Aspects of High Polymeric Chemistry

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INTRODUCTION

WHEN the magnificent structure known as organic chemistry was built up in the second half of last century, it contained not only an enormous number of new substances with interesting and valuable properties, but also embodied a series of more or less general laws on the relations between the structure and the qualities of a molecule. It was realized, for example, that the presence of certain atomic groups (OH, NH₂, HSO₃) had as a consequence solubility in water, that other combinations of atoms impressed on the molecule the property of a dyestuff, others again made it a narcotic, or an explosive, and so on. These laws did not appear suddenly in clear and definite shape, but grew slowly with the development of chemical science. They were nearly all formulated at first as preliminary rules, and their validity checked by the aid of the continually increasing experimental material. Some of them did not successfully pass this test; they are forgotten to-day and many of them are no longer known; others have survived and represent our present knowledge of the possibilities of constructing a molecule with required properties. They can be called the leading principles of preparative organic chemistry, and are of utmost value for all synthetic work in chemical industry.

At present, another organic chemistry is in full development—the chemistry of the high molecular substances. Although they are built up of the same atoms as the normal organic molecules, namely, carbon, hydrogen, oxygen and nitrogen, and only occasionally contain other elements such as sulphur, chlorine, etc., they are of incomparably higher molecular weight. While the single molecule of a normal organic substance such as benzene, urea or naphthalene has (referred to O = 16) a molecular weight of the order of magnitude of a hundred, the high polymeric bodies such as proteins, cellulose, rubber, polystyrene, polyvinylchloride, etc., achieve molecular weights of many thousands. At first they were found only in living bodies as frame-building substances and as resins; to-day we know quite a series of chemical reactions, which enable us to build them up synthetically, and they appear to be growing in importance both scientifically and technically. Almost daily a new polymerization product is built up and studied. In the chemical industry,

we have to face already a host of commercial names, as neoprene, duprene, buna, perspex, victron, distrene, trolitul, mipolam, igelite, etc.

In this state of affairs, while we naturally wish to produce an increasing number of these new bodies, it is also desirable to formulate some general laws on the relations between structure and properties, unless we are to lose all control over this rapidly growing branch of chemical science. When we look back to the development of organic chemistry, we cannot expect that these laws will be at once before us in their full clearness, but they will emerge slowly from the fog, which covers the yet unknown and mysterious region of our science. Hence we are justified in putting forward some preliminary rules on the relationships between structure and properties, even although we are not yet in a position to give them the form of quantitative laws. It must always be remembered that we have to test these working hypotheses very carefully against the experimental material, and that we must give them up at once if they do not work satisfactorily.

SOME IMPORTANT VARIABLES

Our actual experimental knowledge on polymerization reactions enables us to state some characteristic features for a high-molecular sample, on which the final properties of the material depend in a very important way.

(a) The *chemical nature* of the monomeric material; it may be either aliphatic or aromatic; it may be a hydrocarbon, an ester, a chloride or a ketone; it may contain one or more double bonds. Table 1 gives a survey of the most important materials as regards their chemical nature.

TABLE 1.
CHEMICAL CHARACTER OF COMMONLY USED MONOMERIC MATERIALS.

Chemical class of the monomer	Chemical formula of the monomer	Some trade names of the polymers
Hydrocarbons	Ethylene, CH ₂ = CH ₂	Oppanol Buna Victron, Trolitul Natural rubber
	Butylene, C ₄ H ₆	
	Butadiene, C ₄ H ₆	
	Acetylene, C ₂ H ₂	
	Styrol, C ₆ H ₅ .CH=CH ₂	
Esters	Isoprene, C ₅ H ₈	Vinylite Plexigum Perspex
	Vinylacetate, C ₄ H ₆ O ₂	
	Acrylic ester, C ₃ H ₅ O ₂	
Chlorides	Methacrylic ester, C ₅ H ₈ O ₂	Igelite
	Vinylchloride, C ₂ H ₃ Cl	
Ketones	Dichlorethylene, C ₂ H ₂ Cl ₂	
	Methylvinyl ketone, C ₄ H ₆ O	
Alcohols	Vinyl alcohol, C ₂ H ₄ O	Vinarol

(b) The (average) *length of the main valence chains*, which form the background of every high polymeric substance. It depends essentially on the way in which the sample has been produced; whether the polymerization was carried out at low or high temperature, with or without a catalyst and so on. Table 2 provides some idea of the numbers involved.

