray analysis, the conformation and absolute configuration can be determined. Adequate data are not available for crystalline polymer fibres, additional data being necessary, besides the X-ray intensities, for a spatial evaluation of their molecular shapes.

Figure 8: Representation of the 4C₁ and 1C₄ chair conformations of glucose, adapted from Lehmann

Model compound polyoxymethylene (POM)

C. Priesner praised the review on polymerisation published by Hermann Staudinger: “Of fundamental importance for the investigation of polymers of natural and synthetic origin has been an article “Über Polymerisation” published in Berichte der Deutschen Chemischen Gesellschaft issued on June 12, 1920. It can be said without exaggeration that this paper has pointed the direction for modern macromolecular chemistry. The within included thesis has been wholly confirmed by researches in the following years, appearing surprisingly modern in its formulation.”

Formaldehyde was an example, polymerising to a short linear chain of paraformaldehyde or to a longer chain called polyoxymethylene with the same basic chemical units in the chain. Isoprene was also discussed, representing a linear rubber chain, according to Pickels, who did not specify a chain length. Cellulose was not mentioned in this review. In the following years, Staudinger concentrated his investigations mainly on three domains: 1) rubber and synthetic isoprene polymers (Staudinger and Fritschi, Staudinger); 2) synthetic polymers, especially polymeric formaldehyde (polyoxymethylene, Staudinger and Lüthy, Staudinger); 3) cellulose. Staudinger regarded the engagement with synthetic polymers as extremely important, since the monomeric or basic units are well-known, and products with graduated polymerisation are accessible. The results obtained for polyoxymethylene were then transferred to cellulose by analogy. From 1929 on, Staudinger worked experimentally with
cellulose (Priesner), concentrating his numerous investigations on the size and macromolecular character of cellulose.

His studies on the macromolecular character and structure of polyoxymethylene are of exceptional importance, since they combine data of organic chemistry with X-ray investigations to give sound results. These results concern primary valence chains, the length of a linear chain molecule and the formation of fibres. By the scission of high molecular weight polyoxymethylene with acetic anhydride, short chains of polyoxymethylene diacetates were produced. After fractional distillation and crystallisation, they were separated into single individual compounds (up to a degree of polymerisation DP = 22). End group determination and osmosis resulted in the same molecular weights. The analysis of the undissolved residue showed an average DP of ca. 50 (Staudinger et al. 55, 66). The subsequent X-ray investigations on crystalline materials by the Debye-Scherrer method led to the results listed below, with significant consequences.

All high molecular weight POMs with various end groups led to the same X-ray diagrams, from which the same unit cell size was concluded. This unit cell contains the same number of molecular units that have the same basic molecular structure. The shorter polyoxymethylene diacetate with 9 to 19 formaldehyde groups exhibit the same rings in the Debye-Scherrer (powder) diagrams as high molecular weight polymers do, but they are less sharp and are sometimes split into several fine rings, under the influence of end groups. Further reflections appear at very small diffraction angles in the innermost region of the diagram. The spacings of those reflections are influenced by the length of the crystallites of the various fractions. The diagram of POM can be indexed with an orthorhombic (quasi-hexagonal) unit cell with \( a = 4.56 \, \text{Å}, b = 7.89 \, \text{Å}, c = 3.54 \, \text{Å} \). According to density considerations, a unit cell contains four monomeric units placed in two chains – to be consistent with the size of the unit cell, which means that one dimer unit is placed along each chain within the unit cell. The chains are located parallel to the c axis derived from morphological considerations (Fig. 9). With these data, the length of a \(-\text{CH}_2\text{O}-\) monomer unit amounts to \( c/2 = 1.77 \, \text{Å} \), somewhat shorter than the expected and calculated distance of 2.37 Å between the two carbon atoms of C-O-C (bond length C-O and O-C 1.410 Å, angle C-O-C 114°). This shortening has been explained by a tilt of the monomer unit toward the c axis.66 The small-angle X-ray reflection shows for compound \((\text{CH}_3\text{CO})_2\text{O}*(\text{CH}_2\text{O})_n\) a spacing of 25.3 Å for \( n = 9 \) and leads to an increment of 1.8 Å for each additional monomer CH$_2$O-unit. This value corresponds to \( c/2 (1.77 \, \text{Å}) \) for the high molecular weight POM and distinctly shows that the same elongation of the chain is obtained by adding a monomer unit to the chain of polyoxymethylene diacetates. This increment corresponds to the same distance of the continuous monomer units of the chain of high molecular weight POM in the c-direction. Therefore, it can be concluded that a continuous primary valence chain with covalent chemical bonds is running through the unit cell.

Actually, the POM chain forms a helical structure with a 2\(_1\) screw axis parallel to the c axis,67 (Fig. 9) and the POM macromolecule does not exhibit the maximal possible length. Because of regular gauche conformations along the skeleton of the chain, a shortening of the chain occurs in the c-direction of the unit cell. The projection of the distance of adjacent C…C atoms of 2.37 Å of a monomeric unit on the c-axis amounts to 1.77 Å as observed. The ball and stick models with known standard bond lengths and angles that Sponsler and Dore (1926) 68 successfully used for the determination of the crystal structure of cellulose could have also been effectively applied to POM. That modelling would have demonstrated that Staudinger’s idea that regarded macromolecules as rigid rods with the most extended chain length was not adequate either for the solid state, or for solution. POM also provided evidence that the shape of the chain is flexible even in the solid state. A second crystalline modification of POM was obtained and investigated by Hengstenberg69 and Sauter70 with samples from Staudinger’s laboratory, requiring further changes in the conformation (shape) of the chain skeleton.
Figure 9 was drawn with the coordinates of a later performed single crystal X-ray analysis (Gramlich67) with a bond length C-O of 1.410 Å, angle C-O-C of 114.1° and O-C-O of 112.8°, and a torsion angle of 64.5° along the chain skeleton (gauche conformation). The distances between the chains rest on lattice forces (secondary interactions) and have been correctly interpreted.66 The chemical molecular weight of the single fractions of POM agrees with the ones extracted from the chain length from X-ray data. However, X-ray investigations of the molecular weight of high molecular weight materials are unreliable at best.

The sublimation of POM in vacuum led to fibres, whose axis contained the molecular axes, comparable with the cellulose fibres. Staudinger regarded the results as transferable to cellulose and chose POM as a model for cellulose in his subsequent publications. No doubt, POM with a DP ranging from 50 to 100 shows polymer specific properties, but nevertheless the length of the chain or the size of the macromolecules is relatively small in comparison with those of native cellulose or of other synthetic polymers.

Sauter70 continued the X-ray investigations with excellent data from single crystals of high molecular weight POM. To grow such uniquely large polymer crystals was a most challenging task, seldom successful for polymers, but it was achieved for POM by O. Schweitzer.71 Another polymorphic modification with a pseudo-hexagonal orthorhombic unit cell with almost the same base plane, but a longer fibre axis, was published by Sauter, with a = 7.74 Å, b = 4.46 Å, c = 17.35 Å. It had already been identified some years earlier by Hengstenberg69 on the basis of fibre diffraction patterns. The longer c axis gives rise to a longer fragment of the POM molecule within the unit cell containing 9 monomer units. There is a different twisting of the chain skeleton, with C-O-C-O torsion angles of ca. 78° as compared to 64.5° of the first POM modification. This chain structure of POM can be described approximately as a 9/5 helix, i.e. 9 monomer units in 5 turns – actually a 29/16 helix with a fibre repeat of 56.02 Å is still a better approximation - as compared to the 2/1 helix of the first modification. The projection of a monomer unit on the c-axis of the ca. 9/5 helix is somewhat longer and amounts to 1.93 Å, as compared to 1.77 Å of the 2/1 helix shown in Figure 9.

