

THE MECHANICAL PROPERTIES OF HIGH POLYMERS.

A Lecture given by PROFESSOR H. MARK, Director of the Polymer Res. Inst., the Polytechnic Institute of Brooklyn, N.Y., before the Faraday Society at the Royal Institution in London, on 26th June, 1946.

1. Introduction.

High polymeric materials have received much attention by scientists and technologists during the past fifteen or twenty years. The scientific interest centres around three problems.

(1) What kind of structure must a simple organic molecule possess in order to be capable of easy polymerisation and what are the mechanisms of the various types of polycondensation and polymerisation reactions? Studies of this kind require close co-operation between organic chemists and physical chemists; they begin with the preparation of new monomers and culminate in a thorough analysis of the various steps of a polymerisation reaction.

(2) What is the adequate statistical and thermodynamical treatment of macromolecules in solution and in bulk; how do the mechanical, electrical and thermal properties of a polymer depend upon the chemical

nature of the material? Progress in this field has mainly been led by physicists and physical chemists and the fundamental outline of a statistical thermodynamics for polymers has been worked out.

(3) What are the implications of polymer behaviour for the treatment of biological problems, particularly for the properties of protein molecules? This is a highly interesting approach and it seems that a thorough analysis of the typical behaviour of long flexible chain molecules and of their mutual interaction may be capable of contributing valuable aspects to questions such as the contraction and relaxation of muscles, the permeability of animal and plant membranes and the existence of forces which act over comparatively long distances (100 Å. and more).

The great technical interest of polymer chemistry is caused by the vast number of valuable building and constructional materials of all kinds which have been produced during recent years and will, in increasing degree, be developed in the near future. Almost any branch of mechanical, electrical and aeronautical engineering depends to-day essentially upon the availability of new and improved types of rubbers, plastics and fibres, which permit the construction of better functioning elements for the various composite engines and devices. This practical industrial application of polymeric materials is being piloted by the fundamental work as mentioned under (1) and (2) and it is the purpose of this brief article to report on recent progress in this specific direction. It will, however, be attempted, at least, to mention briefly those points where a successful application of recent results of polymer research on biological problems appears to be indicated.

The two main sources for new and improved types of polymers in the last few years have mainly been the use of *new chemical systems* and the capability of producing polymeric materials possessing a better *phase texture* than before. It may therefore be appropriate to discuss these two points one after the other.

2. The Use of New Chemical Systems in Preparing High polymers.

Organic chemical synthesis has principally contributed to this progress, which is not at all confined to preparing a new monomer, but preparing it in a high degree of purity and at low cost. Rather spectacular progress has been achieved in this direction during the last few years.

(a) Hydrocarbon Monomers.—A series of new vinyl derivatives with comparatively heavy aromatic substituents, have been prepared; their polymerisation characteristics and the properties of the polymers have been studied. In general they appear to be all of the *polystyrene type*: colourless, non-crystalline (disordered), transparent resins of high softening point (in some instances up to 150° C.) with low density (around 1.1), excellent electrical properties (dielectric constants between 2.6 and 2.9; power factors around and below 0.0002) and a high resistance against acids and alkalis. It would lead too far in this comprehensive article to enumerate them all and to give a detailed account of their properties, but it seems to be worth while to give a few references about some of them. There have been investigated recently: α -methylstyrene,¹ four isomeric di-methylstyrenes,² several other alkylated styrenes,³ *as*-diphenylethylene,⁴ 2-vinylnaphthalene,⁵ 5-vinylfluorene⁴ and vinylanthracene.⁴ From the point of view of co-polymerisation, these materials represent

¹ Hershberger *et al.*, *Ind. Eng. Chem.*, 1945, **37**, 1073.

² Marvel, Saunders and Overberger, *J. Amer. Chem. Soc.*, 1946, **68**, 1085.

³ Marvel, Overberger *et al.*, *ibid.*, 1946, **68**, 736, 1088.

⁴ Unpublished experiments in progress at the Institute of Polymer Research, Polytechnic Institute of Brooklyn, New York.

⁵ Grimm *et al.*, lecture given at the A.C.S. Meeting in Atlantic City, 10th April, 1946.

hardening and flowpoint elevating components; they can all be activated by radical type initiating systems; most of them also seem to be susceptible to the carbonium-ion type catalysis.

A series of new dienes and trienes have been prepared and their utility in the synthetic rubber field has been studied very systematically. Whether their incorporation into three or four component co-polymers at the side of butadiene and its simple derivatives brings enough advantages to balance their relatively high cost, is a question which cannot yet be answered unambiguously.

Perhaps the most interesting new hydrocarbon monomers are the *cyclo*-polyolefines, which have been recently prepared by Reppe and his co-workers⁶ by simple polymerisation of acetylene under moderate pressure.* Outstanding among them is *cyclo*-octatetraene, which was prepared by Willstätter and his co-workers a long time ago^{7,8} and which seems to be capable of polymerising in various ways to give hard transparent resins of almost saturated character or soft, rubbery products which still contain a certain degree of unsaturation.⁹

(b) Monomers of the Ether, Ketone and Ester Type.—A long series of vinyl ethers⁹ has been prepared and the polymers have been studied; they range from soft rubbers with low brittle points (polyvinyl-*isobutyl* ether) over waxy materials (polyvinylstearyl ether) to relatively hard, colourless resins (polyvinylmethyl ether) and may well prove to be rather interesting components for many types of co-polymers.

Similarly a number of vinyl ketones have been prepared, the polymers of which are mostly resins with general characteristics similar to polymethacrylates.