TABLE 2.
DATA ON APPROXIMATE AVERAGE CHAIN-LENGTHS.

Material	Degree of polymerization, i.e., number of monomers in the chain
Natural rubber	approx. 500-1000
Masticated rubber	" 50- 200
Low polymerized styrene	" 50- 100
Medium " "	" 200- 800
High " "	" 2000-5000

(c) The *internal flexibility* of the main valence chains. According to the fundamental ideas of stereochemistry and statistics of molecular movement, a very long hydrocarbon chain has a certain amount of internal mobility due to the principle of free rotation around the single main valence bonds. This mobility can be reduced by substituents, double bonds, ring formation, etc. Table 3 gives some examples of this property.

TABLE 3.
DATA ON THE FLEXIBILITY OF THE CHAINS.

Material	Internal flexibility of the chains
Cellulose	Very low
Cellulose esters	Very low
Polystyrene	Fairly low
Polyvinyl chloride	Fairly low
Methacrylic ester	Rather low
Acrylic ester	Medium
Polyvinyl alcohol	Medium
Polyisoprene	High
Polybutadiene	Very high
Polybutylene	Very high

(d) *Main valence linkages between the chains*. In certain cases, especially when the monomeric molecule contains more than one double bond, it is possible to create cross linkages between the long chains. This strengthens greatly the whole structure of the resin, makes it resistant to heat, impact and abrasion, but, on the other hand, increases the density and decreases the flowing properties. This 'netting' of the chains may be quantitatively characterized by the 'netting index' (*Vernetzungszahl*), which indicates the number of

TABLE 4.
DATA ON CROSS LINKAGES BETWEEN THE CHAINS.

Substance	Amount of cross linkages (netting index)
Native cellulose	Nearly zero
Native rubber	Nearly zero
Polybutylene	Very low, ~ 3-5
Polystyrene	Very low, ~ 3-5
Polyvinyl chloride	Very low, ~ 3-5
Soft rubber	Medium, ~ 5-10
Polybutadiene	Medium, ~ 5-10
Hard rubber	High, ~ 10-20
Buna	High, ~ 10-20
Bakelite	Very high, ~ 50

cross linkages to a hundred chain linkages. A netting number of 3 would mean that in the sample we have on an average three bonds perpendicular to the chains to a hundred parallel to them. Table 4 gives an idea of the amount of netting in different materials. It must be pointed out that, in accordance to the preliminary state of the whole of our quantitative knowledge in this field, all figures have to be taken as very rough estimations, but nevertheless they form a useful basis for further and better work.

CONNEXION BETWEEN STRUCTURE AND PROPERTIES

After having enumerated some of the important factors, which together characterize in some way the structure of a high polymeric material, we may try to sketch some connexions between these factors and some of the more interesting technical qualities. For the present short survey, we choose the following properties: heat, oil- and water-resistance, impact and abrasive strength, electrical resistance and reversible elasticity. There are others, which may be equally important; for example, the flowing properties, the surface hardness or the dielectric constant, but it would be inappropriate here to deal with them all. For the sake of simplicity, it must suffice to state the results which one can derive from our present experimental knowledge together in a short table, without discussing every one of them in detail (Table 5).

At the top of the table, the different properties are named, and in the columns the four variables above-mentioned, namely: (a) chemical nature of the monomeric molecule; (b) length of the chains; (c) flexibility of the chains; (d) netting number. Two crosses mean that this particular variable has *no effect* on the special property at all; one cross indicates that it has *little effect*; if there is any effect it is stated in words.

We see, for example, that the impact strength is decreased by a small netting number and increased by a large netting number, that the water resistance is lowered by the content of OH and OCH₃ groups and made bigger by the introduction of CH₃ groups or fatty radicals, but that it is not affected by the chain length at all.