The investigations on POM proved that the macromolecules are formed by primary chemical bonds between the basic units (monomers), i.e. that primary valence chains exist. Long linear macromolecular chains are running through small unit cells. It cannot be necessarily concluded from small unit cells that they contain small molecules of the size of the unit cell. Further on, the POM macromolecule forms at least two shapes (conformations) in the solid state with
different total molecular length for the same DP and neither of the two structures shows the most extended form.

**Structural studies on cellulose**

X-ray diffraction represents a suitable method for a complete determination of the structure of crystalline materials, if sufficient intensity data are available, which is rarely the case for diffractions on polymer fibres and powders. The lack of experimental data can be partially overcome by the introduction of molecular models, today carried out by computer-aided simulation and simultaneously evaluated with X-ray data. The packing arrangements and the formation of crystalline structures (crystallites) are determined by the interactions of atoms and molecules and can be represented by potentials attributed to the single atoms of the molecules. The unit cell and the space group, by which the structural unit of a crystal is described, are nevertheless helpful mathematical quantities to reduce the structural investigations to an acceptable level. Therefore, it is possible to introduce a larger “unit cell”, e.g. a multiple of the smallest “correct” unit cell, if not referring to symmetry elements of the proposed cell or introducing common symmetry elements to both cells. In conclusion, a correct result concerning the required structure will be thus obtained.

Sponsler and Dore\(^{68}\) remarked correctly, when performing a structure determination of cellulose ramie fibres, that besides the chemical reactions of the cellulose chain, the physical properties of a fibre must be also considered. For example, anisotropic strength, thermal expansion and swelling in the direction of the fibre axis must be explained by a proposed structure. It was clear to them that the X-ray data alone would provide only a rough conception on the distinct relationship between molecules. Their proposed strategy consisted in creating three-dimensional ball and stick or space-filling models first for glucose and then for cellulose, on the basis of known average bond lengths and angles derived from organic molecules. These models for cellulose should correspond to the length of the fibre axis (repeat distance) obtained by X-ray analysis of 10.25 Å (the current value is 10.38 Å) and should account for the intensities of the strong reflections. They already knew from the work carried out by Irvine *et al.* and Haworth *et al.* that the question of the configuration of glucose, pentagonal or hexagonal ring structure was discussed on the basis of organic chemistry. Sponsler and Dore concluded that a single cellulose chain has to be formed of continuous β-glucose units, in the form of hexagonal rings in Sachse–Mohr chairs (Fig. 10). The glucose units were connected by 1-1, 4-4 linkages to obtain a long primary valence chain. The fibre period of 10.25 Å agrees with the length of two joined glucose units parallel to the fibre axis, permitting the observation that a continuous primary valence chain agrees with a short unit cell dimension (fibre period). The packing of the cellulose molecules in Sponsler and Dore’s unit cell is shown in Figure 11, each unit cell containing four parallel chains without any symmetry elements. As shown in the figure, this cell can be reduced to the current, generally accepted two-chain unit cell (space group P2\(_1\)), first determined by Andress\(^{72}\) (a = 8.35 Å, b (fibre axis) = 10.28 Å, c = 7.96 Å, \(\beta = 84^\circ\)) and the reduction proposed by W. H. Bragg.\(^{73}\)

The projection of the chains along a diagonal of Figure 11, represented in Figure 12, shows the long primary valence chains of 10.25 Å period, parallel to the fibre axis. Between the chains, van der Waals interactions (secondary valences) occur. An attractive interaction between the hydroxyl groups is mentioned, shown by dashed lines, which represents, from our current viewpoint, hydrogen bonds.

The method introduced by Sponsler and Dore is nowadays generally accepted for the structure evaluation of crystalline polymers, with the simultaneous consideration of the structural data by X-ray diffraction, on the one hand, and with the support of these data by molecular models, on the other. The incorrect linkage of the monomer units of glucose was corrected by Freudenberg\(^{75,76}\) and Haworth,\(^{77}\) who trusted the experiments of organic chemistry more than the interpretation of the X-ray data made by
Sponsler and Dore, and proposed exclusively 1-4 linkages along the cellulose chain.

The proposal of Freudenberg and Haworth could not explain the existence of some odd-order meridional reflections of the X-ray fibre diagram of cellulose along the fibre axis, with the accepted monoclinic $P_2_1$ space group of the crystal structure. The structure favoured by Sponsler and Dore does not exclude these reflections. According to Polanyi, these reflections could be caused by other materials, i.e. an additional crystal form. A simultaneously existing second modification was actually much later discovered for ramie fibres, although unable to explain the described phenomena. Further ideas explaining the odd-order meridional spots include a twisting of the microfibrils in the fibres.

Figure 10: Model of $\beta$-glucose, adapted from Sponsler and Dore. Hexagonal ring in the Sachse-Mohr chair conformation with numbering of the atoms

Figure 11: Reduction of the four-chain cell, proposed by Sponsler and Dore ($a = 10.80$ Å, $b$ (fibre axis) = $10.25$ Å, $c = 12.20$ Å), to a smaller two-chain monoclinic unit cell equivalent to the one of Andress for native cellulose. A better agreement can be obtained if the cell of Sponsler and Dore is also described with a monoclinic angle (adapted from Kiessig)

Figure 12: Representation of the packing arrangement of the cellulose chains in diagonal direction of the cell in Figure 11, adapted from Sponsler and Dore

A model with 1-4 linkages of the glucose units, according to the primary valence chains of a cellulose molecule proposed by Freudenberg and Braun, or by Haworth, was published by Meyer and Mark for crystalline cellulose. The linear cellulose chains had been placed in a monoclinic or in an orthorhombic two-chain unit cell,
respectively. However, the monoclinic unit cell of space group \( P2_1 \) was preferred. An orthorhombic or perhaps a monoclinic unit cell was previously introduced by Polanyi\(^2\) in 1921. A problem arises with the introduction of the 1-4 linkage of the glucoses. Since the linear cellulose chain possesses reducing and non-reducing ends, the chain has a direction. Adjacent parallel chains pointing in the same direction are called parallel running chains and those pointing in the opposite direction are antiparallel. The model of Meyer and Mark (1928) prefers the two chains in the unit cell to be parallel running chains, not because of the evaluation of X-ray data, but rather because the authors assumed that a parallel arrangement would arise from their biosynthesis in plants. In a further publication of Mark and Meyer,\(^79\) as well as one by Andress,\(^80\) the relative chain shift (now often called “stagger”) between the corner and centre chains in the unit cell was specified for the two parallel chains. In the work of 1929, the relative shift of one glucose unit\(^33\) was reduced to a shift of half a glucose unit,\(^79,80\) and the coordinates of Andress were used by Mark and Meyer to estimate the intensities of the reflections. This 1929 model for cellulose, in which the basic units are continuous linked glucose molecules, has to be regarded as a setback regarding the chair conformation of the glucose residue provided by Sponsler and Dore (1926). In Mark and Meyer’s, as well as Andress’ proposals, all carbon atoms of the glucose ring lie in one plane,\(^79,80\) only the oxygen atom of the ring deviating from this plane. This plane also contains the oxygen \( O_6 \) of the primary hydroxyl group (Fig. 1). The bond lengths and angles deviate considerably from the standard values established at that time. Mark and Meyer adopted all coordinates from Andress, except those of the glycosidic oxygens. The angles \( \Theta(C5-C6-O6) = 144^\circ \) or \( \Theta(C4-C5-O5) = 134^\circ \) and all bond angles involving pendant O-atoms are far from the standard values in both models. The glycosidic bridge angle can be calculated with the given coordinates to 100° (Mark and Meyer\(^79\)) and to 120° (Andress\(^80\)).