Many new ester monomers have been prepared in the vinyl- and acrylic ester series. They all polymerise and co-polymerise easily and represent a very valuable arsenal of components for various types of co-polymers, which, in one extreme, are sticky adhesives, whereas, in the other extreme, they represent completely colourless plastics of high transparency and remarkable surface hardness, which are extremely interesting materials for optical uses.

An interesting sideline may be mentioned here. For many purposes it is important to impart to a polymer in its final state, as film, coating, or moulded article, a high resistance against solvents and swelling agents and a considerable degree of surface hardness. This is best achieved by a process of controlled cross-linking, in the sense that in the first phase of polymerisation, long linear (un-crosslinked) chain molecules are being produced, which are soluble, plasticisable and thermoplastic. The cross-linking reaction is supposed to set in only *after* the main form-giving process is completed. Obviously such a separation of the formation of the polymer molecules themselves and their interlocking by a cross-linking reaction can be in principle achieved, if the monomer contains two (or more) reactive (functional) groups, which react under different conditions. For instance, if a monomer contains *two double bonds*, one of which polymerises already at low temperatures, whereas the other requires higher temperatures to become activated, it is possible to build up first (under mild conditions) independent long chain molecules, which can be spun, cast, extruded or moulded and to produce later (at higher temperatures)

⁶ Kline, *Modern Plastics*, 1946, **23**, January, February, March and April issues.

⁷ Willstätter and Waser, *Ber.*, 1910, **43**, 1176; 1911, **44**, 3423.

⁸ Willstätter and Heidelberger, *ibid.*, 1913, **46**, 517.

⁹ McKinley *et al.*, lecture given at the A.C.S. Meeting in Atlantic City, 11th April 1946.

* The method of preparation is only briefly described in a few reports issued by W. Reppe in 1944 and 1945. There existed some doubt as to whether Reppe's description actually does lead to such cyclic compounds. Recently, however, several laboratories in England and the United States succeeded in preparing *cyclo*-octatetraene under the conditions as disclosed in Dr. Reppe's reports.

a system of cross-links between them, which results in an insoluble and infusible three-dimensional network. An example for such a monomer is vinyl-allyl-ketone where the vinyl-double bond is much more reactive than the allyl-double bond. Upon co-polymerising vinylpropyl-ketone (90 %) with vinylallyl-ketone (10 %) one first obtains a linear chain vinyl polymer which can be easily handled but contains a (small) number of not yet reacted allyl-double bonds, which, however, can be activated at higher temperatures and produce the desired thermosetting resin. Other cases of similar character are vinyl-isocrotonate and allyl-methacrylate. The success of such a *double reactivity monomer* depends clearly upon the sufficient differentiation in the activation energy of the two double bonds or upon their different sensitivity against various types of activating systems. It seems that a thorough study of the reactivity of a double bond and its dependence upon its substituents should reveal how the effects of *induction* and *polarisation* are being balanced by steric hindrances and should provide a basic understanding as to how the ethylene bond can be activated or deactivated by certain substituents or by a combination of them. Quite generally, it has been found that the vinyl- and acrylic-double bonds are highly reactive, whereas the allyl-, crotyl- and cyclohexenyl-double bonds are much more difficult to activate.

(c) Halogenated and Nitrilic Monomers.—Rather interesting monomers have been obtained by introducing halogens and nitrile groups into various ethylenic compounds. Chloro-acrylo-nitrile and chloro-acrylic-esters give mouldable plastics of improved abrasion resistance mono-, di- and polychlorostyrenes have been rather thoroughly investigated by several workers in the field ¹⁰⁻¹² and are yielding plastics of high density, high refractive index, excellent electrical properties and high heat distortion point. Chlorinated polythene (halothene ¹³ polyisobutylene ¹⁴ and polybutadiene ¹⁴ seem to be of interest for the production of water vapour impermeable, incombustible and tough films and coatings, although their ageing characteristics are still calling for substantial improvement. Other monomers, which have been prepared and the polymerisation of which is now being investigated are α - and ρ -cyanostyrene ¹⁴ and cyanoacrylic esters. ¹⁴ In general the cyano group seems to produce strong intermolecular forces, based on polar interaction and on hydrogen bridges and therefore, favours crystallisation and lateral order.

A most spectacular polymer has been found in polytetrafluoroethylene ¹⁵ a material which is resistant against acids, alkalies and solvents of all kinds and has electrical properties even superior to those of polythene. It is usually obtained in films sheets or test samples, has a very smooth, fatty touch, is strongly water-repellent, and can be heated for long periods to temperatures above 300° C. without decomposing. All of these properties make it a remarkably high-temperature insulating material which is attracting great interest on the part of the electrical engineers particularly in the ultra high frequency field.

(d) Polyesters, Polyamides and other Polycondensation Products.—A large number of new bi-functional and multi-functional alcohols, mercaptans, amines and carboxylic acids have been prepared and have been converted into polycondensation products. They cover the range from rather soft and tacky rubbers, such as Paracon, Paraplex, and the more recent Thiokol types, over thermoplastic and thermosetting resins, such

¹⁰ Michalek and Clark, *Ind. Eng. Chem. (News Ed.)*, 25th September, 1944.

¹¹ Marvel, Overberger *et al.*, *J. Amer. Chem. Soc.*, 1946, **68**, 861.

¹² Styramic HT of the Monsanto Chemical Company has been disclosed to be a polydichlorostyrene.

¹³ Cf. Thompson and Torkington, *Trans. Faraday Soc.*, 1945, **51**, 281.

¹⁴ Unpublished experiments in progress at the Institute of Polymer Research, Polytechnic Institute of Brooklyn, New York.

