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REPORT ON A LECTURE BY PROF. STAUDINGER, FREIBURG i. Br.,
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PROBLEMS IN THE FIELD OF MACROMOLECULAR CHEMISTRY

In his lecture, Prof. Staudinger first discussed the difficulties found in the study of problems of macromolecular chemistry. Unlike the compounds of the smaller molecular weight, the macromolecules do not form uniform pure materials, but mixtures of highly polymerized molecules of a different length of the chains, which can not be separated chemically or physically. The molecular weights of such materials are averages. Experiments with substances of high molecular weights are not perfectly reproducible, because the viscosity of the solutions may vary even in solutions of the same concentrations, depending on the length of the chain. This is particularly true for products of decomposition and for synthetic compounds; natural products appear to have uniform and definite lengths of chains. Compounds of high molecular weight must be dissolved for investigation. These large molecules produce colloidal dispersions, the particles of which are not formed by a condensation of relatively large molecular chains, as in solutions of soaps, but the molecules of which are by themselves sufficiently long to form colloidal dispersions in any solvent. This is the difference between the macromolecules and the micellae.

This view point was confirmed by acetylation of macromolecular compounds, e.g. cane sugar; the acetyl residue was split off, and the degree of polymerization of the regenerated sugar compared with that of the original substance. The degree of polymerization was found to have been left unchanged. If the cane sugar had formed micellae, the reaction would have affected not the micellae as such, but each molecule independently, and the degree of polymerization would have become smaller.

The degree of polymerization is, moreover, the same in the different solvents, which again can not be made to agree with the usual behavior of the micellae, because the forces of cohesion holding the molecules together in the form of micellae vary under different outside conditions (solvents, temperature, etc.).

Molecular weights were determined from osmotic pressure measurements, as well as from viscosity determinations. The determination of the terminal groups was used as a chemical method for the determination of molecular weights. In doing this, the characteristic groups of the molecule (-OH; -COOH) were made use of in the determination, calculating, e.g. the molecular weight of the carbonic acid from the weight of the silver salt.

Changes are frequently produced during the solution, especially of the natural products, by, possibly, the effect of the oxygen of the air or by traces of acids, and they greatly increase the difficulties of study. The molecules present in such solutions are fibrous in structure. According to Dr. Staudinger, these fibrous molecules must be imagined as being fibrous, like glass filaments, which still can elastically vibrate. The fibrous molecule

does not, however, have the mobility of a thread of wool, and can not therefore become converted into a spherical or spiral structure. Viscosities of such solutions are proportional to the length of the fibrous molecules, and the determination of viscosity can therefore be used for the determination of the constitution. The solution must however be sufficiently dilute, so that the fibrous molecules would not affect each other.

The viscosity law derived by Staudinger is:

$$\frac{\eta_{sp}}{c} = K_m \times M,$$

where η_{sp} is the specific viscosity (increase in viscosity of the solvent produced by the solute), c the concentration, M the molecular weight and K_m a constant characteristic for each homologous system of polymers.

The specific viscosity has a definite characteristic value for each substance, which depends on the length of the molecule, and is but slightly affected by the nature of the solvent. The viscosity of the solutions of fibrous molecules, is, therefore, according to this law, dependent on the degree of dispersion: fewer long molecules produce a higher viscosity than many short ones. Prof. Staudinger states the law, that the same length of molecules is present when in the same concentration of two substances the specific viscosities are equal. The specific viscosity is therefore independent from the diameter of the molecules.

The validity of the law was proven by a comparison of the computed and experimentally determined values for the constant K_m . The law of viscosities can be applied only to fibrous macromolecules, and is no longer valid when dealing with spherical structures or lower molecular weight compounds. Exceptions to the law have however been found also with macromolecular compounds, caused by the branching of the chains: a side chain increases only the diameter of the molecule, not its length.

The specific viscosity is either not dependent on the temperature, or else only slightly so (investigations at 20° and 60° C). When, however, the length of the chain exceeds certain limits, the solution becomes more viscous at higher temperatures, because the mobility gradient occurring during the viscosity determinations and the orientation of the molecules connected with it counteract the heat motion.

Prof. Staudinger illustrated his experiments by describing in greater detail rubber, cellulose, starch, albumin, as well as high molecular weight synthetic products. He stressed in particular the difference between Buna and the natural rubber; the natural rubber indicates long side chains on the fibrous molecules, while Buna rubber has many short ones. This results in a poorer formability of the Buna in comparison with the natural rubber, as well as its property to readily form rings and become difficultly soluble.

Signed, Henkels.