In a further investigation by Meyer and Misch,\(^81\) they overturned the established parallel packing of the cellulose chains in a microfibril, and proposed an antiparallel packing arrangement of the two basic chains within the same sized unit cell and space group \( P2_1 \). This arrangement had been justified by the assertion that native cellulose can be further transformed to cellulose II, by a process (mercerisation) that preserves the overall fibre structure, orientation and space distribution. Besides mercerisation, cellulose II is also obtained by regeneration and crystallisation from solution. This regenerated cellulose would necessarily be packed in an antiparallel fashion, according to Meyer and Misch, since the same number of chains in solution point in opposite directions, when they are aligned and crystallised by fibre spinning. Since regenerated and mercerised cellulose show the same structure, it was concluded that native cellulose is also arranged in an antiparallel fashion. Further improvements of the cellulose chain structure, as compared to the original proposals\(^79,80\), consist in the Sachse-Mohr chair conformation of the glucose ring, but some bond lengths and angles are far from the desired standard values. The small glycosidic bridge angle of ca. 105° leads to unreasonable short van der Waals distances between \( H1 \) and \( H4 \) of the adjacent residues of 1.54 Å. The parallel chain model of cellulose elaborated by Andress, which is almost identical with that of Mark and Meyer, was strongly criticised on geometric grounds. However, the main argument for the introduction of parallel packing, \( i.e. \) by the synthesis of the chains originating by the growth of plants, was not mentioned at all.

The conformation of a glucose unit in the cellulose chain was dealt with in details by Hermans,\(^82\) and the established standard geometry, as well as the Sachse-Mohr chair conformation were introduced. He found that the so-called virtual bond length between two adjacent glycosidic oxygen atoms is larger than half of the fibre period, and therefore a chain with tilted (bent) glucose units must be considered. A rotation of two neighbouring glucoses then leads to a theoretically reasonable glycosidic bridge.
angle and to intramolecular hydrogen bonds between the O3 and O5 of adjacent glucose residues (Fig. 1).

The antiparallel arrangement of native cellulose chains by Meyer and Misch has represented the basis of cellulose research in the solid state for decades. Only later in the 1970s, with the introduction of computerized molecular modelling with simultaneous evaluation of X-ray data, was there a return to the hypothesis of the parallel arrangement of native cellulose molecules in the crystalline microfibrils. Meyer and Mark repeatedly insisted that the evaluation of the cellulose structure cannot depend on models but rather only on X-ray data. It should be noted that the preference of the antiparallel packing arrangement of native cellulose, proposed by Meyer and Misch, relies only on ideas concerning the crystallisation process, and the parallel arrangement of Meyer and Mark (1928) relied on ideas concerning fibre growth in plants. The discrimination of the different packing arrangements by X-ray data was not considered in those investigations and would not have led to the proposed goal because of the few reflections observed in their patterns.

Mercerised or regenerated cellulose II is still considered as an antiparallel arrangement of chains, based on computer simulations and X-ray, as well as neutron analysis. This proposal is supported by single crystal X-ray analysis of a longer fragment of cellulose, i.e. oligomer cellotetraose, which exhibits a base plane projected down the molecular axis, almost identical with cellulose II. The unit cell contains two cellotetraose molecules of different conformation, packed in an antiparallel fashion, which is also found in cellulose II (of space group P2₁). Two somewhat different conformations of the two chains running through the unit cell are also possible for native cellulose I, as actually established in a recent investigation.³³

By spectroscopic means, especially by high resolution solid state NMR, it was found that in the fibres of native cellulose there coexist, side by side, two modifications, cellulose Iα and Iβ. They exist in different proportions depending on the species. The above-discussed two-chain unit cell belongs to cellulose Iβ, while cellulose Iα in pure form exhibits a triclinic one-chain unit cell. A detailed discussion of different cellulose structures, as well as their conversions, is provided in an overview by Zugenmaier.³⁴

Fibre diffraction of native cellulose has provided an important contribution to the clarification of natural and synthetic polymers. Especially the cellulose chains in the crystalline state with primary valence linkages along the chains, hydrogen bonds and van der Waals interactions to neighbouring chains can be determined with high precision, according to the structural determination techniques pioneered by Sponsler and Dore. The methods for structure evaluation introduced by these two authors are still used today with great success, with considerable improvement however as to the representation of models.

A concise report on the development of X-ray diffraction and a critical discussion of the results obtained for native cellulose before the end of the 1930s is provided in a review by Schiebold.³⁵ In this review, Schiebold criticised K. H. Meyer for quoting improperly or insufficiently essential scientific papers or results, and was supported by Staudinger – as revealed by the document reproduced in the Appendix. Staudinger typed and glued this document on the inside of the cover of Meyer and Mark’s book found, in its last edition, at the library of the Institute of Macromolecular Chemistry in Freiburg.³⁶ Also, the term “macromolecule”, introduced by Staudinger in 1922, by extending the usual term “molecule”, was first rejected by Meyer and Mark. Therefore, Staudinger’s complaints should be considered as adequate.

Size of cellulose macromolecules

In the investigations discussed so far, the structure of cellulose could be established as a linear primary valence chain with the monomeric unit of β-D-anhydroglucopyranose linked in 1-4 position. The size and length of the native macromolecules could only be estimated by methods available at that time, since the precise assessment of molecular weights could not be provided for large molecules until 1930.
Certainly, the molecular weight of the degradation products could be determined by the end group method. Osmosis and depression of the freezing point led to molecular weight determinations of up to 10000 (DP = 60 for cellulose) with high precision. It was assumed that the values for native cellulose might be far higher, but they could not be evaluated. The determination of the size of macromolecules by X-ray investigations was not possible, as expressed by many authors, since the necessary correlation between crystallite size and molecule size could not be provided. Consequently, the values of the crystallite size of ramie fibres, determined by Meyer and Mark, could not describe the length of cellulose molecules. According to the current view, macromolecules can be folded, as also observed on small molecules with a flexible spacer between two stiff terminal groups, or they might form fringed micelles, a frequently seen packing model of cellulose (Fig. 13). This means that the required correlation between crystallite size and molecule size does not exist. Both packing models and some further proposals are not suitable for determining chain lengths. In the 1960s, especially Husemann and Bittiger dealt with problems of packing arrangements and chain folding of cellulose derivatives in the solid state by electron microscopic investigations.