¹⁵ Renfrew and Lewis, lecture given at the A.C.S. Meeting in Atlantic City, 11th April, 1946.

as the novel soluble glyptal and alkydal modifications, the various Columbia resins and the newer types of Bakelite to certain new types of Nylon, the strength and recovery of which is even superior to that of the commercial 6-6-Nylon (polyhexamethylene-diamine-adipamate). A particularly interesting effect has been achieved by replacing a certain fraction

of the amide-bonds $\left(\begin{array}{c} \text{H} \\ | \\ -\text{C}-\text{N}- \\ || \\ \text{O} \end{array} \right)$ in normal polyamides, by methylated amide-bonds $\left(\begin{array}{c} \text{CH}_3 \\ | \\ -\text{C}-\text{N}- \\ || \\ \text{O} \end{array} \right)$, which have the same strength as far as the

individual chain is concerned but which eliminate the possibility for the establishment of a hydrogen bond and, therefore, reduce very substantially the tendency for lateral chain attraction. In such a polyamide the mutual forces between the parallelised chains in the extended state of a fibre or a film are not strong enough to keep the individual chains in their ordered crystal-like state, but are liable to succumb to the random thermal motion of the chain segments. This has the consequence that a sample, if stretched and oriented, cannot maintain the extended state of low entropy after the external forces ceases to act, but relaxes into a contracted state of higher entropy against the action of the intermolecular forces, which are too weak to enforce the ordered state on the system. In this way it has been possible to produce elastic Nylons, which combine in a most remarkable way the properties of a strong and tough fibre with those of an extensible and snappy rubber.¹⁶ In this connection it deserves to be mentioned that fibres exhibiting high elasticity have also been produced from vinylchloride co-polymers (Vinyon E) and from certain polyesters.

It seems that the elasticity of proteins which is so essential for many biological processes, such as muscle contraction, respiration, etc., can be reasonably well understood on the basis of limited lateral chain attraction and can be very successfully influenced by carrying out certain chemical adjustments at the various substituents along the length of a protein chain.¹⁷⁻¹⁹ By assisting the establishment of strong lateral bonds by stretching under appropriate conditions, it has been possible to produce strong fibres out of globular proteins, which exhibit a surprising degree of crystallinity²⁰ and, therefore, a comparatively good wet strength.

(e) Polymeric Silicon Compounds.—An extremely interesting group of new polymers is based on monomeric silicon compounds, such as alkyl- or aryl-siliconhalides or esters. Silicon is tetravalent and may be expected to enter into many structures analogous to those encountered in carbon chemistry. The simplest is that corresponding to methane (CH₄), namely, silane (SiH₄). The hydrogens of silane are readily replaced by halogens, forming the various halosilanes. Virtually all of these compounds have been investigated and their properties reported in the literature. Technologically, the most important is silicon tetrachloride (SiCl₄), produced in large quantities from ferrosilicon and chlorine, or from free silicon and chlorine. Silicon tetrachloride is highly reactive. It hydrolyses readily to the unstable orthosilicic acid, Si(OH)₄, which quickly loses two moles of water to form the oxide, silica, SiO₂.

If, however, one or more of the halogens is first replaced by an organic

¹⁶ Wittbecker *et al.*, lecture given at the A.C.S. Meeting in Atlantic City, 10th April, 1946.

¹⁷ Croston, Evans and Smith, *Ind. Eng. Chem.*, 1945, **37**, 1194.

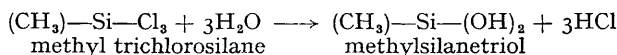
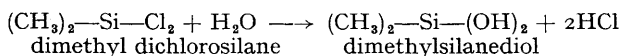
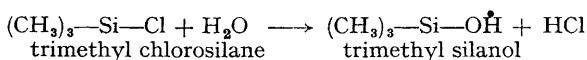
¹⁸ Peterson *et al.*, *ibid.*, 1945, **37**, 492.

¹⁹ Cf. also Alexander, *Colloid Chemistry*, Vol. VI (Reinhold Publishing Company, New York, 1946), pp. 1129 and 1140.

²⁰ Lundgren and O'Connell, *Ind. Eng. Chem.*, 1944, **36**, 370.

452 MECHANICAL PROPERTIES OF HIGH POLYMERS

group such as the methyl radical, and then hydrolysis occurs, there results a series of compounds called silanols. For example :

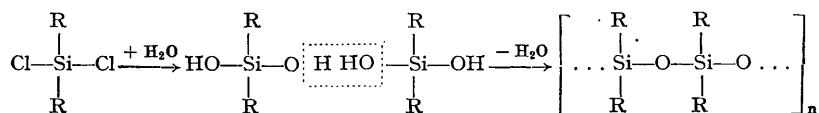


Kipping sought to isolate and to study the silicols and their reaction products.²¹ After extracting crystalline products from the reaction mixture, attempts to determine melting points often caused changes in solubility, in physical form, and in the melting point itself. It is common to read in his work of a "lower melting" material readily converted to a "higher melting" substance, or even to an oil or gelatinous mass, merely by the heat of the melting point bath. Nevertheless, Kipping was able to prepare and characterise a considerable variety of organo-silicon compounds during forty years of research.

Beginning in 1935 in the United States, several investigators embarked upon a study of organosilicon compounds from a different point of view. They were willing to admit the difficulties of classical chemical research in this field. But their impetus was not academic; it was highly practical. Rather than aiming at isolating pure, crystalline products, they attempted to make use of the oily and gelatinous masses which had interfered so frequently with Kipping's efforts. It seemed reasonable to assume that these complex substances were condensation polymers of the silanols, which had united to form siloxane (Si—O—Si) linkages, with the loss of water. These products were termed "silicones," a classification that now includes all compounds containing the siloxane linkage, in which organic groups are bonded to the silicon by means of the C—Si bond.