It is easy to see how such a survey can be used. Let us assume we want a material with high heat-, water- and electrical-resistance and great impact strength. Then we shall take a hydrocarbon with long chains (whether they are flexible or not is immaterial) and strong netting. If we want a rubber-like material, we have to make use of very long and flexible chains without too much netting. If it is to be oil-resistant we shall try to avoid

CH₃ groups in it, and we find that, as regards the flexibility and the netting number, the two qualities of oil resistance and high reversible elasticity require opposite factors. Then it will depend on whether oil resistance or high elasticity is more important, and the choice will fall on a netting number in favour of the more valuable quality. In the case of artificial rubber, for tyres,

It is easily realized how many possibilities for building up substances of very interesting properties are already available in such a rough and unexact scheme as Table 5 represents. Nevertheless, it must be pointed out very clearly that it is absolutely necessary to work out every single case very carefully, and to weigh against each other all the required properties and possible results.

TABLE 5.
RELATIONSHIP BETWEEN STRUCTURE AND PROPERTIES OF HIGH MOLECULAR POLYMERS.

Heat resistance		Oil resistance		Water resistance		Impact strength		Abrasiveness strength		Reversible elasticity	
decreased	increased	decreased	increased	decreased	increased	decreased	increased	decreased	increased	decreased	increased
(a) ×	×	by CH ₃ , OCH ₃ , and fatty groups	by OH groups and O-bridges	by OH, NH ₂ , OCH ₃ , HSO ₃ , COOH groups	by CH ₃ , C ₆ H ₅ , and fatty groups	×	×	by CH ₃ , or fatty groups	by OH groups	×	×
by (b) short chains	by long chains	×	×	×	×	when chains are short	by long chains	by short chains	by long chains	by short chains	by long chains
(c) × ×	× ×	by very flexible chains	when chains are not too flexible	when chains are very flexible	by rigid chains	×	×	×	×	by rigid chains	very much by flexible chains
(d) low netting index	very much by high netting index	by low netting index	very much by high netting index	when netting index is very low	by high netting index	by low netting index	very much by high netting index	by low netting index	very much by high netting index	very much by high netting index	by low netting index

for example, the range of reversible elasticity must not be very high (about 100 per cent) but abrasiveness strength and oil resistance are so important that one would prefer a considerable amount of netting, as is indeed the case in all synthetic materials used for this special purpose, as neoprene, buna, sowprene or thiokol.

At the present time, it is not possible to write down mathematical expressions for the relations between structure and properties of high polymeric substances, but it is possible to derive some preliminary and imperfect rules, which will help us to find our way in this new and very promising field of modern chemistry.

An African Survey*

THIS great survey of the problems of Africa south of the Sahara carried out by Lord Hailey originated in a suggestion made by General Smuts in his Rhodes Lecture at Oxford in 1929, when he pointed out that Africa was developing under the control of a number of European powers, that different, and often conflicting principles were being applied in the administrative, social, educational and legal fields, but that nowhere was there any survey of what was taking place in Africa as a whole. His plea for a survey of the extent to which modern knowledge was being applied to African problems was met by the appointment of a committee consisting of Lord

Lothian as chairman, Prof. Henry Clay, Prof. Reginald Coupland, Mr. Lionel Curtis, Sir Richard Gregory, Prof. Julian Huxley, Mr. Ivison Macadam, Dr. J. H. Oldham, Sir John Orr and Sir Arthur Salter, with Miss Hilda Matheson as secretary. The funds for the survey were chiefly provided by the Carnegie Trustees and later by the Rhodes Trust.

In 1933, Lord Hailey accepted an invitation to undertake the survey, but was unable to undertake personal work until 1935, though certain preliminary inquiries were set on foot in the meantime. It was intended originally that the scope and form of the report—the conception of Lord Hailey—should be of a general character only; but as a result of a year's journey through Africa from the Cape to the Sahara, in which a distance

* An African Survey: a Study of Problems arising in Africa south of the Sahara. By Lord Hailey. Issued by the Committee of the African Research Survey under the auspices of the Royal Institute of International Affairs. Pp. xxviii + 1838. (London, New York and Toronto: Oxford University Press, 1938.) 21s. net.