As to the size of the cellulose molecule, in 1929, Fritz Haber considered that: “The new arguments (Meyer and Mark) that favour large units linked by primary valences are no proof (for Haber), but must be considered as more plausible than conclusive, while the possibility of a set-up by small chains cannot be neglected.” – cited according to Willstätter and Zechmeister. At the same time (1929), Karrer expressed the opinion that cellulose and starch exist as colloidal micelles with associated molecules in solution.

The problems that researchers confronted around 1930 included two questions: whether, in solution, there exist dispersed single cellulosic molecules or micelle particles composed of associated molecules; and what is the size of the cellulose molecules (molecular weight MW or DP).

The molecular weight as a measure for the molecule size is usually obtained by colligative properties, such as vapour pressure, freezing point depression etc., for dissolved molecules, or by the end group method. However, those investigations are restricted to small molecules with MW up to ca. 10000. For larger molecules, osmotic pressure, increase in viscosity, as well as diffusion and sedimentation experiments in an ultracentrifuge proved to be effective in determining molecular weights, such data permitting to assess the size of macromolecules. Later, more efficient methods were added, such as static and dynamic light scattering etc., or gel permeation chromatography, which, in addition, offered insight into the molecular weight distribution. These later introduced methods will not be discussed here. All methods for determining chemical molecular weight assume that the effective particles in solution are actually single molecules, i.e. a molecular disperse solution is present. Although this assumption is often valid, sometimes and especially in investigations of cellulosics, associations of molecules occur, which means that the existence of single

Figure 13: Schematic representation of fringed micelles of cellulose adapted from Fink and Walenta
macromolecules in solution must first be addressed.

**Viscosity**

Viscosity measurements played an important role in the clarification of the constitution of particles in dilute solution. Investigations were carried out at various pressures, concentrations, temperatures and with different solvents to exclude the possibility for associated micelles to be present. Later studies included “polymer analogous conversions” that supported the existence of single molecules in dilute solutions. In this case, it must be verified whether the DP is not changed by chemical conversions and whether measurements in different solvents lead to the same DP. Such experiments are definitely qualified to rule out the existence of micelles.

Capillary viscosimetry is still the simplest method for determining molecular weights of long-chain molecules. However, certain conditions must be observed (Marx-Figini and Gonzalez"). For instance, the flow has to lie in the Newtonian regime – in the 1930s, the fulfilment of the Hagen-Poiseuille law was stated as a condition, which means that the velocity gradient should be very low. High dilution with molecular disperse molecules is a precondition, which means that the molecules should move independently from each other. Between the limiting viscosity number, also called intrinsic viscosity \([\eta]\) and molecular weight \(M\), there exists the following empirical relationship as an approximation at certain molecular weight intervals of a substance (definition of intrinsic viscosity, c.f. Appendix):

\[
[\eta] = K_M^* M^a \quad (1)
\]

Constant \(K_M\) and exponent \(a\) depend on the solvent, temperature and spatial structure of the polymer, and may in part represent constants in a certain molecular weight region, which has to be larger than \(2 \times 10^6\). Generally, the value of exponent \(a\) lies between 0.5 and 1.0, and mostly between 0.7 and 0.8 for chain molecules. Experiments have shown that, for poor solvents (theta solvents) \(a = 0.5\) is to be expected and \(a \sim 0.8\) for good solvents. In the case of \(0.5 < a < 0.8\), flexible chains are suggested, for \(a > 0.8\) semi-flexible chains and for \(a = 2\) absolutely stiff rods, such as those that occur in tobacco mosaic virus. If molecular weight distribution is present, then the so-called \(M_n\), the viscosity average value of \(M\), may be determined (c.f. Appendix eq. (A3)), which differs little from the weight average \(M_w\) for semi-flexible molecules. Formerly, \(M_w\) was determined by diffusion experiments and today much simpler, by light scattering.

The intrinsic viscosity of a macromolecular solution is a measure of molecular weight, as long as macromolecules increase the viscosity of a solution depending on molecular weight. A relationship between the viscosity of a solution and the size of the soluble particles or micelles was concluded many times before Staudinger and co-workers (first published by Staudinger and Heuer for polystyrene). Fikentscher and Mark established a useful relationship for stiff rods. In a first step, Staudinger tested this relationship for specific viscosity – eq. (2) – at low concentrations for small macromolecules, the molecular weight of which was available especially by colligative properties, and extrapolated the validity of the relationship with the same \(K_m\) value, to large molecules. Note that relationships (2) and (1) are equivalent when \(a = 1\), and with extrapolation of \(\eta_{\text{spec}}\) to very low concentrations of the solution \(c \rightarrow 0\), and small shear rates \(\dot{\gamma} \rightarrow 0\).

\[
\eta_{\text{spec}} = K_m c M \quad (2)
\]

The extrapolation \(c \rightarrow 0\) can be carried out by a number of graphical and computational methods. A very simple computational method was published by Schulz and Blaschke. The extrapolation of shear rate \(\dot{\gamma} \rightarrow 0\) requires numerous measurements. Therefore, a standardisation was proposed with the same low shear rate in normalised viscosimeters, and a choice of concentration with little variation in the flow time was preferred (Schulz and Cantow).

The validity of the linear \(\eta_{\text{spec}} - M\) relation eq. (2) assumed, as Staudinger did for low to high molecular weights, the same constant \(K_m\) is obtained according to eq. (3). Further on, the same concentration \(c\) is required for the polymers in solution, as well as similar
polymer homologous products (equivalent molecular weight distributions):

\[ (\eta_{\text{spec}}/M)_a = (\eta_{\text{spec}}/M)_b = ... (\eta_{\text{spec}}/M)_x = K_m \quad (3) \]

On the other hand, if \( K_m \) and specific viscosities \( \eta_{\text{spec}} \) are known, molecular weights can be determined with eq. (3).

In support of the viscosity–molecular weight relationship, Staudinger proposed a model of stiff rods that move only in a plane. As to the form of chain molecules, Staudinger was convinced that they have stiff elastic structures. He wrote:\(^93\) “A chain molecule has to be regarded as a stiff elastic structure. The established relationship between viscosity and chain length is only understandable by a stiff form of the chain molecules, but not with the assumption that these chain molecules in solution bend and wind or twist helically, as sometimes assumed for rubber molecules. A chain molecule is more likely comparable to a stiff elastic glass thread than to a loose thread of wool, which can adopt any form. The chain molecule in solution has, on the average, the same shape as in the crystal. The capability of high molecular compounds to crystallize out of solution depends on this property. The long chain molecules are collected as in a bundle of glass threads and form a macromolecular lattice.”

Staudinger never abandoned this early view of the shape of macromolecules, except for a few compounds, such as polyester, and he correlated the exponent \( a = 1 \) in the viscosity equation (1) with the stiff rod form of the chain molecules. In hindsight, he overlooked the concept that dissolution and crystallisation are driven by the change of Gibbs free energy. The shapes of molecules depend on enthalpy as well as on entropy and temperature. In the course of time, exponent \( a \) was found \( \neq 1 \) for many chain molecules.