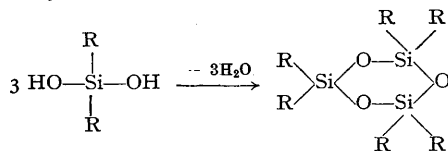
During the last few years, a large number of very able investigators^{22–25} have developed a host of commercially valuable polymers for use as insulators, saturants, varnishes, greases, oils and elastomers, and have contributed to the chemistry as well as to the technology of these compounds.

Simple condensation of a silanediol, resulting from the hydrolysis of the corresponding dihalide, yields a linear system of siloxane linkages :



where R is a simple organic group, such as CH₃, C₆H₅ etc.

Cyclic polymers can also be formed by simple condensation of a silanediol, e.g., the cyclic trimer shown below :



²¹ Cf. Kipping, *Proc. Roy. Soc. A*, 1938, **159**, 139.

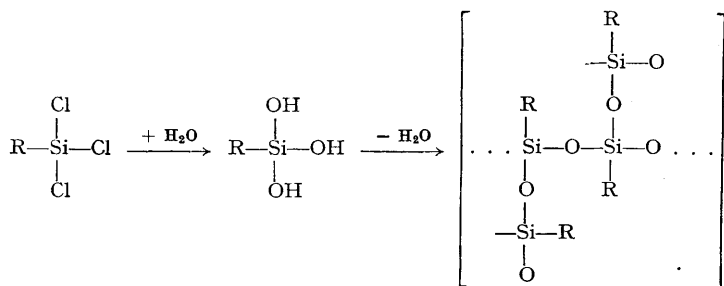
²² Andrianov, *Org. Chem. Ind., U.S.S.R.*, 1941, **6**, 203.

²³ Hyde and de Long, *J. Amer. Chem. Soc.*, 1941, **63**, 1194.

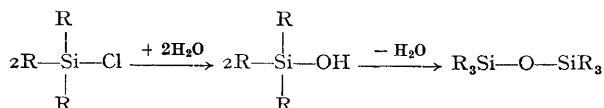
²⁴ Rochow and Gilliam, *ibid.*, 1941, **63**, 798.

²⁵ Norton, *General Electric Rev.*, 1944, **47**, 6.

Simple condensation of a silanetriol yields a highly branched siloxane network :



On the other hand, condensation of silanols can result only in the formation of the dimeric ether :



Carothers, Hill and others,^{26, 27} have discussed the necessary conditions for the production of a linear carbon chain polymer of high molecular weight by polycondensation of bifunctional monomers. In the first place, purity is of very great importance. In the case of Nylon, for example, this demand for purity can fortunately be met by successive recrystallisation of the proper aminocarboxylic acid salts. A second factor lies in the competition between cyclisation and chain condensation. In the case of carbon compounds, only five-, six-, and seven-membered rings are formed to any appreciable extent. In the silicones, however, the formation of larger rings seems to take place much more readily than among the carbon compounds, and hence cyclisation is a more serious competitor of chain formation.

For the preparation of a linear polymer of high molecular weight, dichlorosilanes are the obvious starting materials. Traces of monohalide will decrease the attainable molecular weight. For example, the presence of 1 % (on a molar basis) of monohalide would limit the polymerisation degree to 200, even if condensation could go absolutely to completion. The "practically attainable" polymerisation degree, of course, will be much lower than 200 if 1 % of monohalide is present in the dihalide.

Presence of traces of trihalide in the dihalide will lead to branched structures and eventually to gelation. If both monohalide and trihalide are present in appreciable amounts in the dihalide, polymer structures will be obtained which are characterised by frequent cross-links between short chains.

The above considerations emphasise the important role of "monomer purity" in the production of useful polymers of this type. The high mechanical strength of rubber, cellulose, silk, and Nylon results from the long, linear, threadlike molecular chains which compose most of their total mass. A moderate number of cross-links between chains reinforces the structure and increases the mechanical strength of a given material.

At the beginning it was difficult to obtain sufficiently pure monomers to build up very long linear chain molecules, but recently both the investigators in the General Electric and in the Dow-Corning group have succeeded in producing silicones of very high molecular weight. Considering the structure of a linear methyl-, ethyl- or phenyl-silicone it

²⁶ Carothers, *Collected Papers* (Interscience Publishers, Inc., New York, 1941).

²⁷ Cf. also Alfrey, Honn and Mark, *J. Polymer Sci.*, 1946, **1**, 102.

appears that each individual molecule represents a thin thread of quartz ($-\text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si}-$) wrapped into a molecular layer of paraffin. This combination accounts, in fact, for the two most spectacular properties of the silicones: high stability against elevated temperatures and considerable repellency against water. These two qualities together cause the silicones to be among the most interesting modern insulating materials, which allow motors, generators and transformers to run at much higher working temperatures (200°C . and more) than is possible with the conventional resins or fabrics. Higher current densities can be used and as a consequence the efficiency of the system is very much increased. The remarkable water repellency as such suggests interesting uses in the coating of paper, fabrics and leather. Using the above-mentioned principle of cross-linking with the aid of small amounts of trichloroalkylsilanes one has succeeded in producing elastomers on the silicon basis, which excel because of the fact that they possess a very wide range of rubberiness. Silicone rubbers maintain their elasticity and flexibility down to temperatures of -80°C . and are still resistant to permanent deformation and chemical deterioration at 250°C . and more. The presence of long chains with rather limited internal flexibility and with very small mutual interaction creates rheological conditions, which are most unusual for normal organic polymers, but have already been observed with swollen silica gels and have been called *dilatancy*,²⁸⁻³⁰ A particularly spectacular case for this behaviour is a moderately cross-linked dimethylsilicone which contains an inorganic filler and is known as "bouncing puddy". This material yields easily, so long as the deformation can take place slowly, but reacts like a rigid elastic body towards rapid and sudden impacts or shocks. Considering the relatively limited period (about ten years) during which silicones have been prepared and investigated, it seems entirely probable that many interesting and useful materials will emerge from further studies of these peculiar polymers.