Mark\(^94\) regarded Staudinger’s viscosity formula, eq. (2), as experimentally verified in the short chain regime, however rejected Staudinger’s model that assumed that stiff rod-like molecules move in a plane, arguing that: “The viscosity formula of Staudinger can only be regarded as an empirical relation and can only be applied where it is experimentally verified.” He himself proposed a relation in which specific viscosity is represented as a sum of two terms \( \alpha M + \beta M^2 \), which leads, for small molecular weights, to Staudinger’s formula and, for high molecular weights, to the proportionality \( \propto M^2 \), which had been introduced by Fikentscher and Mark for stiff rods, which means that linear macromolecules behave like stiff rods in certain molecular weight regimes.

Staudinger’s response to the criticism of Mark concerning molecular weight determination is interesting:\(^94\) “At present, the determination deals only with the estimation of molecular weights to show that single large molecules are present in solution and not micelles aggregated from small macromolecules (Meyer and Mark), or from a few monomeric units (Karrer, Hess etc.).” He also rejected the doubts on the \( \eta_{\text{spec}}-M \) law for large molecules. According to the present view, Staudinger overlooked that a specific \( \eta_{\text{spec}}-M \) relationship according to eq. (3) is only valid in certain regions with \( a = 1 \), and especially that the average \( M_n \) is used for the calibration of different molecular weight distributions (polydispersity). Generally, this means that the same \( K_m \) cannot be transferred from small to large macromolecules or from a distinct molecular weight distribution to another one. In comparison to the osmotic determination of molecular weight with regard to viscosity measurements, it was clear to Staudinger that the molecular weight distribution had to be considered. However, the exact relationships between the various averages of \( M_n, M_w \) and \( M_\eta \) were not known to him.

The essential pre-requisite for the determination of the molecular weight of celluloses in dilute solution, \( i.e. \) the fact that they represent single macromolecules and not micelles with associated molecules, was demonstrated by Staudinger and Schweitzer\(^95\) for cellulose derivatives. Further viscosimetric studies, especially for the estimation of DP were carried out by Staudinger and Freudenberger.\(^96\) They investigated acetolytically degraded cellulose triacetate with various chain lengths, determined by the iodometric end group method. \( K_m \) in eq. (3) could be then obtained for single macromolecules of different sizes in m-cresol and they demonstrated that \( K_m = \)
1.6 $10^{-3}$ is constant for all samples with DP = 7-80. The DP of larger degraded cellulose macromolecules determined with this constant exceeded 150 glucose units, much larger than the crystallite lengths in ramie fibres with 30-50 glucose units.

The stiff rod shape of macromolecules in solution, proposed by Staudinger, was strongly criticised by many scientists. Kuhn\textsuperscript{97} opposed the statement of Staudinger that cellulosics represent elongated stiff threads in solution, since the intrinsic viscosity $[\eta]$ should then be expressed by $\propto M^a$, according to Kuhn’s own considerations, and as proposed by Fikentscher and Mark. For semi-stiff chain molecules of cellulose and their derivatives, a value $a < 1$ should be obtained.\textsuperscript{98} Kuhn expected $a = 0.5$ in case of an irregularly coiled chain molecule without considering the molecular volume, with free and also with limited free rotation around the chemical bonds. The changes in the shape and size of the chain molecules, considering the volume of the molecule and especially hydrodynamic effects from the solvent, led to values of 0.8 to 0.9, close to the empirical value of $a = 1$, obtained by Staudinger. Kuhn requested a change in the assumption about the shape of the particles.\textsuperscript{98} The specific viscosity increase according to $\eta_{\text{spec}} = K_m c M^a$ led to $a$ values of 0.5 < $a$ < 0.9 for chain molecules (Kuhn\textsuperscript{98}).

Kuhn’s ideas were taken up by Mark,\textsuperscript{99} who proposed that inner molecular statistics represent a possible quantitative explanation of the deviation from Staudinger’s empirical formula. Although the quantitative views cannot be considered as settled, at a first approximation, the relationship $\eta_{\text{spec}} = K_m c M^a$ can be established, \textit{i.e.} the same functionality preferred by Kuhn. Depending on the assumption of the excluded volume and of the van der Waals forces within a chain, exponent $a$ takes values between 2/3 and 3/2, which deviate from the currently accepted values of Kuhn. Mark concluded that rigid rod-like molecules could not be valid.

Houwink\textsuperscript{100} tested the viscosity relationship of Kuhn with variable exponent $a$ for a number of polyesters for which Staudinger \textit{et al.}\textsuperscript{101} observed discrepancies between DPs determined by viscometry and by osmosis. Fitting exponent $a$ of Kuhn’s formula $\eta_{\text{spec}} = K_m c M^a$ to the experimental data, he confirmed an exponent of $a = 0.6$. Further $\eta_{\text{spec}}$--$M$ relationships proposed by various authors will not be discussed, since the viscosity formula of eq. (1) is commonly accepted today.

Wo. Ostwald\textsuperscript{102,103} generally expressed doubts that a simple universal relationship between viscosity and size of particles exists and referred to the schematic graphic representation of this relationship (Fig. 14). The S-shaped curve can only be replaced by a straight line (linear $\eta_{\text{spec}}$--$M$ relationship), as required by Staudinger, within very narrow intervals. For small molecular weights, the straight line D is obtained, which considerably underestimates high molecular weights and can only lead to lower limit values with a calibration using this low value $K_m$ constant. Staudinger first stated a DP > 150 for degraded cellulose, using this low $K_m$ constant. Nevertheless, this DP value lies by far higher than the one provided by Meyer and Mark with DP = 30-50.

Considering the tangent on the S-shaped experimental curve, \textit{i.e.} the straight line B, and assuming the molecular weight determined by calibration with osmosis at high molecular weights, the molecular weights are accessible with sufficient accuracy in the region considered. An average straight line, \textit{e.g.} curve A, shows the $\eta_{\text{spec}}$--$M$ relation for the total molecular weight region, as required by Staudinger. Consequently, Wo. Ostwald rejected Staudinger’s viscosimetric evaluation for taking the quantitative determination of molecular weights as a law governing over the entire region.

A double logarithmic plot of viscosity for cellulose derivatives (cellulose tricarbanilate CTC or cellulose trinitrate CTN) \textit{versus} $M_w$, determined by light scattering, can prove the empirical relationship of eq. (1), $[\eta] = K_M M^a$, within limited regions of molecular weights. Sutter and Burchard\textsuperscript{104} obtained for CTC the curve shown in Figure 15. For CTC dissolved in 1,4 dioxane for $M_w > 10^4$, as well as for ATC (amylose tricarbanilate) in the same solvent, the experimental curve can be described with $a = 0.90$ ($K_M = 3.9 \times 10^{-3}$) at higher $M_w$ region for CTC, and $a = 0.88$ ($K_M$...
Cellulose

As soon as reliable molecular weights in the higher weight regime were available by absolute osmotic measurements, Staudinger and co-workers used these results for calibration purposes of their viscosity measurements and corrected their earlier results. According to the plots represented in Figures 14 and 15, it is obvious that the curves in the region up to $M = 10^7$ cannot be extrapolated for the determination of molecular weight at higher values. Staudinger and co-workers addressed these problems from 1937 on. The results proved to be satisfactory for DP of semi-stiff celluloseic materials, since exponent $a$ in eq. (1) is close to the value assumed by Staudinger of $a = 1$. Staudinger and Daumiller found for constant $K_m$, eq. (2), $K_m = 6.3 \times 10^{-4}$ for cellulose triacetate with DP = 80-780 in m-cresol and $K_m = 5.3 \times 10^{-4}$ in chloroform (only soluble until DP = 400). For cellulose trinitrate, $K_m = 11 \times 10^{-4}$ was obtained, leading to a DP of nitrated cotton linters of 3000 and of ramie of 3500 (Staudinger and Mohr) with calibration by osmosis. Staudinger and Reinecke provided a comprehensive compilation of results for methyl and ethyl derivatives, among other compounds. From all these investigations can be concluded that cellulose trinitrates are excellently suited for DP determination of cellulose, since derivatisation can be simply

Figure 14: Schematic representation of the dependency of specific viscosity on molecular weight, curve C, adapted from Wo. Ostwald and R. Riedel

Figure 15: Intrinsic viscosity $[\eta]$–molecular weight $M_w$ relationship in a double logarithmic plot for narrow molecular weight distributions of cellulose tricarbanilate CTC $(M_w/M_n = 1.10)$ and amylose tricarbanilate (ATC) in 1,4-dioxane (adapted from Sutter and Burchard)

$= 2.36 \times 10^{-3}$) at higher $M_w$ region for ATC. Marx-Figini and Gonzalez decomposed the curve for CTN dissolved in acetone into two parts and obtained $a = 1.0$ ($K_M(DP) = 0.82$) for $DP_w < 1000$ and $a = 0.76$ ($K_M(DP) = 4.46$) for $DP_w > 1000$, which means that exponents $a$ for semi-flexible chains deviate little from 1.0. The linear intrinsic viscosity–molecular weight relation, $[\eta] = K_M M$, introduced by Staudinger is not generally valid over the entire molecular weight regime, nevertheless, it represents an empirical approximation with sufficient accuracy within certain intervals. However, it is hard to understand that Staudinger drew the conclusion that macromolecules in solution, as well as in the solid state, have a stiff rod-like shape, from the linear relationship with $a = 1$, and that he did not consider Kuhn’s arguments on the existence of coils caused by free or hindered rotation around single bonds. Staudinger declared this idea misleading and did not follow Kuhn, who considered an exponent $a$ of 0.9 to almost 1.0, if the macromolecular coils are disturbed. Staudinger ignored the experimental results for many macromolecular materials, among others, for some semi-flexible cellulose derivatives that exhibit $a \neq 1$. 
performed, little degradation occurs and the derivatives are easy to dissolve, which is also the case of cellulose tricarbanilate.

In the above-mentioned publications, the state of dissolution was also addressed and “polymer analogous conversions” on materials of various particle sizes were carried out. The existence of macromolecules is extremely convincing, when studies are not only performed on a single material but rather on various related compounds of a polymer homologue series\(^{108}\) such as performed in the case of polysaccharides (first for cellulose, c.f. Staudinger and Schweitzer\(^95\)). Since 1937, these polymer analogous conversions on cellulosics have been systematically improved.\(^{105-107}\) Cellulose has been converted to polymer analogous triacetate, subsequently saponified to cellulose or analogous 2.5 acetates, and further to methyl and methyl acetyl celluloses. Cellulose was also converted to polymer analogous trinitrates. In all these conversions, a corresponding degree of polymerisation was obtained (original material with DP up to 2000) and the existence of single macromolecules in solution was assessed. The similarity of the \(K_m\) constant in eq. (2) for the different derivatives was interpreted with an elongated and unbranched shape of the cellulose derivatives in dilute solution, the same shape as that present in the solid state.

The unbranched shape of the cellulose derivatives was also experimentally confirmed by polymer analogous conversion comparing the molecular weight determined by various methods, such as the end group method with viscosity or osmosis measurements. The agreement of DP values points towards a linear macromolecule\(^{107}\) structure for cellulose, in contrast to amylopectins and glycogens, which are branched macromolecules. For native cotton fibres, as well as for ramie, a DP > 3000 was established. Exact values were difficult to obtain, since the purification of the materials required a preliminary treatment with an unknown effect for the size of the molecules. The idea of a packing arrangement of the fibres, as shown in Figure 6, can be eliminated when discussing the size of a cellulose molecule. A crystallite with a dimension of 30-50 glucose units as shown in Figure 6 could not accommodate a cellulose chain with ~3000 glucose units, especially since chain folding can be excluded because the chains are arranged in isodirectional fashion (parallel packing). Instead, a cellulose chain may be passing through several crystallites, as revealed in Figure 13.

Despite these convincing experimentally supported arguments for the presence of single macromolecules in dilute solutions, other conceptions as to the structure and size of cellulosic materials were presented around 1935 and later. Haworth et al.\(^{109}\) considered that native cellulose is organised in molecular aggregates of which a single molecule contains no more than 200 glucose units. McBain and Scott\(^110\) proposed that cellulose in dilute solution appears as association colloids, as found for soaps. Also, in 1940, Mark commented on Staudinger’s thesis on the existence of single molecules:\(^{111}\) “The macromolecular-isolated state is only in part correct for the claimed cases. Especially for celluloses and their esters, another state is present in solution. In recent years, extremely important reasons for the existence of micelle-like chain molecular aggregates have been brought forward by Lieser.”\(^{112}\) Chain molecular aggregates consisted, from the viewpoint of Mark, Haworth et al., McBain and Scott, of primary valence chains of limited length. P. H. Hermans\(^113\) wrote in 1942: “The opinions are still split for the often discussed problem if in technical solutions for fibre spinning a dispersion to micelles or to chain molecules occurs... As a consequence, almost all theoretical considerations about the spin and deformation process prefer the micelle theory... No decision is so far reached between the two extreme ideas.”

**Osmosis**

The evaluation of osmotic pressure is an excellent method for determining particle or molecular weights. It leads to absolute values, in contrast to viscosity measurements, which allow only the determination of relative values. The osmotic pressure represents the difference in pressure between a solution and a pure solvent, which
are separated by a semi-permeable membrane through which particles of a certain larger size cannot permeate. Such membranes are difficult to produce for low molecular weight substances, but easier to generate for macromolecules or large particles. The reduced osmotic pressure $\Pi/c$ is given by the following expression:

$$\Pi/c = RT/M + A_2c$$  \hspace{1cm} (4)

where $\Pi$ – osmotic pressure, $c$ – concentration of the solution, $R$ – gas constant, $T$ – absolute temperature, $A_2$ – second virial coefficient, representing a complex measure of the size and interaction of the solute and the solvent. Further terms in the expansion play a minor role and are not referred to. For an ideal solution $A_2$ vanishes ($A_2 = 0$), as found especially for small molecules and eq. (4) is then called van’t Hoff’s law. Relation (4) contains the number averaged value $M_n$ of the molecular weight distribution (c.f. Appendix).