3. Phase Changes in Polymeric Systems.

Let us now suppose that for some good reasons a chemist or a company has decided to use a given chemical material, such as cellulose acetate or Nylon. Is there still a chance left to vary the mechanical properties of fibres, films or moulded pieces of such a given material, thereby making it possible, at least to a certain degree, to adjust the properties of the final samples to some given specifications? Experience has, in fact, shown for a long time that, out of the same polymer, samples with very different mechanical properties can be made depending upon the *state of order* in which the polymer is brought in the course of the various processing steps, such as spinning, casting, drawing, extruding, moulding, etc. We are faced here with an *organic chemical metallurgy and metallography* in which the characteristic features of the *condensed state* are *superimposed* over the *fundamental chemical properties*. Therefore, the question arises: do we know what connections exist between the principal structural features of a given polymer and the mechanical properties of samples made from it? Such knowledge, if it exists, obviously would be of great value in designing polymers for special purposes and in improving their properties. A fair answer to this question seems to be that we have no well-developed mathematical theory which connects *quantitatively* the structure of a given polymer with its properties, but we do know a number of general rules and principles which correlate properties and structures and which have been helpful in many cases in obtaining materials with superior properties.

²⁸ Reynolds, *Phil. Mag.*, 1885, **20**, 469.

²⁹ Cf. Fischer and Gans in J. Alexander, *Colloid Chemistry*, Vol. VI, p. 287.

³⁰ See also Green and Weltman in *ibid.*, Vol. VI, p. 332.

There are, as already mentioned, two main factors that influence the ultimate behaviour of a polymer: (i) the structural configuration of the long chain molecules themselves; and (ii) the way in which these molecules are arranged in the sample of the polymer. The same distinction can also be expressed in a somewhat briefer form in terms of (i) the chemical structure of the molecules and (ii) the physical texture of the macroscopic sample. We shall now attempt to discuss these two factors in order.

Details of Chain Structure and Mechanical Properties of Polymers.

Let us first enumerate the most important structural details of high polymer molecules and briefly report our present knowledge on their significance for the mechanical properties of polymers. There are, first of all, the average molecular weight and the average D.P.* of the substance, which according to Table I, vary from 20,000 to 1,000,000 and from 100 to 5000, respectively. There is the molecular weight distribution, which describes the heterogeneity of the material and is comparatively narrow in some cases and fairly wide in others, and there is the internal flexibility of the individual chains, which is a consequence of the chemical nature of the bonds between the monomers.

The connection between mechanical properties and average D.P. has been frequently investigated.^{31, 32} The general result is that, in order to obtain mechanical strength at all, a certain minimum D.P. which ranges between 40 and 80 is necessary. As soon as this critical value is exceeded, the material starts to exhibit mechanical strength and its ultimate tensile strength increases from now on continually with the average D.P. It was found that up to a D.P. between 40 and 80 the tensile strength of a film cast from this material is negligible and that it then increases about in proportion to the chain length. The proportionality between mechanical strength and D.P. holds up to a D.P. of about 250. Then the curve bends, and after a D.P. of about 600 is reached, the mechanical properties depend but moderately upon D.P.

While the influence of the average D.P. on the mechanical strength is fairly well established, the significance of the molecular weight distribution is still an unsolved problem. Promising attempts have been made recently to establish a connection between the distribution curve and the mechanical properties of high polymers; it is found that relatively small amounts (between 10 and 15 % by weight) of constituents having a D.P. below 150 are detrimental for such mechanical properties as tensile strength, resistance to flexing, fatigue performance, and so forth. Removal of such constituents of low molecular weight improves the material considerably.³³

Let us next consider the internal flexibility of the individual molecules. It is a well-established fact that each atom in a small molecule carries out rapid vibrations, the energy of which represents the main part of the heat content of a solid (crystallised) material and can be studied by the molecular spectrum (ultraviolet, infra-red, Raman) and the temperature dependence of the thermal capacity. In larger molecules, such as the polymers listed in Table I, there exist, in addition to these rapid vibrations of the individual atoms, comparatively slow vibrational and rotational movements of certain parts or segments of a large molecule. This does not imply that the rotation about the single C—C bond is actually free. In fact, recent investigations have shown that, owing to the mutual interaction of the substituents, subsequent CH₂ groups in a long chain paraffin

³¹ Sookne and Harris, *Ind. Eng. Chem.*, 1945, **37**, 475.

³² Mark in E. Ott, *Chemistry of Cellulose and Its Derivatives* (Interscience Publishers, Inc., New York, 1944), p. 990.

³³ Mark, *Paper Trade J.* 1941, **113**, 34.