In the first publications of Schulz,\textsuperscript{114} the deviation from van’t Hoff’s law has been taken care of with a relationship comparable to the real gas law by introducing a co-volume $b$:

$$\Pi/c = RT/[M (1-b)]$$  \hspace{1cm} (5)

The virial expansion is to be preferred since $A_2$ also appears in the light scattering formula and can therefore be independently determined and compared.

The extrapolation of $c \rightarrow 0$, that is $\lim_{c \rightarrow 0} \Pi/c$ in eq. (4), leads to the determination of particle or molecular weight. The extrapolation may cause problems since the form of the experimental curves of the reduced osmotic pressure as a function of concentration is not linear and the investigations must be carried out at very low concentrations.

The deviation from van’t Hoff’s law was a big obstacle to theoretical interpretation. Here, as in viscosity studies, it appeared that the experimental investigations provided conclusive results, whereas the theoretical foundations often relied on incorrect assumptions (c.f. the above comment by John von Neumann concerning models).

In 1937, A. Doby\textsuperscript{115} reviewed her osmotic investigations on cellulose nitrate (Fig. 16). The extrapolation of the reduced pressure $c \rightarrow 0$ for various different solvents led to a constant value of molecular weight of $M = 111000$ (DP $\sim$ 320), which represents the true weight and not associated micelles. In the presence of micelles, a dependency on $M$ had to be observed for various solvents. Staudinger’s idea on disperse single macromolecules in dilute solution was confirmed again. Molecular weight determination was placed on a secure foundation with the introduction of the absolute osmotic method; equally, viscosity measurements gained in reliability by the calibration of the viscosity–molecular weight relationship.

The exact determination of macromolecular sizes caused difficulties even in the 1930s, since comparisons were rarely possible among the few readily available methods and because of different original materials and their purification. No firm base was available for a theoretical foundation. The idea of stiff molecular models hindered the viscosimetric determination of molecular weight, as well as the $[\eta]$–$M^a$ functionality, delaying an overdue development. An experimental discrimination between different geometric models was first obtained with the determination of the radius of gyration of macromolecules with light scattering measurements in the 1940s and 50s. That moved the concept of macromolecules very much to the awareness of science.

From today’s point of view,\textsuperscript{116} the empirical $[\eta] = K M^a$ relation in eq. (1) can be extended to $M = M_n$ (and $K = K_n$) or $M = M_w$ (and $K = K_w$) with certain limitations (similar polydispersity, i.e. a similar ratio $M_w/M_n$, especially when using $M_n$). If $M_n$ is to be determined, molecular weight distribution has to be taken into account by a correction factor, which depends on exponent $a$, as well as on the $M_w/M_n$ ratio. These correction factors are especially large in a conversion from $M_n$ to $M$ (i.e. $M_n$) or at different polydispersity $M_w/M_n$ of the materials investigated. They can be omitted for standard measurements with the use of $M_w$ for calibration purposes, e.g. for $M_w/M_n = 2$ and $a = 0.7$, the ratios $K_w/K = 1.54$ and $K_w/K = 0.95$ are obtained.
Figure 16: Reduced osmotic pressure, p/c, as a function of concentration, c = gn/(1000 cm³), of a cellulose nitrate in various solvents, adapted from Dobry.115 1 – ethyl benzene; 2 – methyl salicylate + 20% methanol; 3 – acetophenone + 3% ethanol; 4 – cyclohexane + 5.8% ethanol; 5 – ethanol; 6 – glacial acetic acid; 7 – methanol; 8 – nitrobenzene

This means that, for the determination of \( M_\eta \), the calibration of the viscosity constant with \( M_w \) is to be preferred. In this case, the corrections lie generally within the experimental error. An evaluation concerning the influence of physical quantities on constants \( K \) and \( a \), i.e. the size and shape of molecules, hydrodynamic effects etc. will be omitted here. Many different models were introduced and are discussed in reviews. Under certain conditions, the theoretical evaluation leads to an exponent \( a = 1 \) without introducing the rigid rods of Staudinger. At this point, it should also be stressed that, at high dilution of solutions of incompletely substituted cellulose derivatives, associations occur or so-called duplex structures may appear and the single molecules are connected by stronger forces.

CONCLUSIONS

The application of today’s experimental and theoretical methods converged to well-characterised and well-defined structures for cellulosics, as well as for polymers in general. The characterization and the determination of the cellulose structure are inseparably connected with the historical development of macromolecular chemistry, and have been extremely dependent on the progress of the experimental methods available over time. The constitution of cellulose was introduced as a linear chain of variable length of 1-4 linked \( \beta \)-D-anhydroglucopyranoses by Freudenberg and Haworth in 1928, shortly after Haworth established \( \beta \)-D-glucose as a six-membered ring in contrast to the formerly accepted five-membered ring.4 The length of the chain could not be determined by means of organic chemistry. Sponsler and Dore investigated the structure of ramie fibres and introduced, with the help of molecular models and the interpretation of X-ray data, a linear chain model for cellulose and simultaneously the conformation of the monomer units of cellulose, i.e. glucose, as a chair in the Sachse-Mohr conformation. Two monomers form the repeat unit of the cellulose chain in the crystalline state. Their investigations contradicted the general opinion of the 1920s that cellulose consists of aggregates of small molecules, e.g. anhydrocelllobiose or even of anhydroglucose. But the 1-1, 4-4 linkages of the glucoses in their model were incorrect, the error being remedied by Freudenberg and by Haworth. Mark and Meyer, as well as Andress, embodied this concept in a model for crystalline fibres of native cellulose. This model, which rested on parallel packed chains pointing in one direction, was transposed to an antiparallel chain arrangement by Meyer and Misch, which was the generally accepted model until the 1970s. Only then, with improved experi-
mental methods and computer-aided model simulations, a data-based proposal was introduced for parallel chain arrangement of native cellulose in the fibres. The clarification of the structure of native cellulose became more difficult, inasmuch as two cellulose polymorphs were perceived to be simultaneously present in a fibre. Further, inter-convertible modifications of cellulose have been discovered over the years, enriching the field of cellulose research.

The sizes of cellulose molecules and their size distributions, that is their molecular weight or DP, and, correlated with it, the concept of macromolecules, could not be resolved with X-ray investigations. Similar to the molecular weight determination of small molecules, the properties of macromolecules in solution were considered. The increase in viscosity with molecular weight represented the empirical quantity on which Staudinger et al. concentrated a large part of their investigations. The initial, inaccurate determination of molecular weight of macromolecules by viscosimetry was placed on a secure basis when the absolute osmosis method was introduced from 1937 on. Average values for DPn of cotton linters and ramie fibres of > 3000 were obtained. The determinations of sedimentation and diffusion coefficients with the ultracentrifuge represent further milestones in the clarification of molecular weights and their distribution at considerable expenditure. At the beginning of this development, the limited theoretical basis of the viscosimetric method caused heated discussions about the applicability of these studies and only later led to sound results. After a broad palette of investigations, the size of cellulose and of its derivatives was finally determined in molecular disperse solutions.