* D.P.: Degree of polymerisation.

molecule cannot rotate freely about the connecting bond. However, vibrational movements within angles of about 10° are much less inhibited, and as a consequence a chain of many CH_2 groups—say a thousand or more—will exhibit as a whole a considerable degree of internal flexibility. There are no sharp bends to be expected within the range of a few CH_2 groups but the chain as a whole will be capable of assuming a large number of slightly curved or coiled geometric configurations, and the probability of finding such a large molecule in its most extended state is extremely small. If an isolated long chain molecule is brought into this state of extreme elongation by external forces (mechanical stretching), it has the tendency, under the influence of its random thermal motions, to return to the most probable configuration, which is characterised by a certain degree of folding and curling. This represents a tendency of the long chain to contract if it is once extended.

The *rate* at which it contracts, however, will not depend upon how much more probable the final (contracted) configuration is than the

TABLE I.—MOLECULAR WEIGHTS AND DEGREE OF POLYMERISATION OF SOME REPRESENTATIVE POLYMERS.

Material.	Elements.	Molecular Weight.	Degree of Polymerisation.
Cellulose in native cotton	C, H, O	<i>ca.</i> 1,600,000	<i>ca.</i> 10,000
Cellulose in wood pulp .	C, H, O	<i>ca.</i> 500,000	<i>ca.</i> 3000
Cellulose in rayon .	C, H, O	80,000-160,000	500-1000
Cellulose acetate in rayon	C, H, O	80,000-140,000	300-500
Cellulose acetate in film .	C, H, O	100,000-160,000	400-600
Native rubber .	C, H	200,000-400,000	3000-6000
Buna-S .	C, H	100,000-150,000	1500-2000
Polyvinyl chloride (Geon)	C, H, Cl	100,000-200,000	1500-3000
Polyvinylidene chloride (Saran) .	C, H, Cl	100,000-300,000	1000-3000
Polyvinyl chloride acetate (Vinylite) .	C, H, O, Cl	100,000-200,000	1500-3000
Polystyrene .	C, H	100,000-300,000	1000-3000
Polymethylmethacrylate (Lucite) .	C, H, O	100,000-200,000	800-1600
Protein in native silk .	C, H, O, N	<i>ca.</i> 150,000	2500
Polyamides (Nylon) .	C, H, O, N	<i>ca.</i> 25,000	250

original (extended), but upon how fast the chain-like molecule can pass from the extended into the curled-up state, which in turn will depend upon how quickly the individual segments of the molecule can swing from one geometric position to another that is separated from the first by a certain energy barrier. Thus, the rate of contraction of a polymer is a matter of the rate of chain segment diffusion in the face of energy barriers that separate the possible positions of the individual chain segments from one another. In an isolated long-chain molecule these barriers depend upon how much the free rotation about the consecutive bonds in the chain is hindered, either by the intrinsic rigidity of the bond or by the mutual interaction of substituents. It must be added that in an actual piece of rubber there are no *isolated* chain molecules, but a condensed multitude of them in a state of irregular entanglement, attracting each other with intermolecular (van der Waals) forces. This mutual interaction also contributes to the hindrance of the free mobility of the individual molecules and their segments and hence affects the rate of contraction of the material.

There is another aspect of the hindered internal flexibility of the molecules in a polymer. The reason for this hindrance is the existence

of energy barriers which have to be overcome as the segments move into less and less geometrically biased positions. Each elementary step of recovery, therefore, requires a certain activation energy, which is responsible for the influence of temperature on the rate of segment diffusion and hence on the rate of recovery. If the energy barriers over which the segments have to go are high, it will, at low temperature, become more and more difficult for an individual segment to acquire this energy and the rate of recovery will be considerably reduced. This means that the material will be slow in adapting itself (by segment movement) to the external stress, and hence it may develop brittleness.

Thus we may conclude that the intrinsic flexibility of the individual chains is of great importance for the mechanical characteristics of elastomers and affects mainly the rate of recovery from the extended state and its temperature dependence, particularly the point at which the material begins to exhibit brittleness.

It may be added here that the chemical nature of a given polymer is of great importance for its chemical reactivity, swelling, and solubility. Thus polyhydrocarbons, such as natural rubber, polystyrene, polyisobutylene, and so forth, are very resistant to acids and alkalis, and do not absorb water, but eventually swell and dissolve in hydrocarbons and other typically organic solvents. Polymers containing many hydroxyl groups, such as cellulose or polyvinyl alcohol, are in turn very resistant to the action of organic solvents but absorb moisture and eventually even dissolve in water or in weak alkali. It seems, however, that the mechanical properties of polymers depend not so much upon whether the monomer is a hydrocarbon, an ester, a sugar, or an alcohol, but rather upon the chemical characteristics as embodied in the molecular chain structure and expressed by average D.P., D.P. distribution and internal flexibility of the chain molecules. In fact, Table I shows that fairly strong fibres can be made from materials that are very different chemically.

After having now briefly discussed how the structural details of the individual chains affect the mechanical properties of a polymer, let us pass to the importance of the mutual arrangements of the chain molecules in a sample.

Arrangement of the Chain Molecules and Mechanical Properties of Polymers.

It may be worth while to consider very briefly the behaviour of an ordinary organic substance. At the freezing temperature a liquid of low molecular weight, such as benzene, toluene or isoprene, undergoes a very distinct change in mechanical properties within a narrow temperature range. Below the freezing temperature ordinary substances are crystalline solids; they respond to shearing stress by undergoing small (1 % or less) predominantly reversible deformations and exhibit the long range order (100 Å. or more) of a three-dimensional crystal lattice. Each molecule is held by attractive and repulsive forces of all surrounding particles in a relatively well-defined equilibrium position, about which it performs rapid, quasi-harmonic vibrations. Transition of an individual molecule from one equilibrium position to another (self-diffusion) is extremely infrequent, the average amplitude of the vibrations amounting only to about 5 % of the distance between adjacent equilibrium positions. Such systems appear to us as rigid, hard substances, having a definite shape and all other characteristics of a solid body.