With the linear [η]–M relationship, Staudinger came very close to the description of semi-flexible celluloses by the currently accepted empirical formula \([\eta] \propto M^a\) \((a = 0.8 - 1.0)\), but the stiff rod-like model he introduced as an explanation was far from any reality. On the other hand, the stiff rod model of Fikentscher and Mark, which relied on sound theoretical considerations and provided the exponent \(a = 2\), was unable to describe intrinsic viscosity for semi-flexible chain molecules. Kuhn’s coil model actually represented a simple solution for flexible and semi-stiff chain molecules with \(0.5 < a < 1.0\).

Further detailed information on the historical development of the macromolecular character of cellulose until the middle of the 1930s can be found in the comprehensive publications of Haworth, Freudenberg, Staudinger, Meyer and Mark, Saechtling, Marsh and Wood, Purves and Hess.

**APPENDIX**

**Macromolecules**

The term “macromolecule” was introduced by Staudinger and Fritschi in 1922, to designate a compound with a molecular weight above 10000. Macromolecular compounds consist of molecules, similar in their composition, chemical structure and size. In accordance with this convention, a pure corpuscular protein may be a macromolecular compound, but even a “pure” high polymer, other than a fraction, which is precisely “molecularly homogeneous”, is always a mixture of homologous polymeric compounds.

The molecular weight distribution may be determined, e.g. by gel permeation chromatography, and different moments (averages) of the distribution are accessible by various methods.

The *number-average molecular weight* \(M_n\) (eq. (A1)), obtainable from end group determination or by proper extrapolation to infinite dilution of cryoscopic, ebullioscopic, or osmotic pressure data, is the ordinary kind of average, equal to the total mass of the molecules (in atomic weight units), divided by the number \((N = \sum_{i=1}^{\infty} n_i)\) of molecules \((n_i – \text{number of molecules with molecular weight } M_i)\):

\[
M_n = \frac{\sum_{i=1}^{n} n_i M_i}{\sum_{i=1}^{\infty} n_i} \quad (A1)
\]
The weight-average molecular weight $M_w$ (eq. (A2)), obtainable, for example, by appropriate extrapolation of turbidity, light scattering etc. data to infinite dilution, equals the sum of the squares of the masses of the molecules, divided by the total mass ($W = \sum_{i=1}^{\infty} w_i$, $w_i$ – total mass of the molecules with molecular weight $M_i$).

$$M_w = \frac{\sum_{i=1}^{\infty} \eta_i M_i^2}{\sum_{i=1}^{\infty} \eta_i M_i} = \frac{\sum_{i=1}^{\infty} w_i M_i}{\sum_{i=1}^{\infty} w_i}$$ (A2)

The viscosity-average molecular weight $M_\eta$ (eq. (A3)) for a specified value of $\alpha$, obtainable by extrapolation of solution viscosity $\eta$ data to infinite dilution, if the limiting viscosity number $[\eta]$ depends on molecular weight, according to relation (A4), $K_M$ constant.

$$M_\eta = \frac{\left(\sum_{i=1}^{\infty} w_i M_i^\alpha\right)^{1/\alpha}}{\sum_{i=1}^{\infty} w_i}$$ (A3)

$$[\eta] = K_M \cdot M^\alpha$$ (A4)

It should be emphasized that this kind of average is indefinite, unless the dependence of the limiting index on molecular weight is known. This dependence is a function of solvent and temperature. If $a$ has the value of unity, the viscosity-average is identical with the weight-average. All such foregoing types of averages, except the number-average, are “weighed averages”, differing in the extent to which the relatively high (or low) values are “weighed” during averaging.

Degree of polymerization, DP

The degree of polymerization is defined as “the (average) number of base units per molecule”, if the molecules are composed of regularly repeating units, or as “the (average) number of mers (monomeric units) per molecule”, leading to $DP_n$, $DP_w$, $DP_\eta$.

$$M = DP \cdot M_o$$ (A5)

(taken over from the “Report on Nomenclature in the Field of Macromolecules”, J. Polym. Sci., 8, 257 1952)

Viscosity

The viscosity of a liquid $\eta$ describing the fluidity of a liquid, can be determined by the flow through a rod-like cylinder with the application of the Hagen-Poiseuille law. To determine the average molecular weight, the limiting viscosity number (intrinsic viscosity) $[\eta]$ should be known. The following relationships hold true:

- Viscosity of a solution: $\eta$
- Viscosity of the pure solvent: $\eta_o$
- Relative viscosity: $\eta_r = \eta / \eta_o$
- Specific viscosity: $\eta_{spec} = (\eta - \eta_o) / \eta_o = \eta_r - 1$
- Viscosity number (reduced spec. viscosity): $\eta_{red} = \eta_{spec} / c = (\eta_r - 1) / c$
- Limiting viscosity number (intrinsic viscosity): $[\eta] = \lim \eta_{spec} / c = \lim \eta_{red}$ with $c \to 0$ and shear rate $\to 0$

Polymer analogous reaction

The transfer of a macropolymeric compound in a derivative of the same degree of polymerisation is termed as a polymer analogous reaction. The size of the macromolecules does not change with temperature and concentration, or by changing the solvent, only if a chemical reaction occurs, leading to degradation or to molecular built-up of the macromolecules.

Micelle

The term “micelle” is used in different ways:

According to Nägeli and Ambronn, the term “micelle” describes particles (crystallites, small crystals) with definite boundaries in the solid state. The regular repetition causes orientation birefringence and broadening of the X-ray reflections. The term “micelle” does not provide any information on the molecular structure of crystallites.

In contrast to the above definition, McBain uses the term “micelle” for supermolecular complexes in aqueous soap solutions.

The word “micelle” is less appropriate for crystallites; its use should be restricted only to colloidal particles or aggregates in solution.
**Excerpt** from the reference letter for Einstein’s election to the Prussian Academy of Sciences on July 24, 1913:

“Zusammenfassend kann man sagen, dass es unter den großen Problemen, an denen die moderne Physik so reich ist, kaum eines gibt, zu dem nicht Einstein in bemerkenswerter Weise Stellung genommen hätte. Dass er in seinen Spekulationen gelegentlich auch einmal über das Ziel hinausgeschossen haben mag, wie z.B. in seiner Hypothese der Lichtquanten, wird man ihm nicht allzu schwer anrechnen dürfen: denn ohne einmal ein Risiko zu wagen, lässt sich auch in der exaktesten Naturwissenschaft keine wirkliche Neuerung einführen. Gegenwärtig arbeitet er intensiv an einer neuen Gravitationstheorie... Der eigenen reichen Produktivität gegenüber steht die besondere Begabung Einsteins, fremden neu auftauchenden Ansichten und Behauptungen schnell auf den Grund zu gehen und ihr Verhältnis zueinander und zur Erfahrung mit überraschender Sicherheit zu beurteilen.”


Figure A1 a, b: H. Staudinger and E. Husemann in conversation and on the motor scooter

Figure A2: E. Husemann (left) with assistant A. Bauer-Carnap at the electron microscope
Bemerkungen zur "Makromolekularen Chemie" von K. H. Meyer

Wie die erste, so kann ich auch die vorliegende zweite Auflage des Buches von K. H. Meyer nicht ohne einen Hinweis in die Bibliothek des Forschungsinstitutes einreihen.


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