As the temperature is increased, the vibrations of the individual particles become more and more vigorous until, at the melting temperature, the forces between the constituents of the lattice can no longer maintain the long range order of the crystal, and the whole structure breaks down. The result is a liquid, characterised by the absence of any far-reaching geometric order. The nearest neighbours of any individual molecule,

458 MECHANICAL PROPERTIES OF HIGH POLYMERS

it is true, are arranged about the latter in much the same manner as in the crystalline state, but molecules a few Angstroms farther away are distributed practically at random. Each single particle, again, carries out rapid quasi-elastic vibrations about an equilibrium position; but this equilibrium position itself (being a position of minimum potential energy) is not fixed in its location and the molecule undergoes, in addition to vibrations, an irregular translational Brownian movement, which makes it change its place rather frequently—self-diffusion is rapid. The lack of long range order prevents a liquid from sustaining shear or stress and from assuming a definite shape; it flows. Eyring, Lennard-Jones and their co-workers have succeeded in giving a very satisfactory explanation of many important properties of liquids on the basis of this picture.

A liquid can be undercooled below its equilibrium melting temperature, thus retaining the characteristics of its disordered (amorphous) geometric structure. The coefficient of viscosity η decreases with increasing temperature, roughly following an exponential relationship,

$$\eta = A e^{B/T}$$

where A and B are constants and T is the temperature, and at a sufficiently low temperature the material becomes hard and brittle; it is then called a glass. The transition from rigid glass to viscous liquid frequently occurs in a relatively narrow temperature range (the softening point) with no sudden change in structure and with no discontinuity in the primary thermodynamic variables, such as heat content, free energy and specific volume. Thus in the case of ordinary (low molecular weight) organic substances, the relationship between the crystalline, glassy and liquid states can be represented by the scheme of Table II.

TABLE II.—COMPARISON OF THE VARIOUS STATES IN WHICH ORDINARY ORGANIC SUBSTANCES CAN EXIST.

State.	Extent of Geometric Order.	Viscosity.
Crystalline . .	Long range (more than 1000 Å.)	High
Glassy . . .	Short range (only a few Å.)	High
Liquid . . .	Short range (only a few Å.)	Local viscosity low

High polymers consisting of long chain molecules exhibit a more complicated behaviour. The strong chemical bonds inside the individual chains are seldom, if ever, severed during the normal mechanical deformation of the polymer, such as stretching of rubber or spinning of Nylon, or during the various thermal treatments, such as annealing or moulding. The changes in shape which take place during these processes occur at the expense of opened (and reclosed) bonds between the individual chains, which are not due to chemical forces, but to the various types of intermolecular interaction, such as hydrogen bridges and van der Waals forces.

Let us, from this point of view, compare the crystal lattice of isoprene with that of stretched (or frozen) rubber and consider what happens if the temperature of both systems is increased. In frozen isoprene, each individual molecule (C_5H_8) is located in a definite equilibrium position, about which it undergoes irregular, quasi-harmonic vibrations. The distance between any one molecule and its next neighbour is about 4 to 5 Å., while the interatomic distances within the molecule are only 1.0 to 1.5 Å. This elucidates the fact that the C_5H_8 molecule is held together by strong chemical bonds, having dissociation energies of 70 kcal./mole. or more, so that it forms a well-defined unit in the lattice, while the forces

between the molecules are of the much weaker, van der Waals type (about 5 to 8 kcal./mole.). Nevertheless, below the melting temperature, the bonds between molecules suffice to maintain the long range order of a crystal lattice, and frozen isoprene is a hard, rigid substance. Above the melting temperature, however, all long range connections between the molecules disappear and the result is a liquid with rapid self-diffusion of the individual molecule and small coefficient of viscosity (about 10^{-2} poise).

In frozen rubber, each individual isoprene residue (C_5H_8) as well as each C and H atom within it, vibrates about a definite equilibrium position; but a thorough investigation of the lattice shows that each isoprene residue is particularly close to two other residues, indicating that long linear chains of residues exist, within which all next-neighbour distances correspond to strong chemical bonds. The main valence chains of isoprene extend parallel to the direction of the stress have a length of several thousand monomers and represent the backbone of the whole structure. In all directions perpendicular to the axes of the chains the distances between adjacent molecules are determined by normal van der Waals forces. This lattice therefore is highly anisotropic with strong forces along the parallelised chains and weak forces perpendicular to them. As the temperature is increased the weak intermolecular bonds gradually are severed and thus the lateral arrangement of the chains is disturbed and eventually destroyed. The chains start rotating about their axes, changing their mutual distances and eventually curling and coiling up in an irregular way. However, while the weak bonds between the individual chain molecules are opened the strong (chemical) linkages within them remain unaffected. The molecules are not degraded at temperatures at which the lattice structure has already broken down. This has the important consequence that although the long range geometric order of the lattice disappears upon raising the temperature to the softening point a long range entanglement due to the unaltered existence of the long chain molecules is maintained. This long range entanglement is responsible for the fact that at the softening point of a polymer, we get not a liquid, but a rubbery solid.

An individual isoprene residue in (amorphous) unstretched rubber vibrates with about the same intensity as does an isoprene molecule at the same temperature in liquid isoprene, and it will also carry out about the same short range Brownian movement; but, owing to its position in the chain molecule, it will not be able to diffuse farther away from its original positions without affecting other parts of the chain to which it belongs. This geometric restriction of the various segments of the flexible linear macromolecules due to the strong bonds between them produces a long range entanglement, which enables the material to sustain moderate stresses of shears, hence to maintain a certain definite volume and shape and resist elastically any attempt of deformation. In this sense rubbers have a state between the solid and liquid, just as glasses do, and one may say that glasses are liquids with high viscosity, whereas rubbers are liquids with long-range entanglements (see Table III). The self-diffusion of chain segments is not essentially affected by the long range entanglement and, therefore, is rapid, whereas any displacement of the large linear molecules as a whole, is impeded by their mutual interaction over long ranges and therefore is very slow. The irregular motion of portions of the chains under the influence of the temperature has been termed, by Kuhn³⁴ internal, or micro-Brownian movement; the displacement of the macromolecules as a whole is referred to as external, or macro-Brownian movement.³⁵

Using these terms, we can say briefly (and with a certain degree of oversimplification) that rubbers are materials that have rapid internal,

³⁴ Kuhn, *Kolloid Z.*, 1936, **76**, 258.

³⁵ Cf. also, Mark, *Amer. J. Physics*, 1945, **13**, 207.

460 MECHANICAL PROPERTIES OF HIGH POLYMERS

TABLE III.—TRANSITION POINTS FOR ORDINARY SUBSTANCES AND HIGH POLYMERS.

(a) Behaviour of Ordinary Substances :*Melting Point.*

Long range molecular order No Brownian motion Sustains external forces ; exhibits short range, high modulus elasticity	Short range molecular order Rapid Brownian motion Does not sustain external forces flows and has low viscosity
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(b) Behaviour of Polymers :*Brittle Point.**Flow Point.*

Solid State.	Rubbery State.	Liquid State.
Long range molecular order	Short range molecular order, but long range entanglement	Short range molecular order
Both Brownian movements are frozen in	Internal Brownian motion rapid ; external Brownian motion still frozen in	Both Brownian motions are activated
Sustains external forces ; exhibits short range, high modulus elasticity	Sustains external forces ; exhibits long range, low modulus elasticity	Does not sustain external forces ; flows and has medium viscosity

but slow external Brownian movement. It is this combination that characterises the rubbery state.

Significance of the Two Different Brownian Movements.

Let us first consider for which essential feature of rubberiness the two types of Brownian or molecular motion are responsible. If we start stretching a rubber, we expect it to begin deforming at comparatively low stresses ; it is supposed to be a soft, extensible material, having a small initial Young's modulus. For typical elastics (soft rubbers or gum stocks), Young's modulus is between 10^6 and 10^7 dyne/cm.² (15 to 150 lb./in.²). If a material is to extend appreciably under the influence of such small stresses, it needs a considerable degree of internal mobility, much like a normal liquid. In fact, rubbers have many properties in common with ordinary liquids. They possess a compressibility very similar to that of liquids. Poisson's ratio for all "soft" elastics is in the neighbourhood of 0.50 ; the thermal expansivity of rubber is of the same order of magnitude as that of ordinary liquids, and (perhaps most surprising) the solubility of gases (hydrogen, oxygen, etc.) and solids (sulphur, selenium, etc.) in rubbers resembles rather closely the solubility of the same materials in ordinary liquids. The "local" fluidity of elastics produced by the fast internal Brownian motion is also responsible for this rapid contraction. In a stretched rubber certain segments of the individual chains assume configurations the free energy of which is larger than in the unstretched condition. Therefore, as soon as the external force ceases to act, these portions will start to diffuse back into their unstrained (equilibrium) positions, which correspond to a minimum free energy and represent the relaxed state of the sample. How quickly this contraction takes place depends upon the rate of segment diffusion, which determines the "local" fluidity of the material.

Certain materials "snap" back into their original shape, because segment motion is fast ; others "creep" back, because the local mutual

interaction of the chain segments is strong and prevents them from assuming their unstrained positions with a short time. Natural rubber, Neoprene, Butyl-rubber and the Buna types are examples of the first case; polystyrene above 80°C. , Vinylites and moist polyvinyl alcohol, of the other. In order to get a good, snappy elastic, one has to keep the internal Brownian motion as rapid as possible, which means that one has to accentuate the local liquid character of the system.

On the other hand, if we provide in an elastomer for *nothing* but this high local fluidity and keep a macroscopic sample of the material under stress for a certain length of time, the material will *flow*. It will not sustain the imposed stress or shear, but, with the very aid of the rapid internal Brownian motion, will relax into the extended state instead of into the contracted. Hence it will behave like a viscous liquid or plastic rather than like a rubber. To prevent this permanent loss of shape, one has to provide for *strong long-range entanglement*, which makes the external Brownian movement (slipping of whole chains along one another) so slow that it cannot produce any appreciable permanent set within the time the sample is in its extended state. In general, the mutual attraction of the chain by van der Waals forces alone does not provide for a sufficiently stable long-range entanglement to conform with practical requirements. Therefore, one usually produces a system of irregularly distributed, widely spaced fix points. They provide a stable, but highly deformable network throughout the sample, which can be stretched several hundred per cent. and will return to its original shape, because its individual knots are connected with one another by flexible chain molecules. Such fix points can be made in different ways. One way is to produce strictly localised, strong chemical bonds between the individual chains, such as sulphur, oxygen, or methylene bridges, as is presumably done during the various processes of curing and vulcanising. Another way is to have groups of particularly strong molecular interaction (hydrogen bonds, strong dipoles, highly polarisable groups) or of great bulkiness (phenyl, benzyl or naphthyl groups) randomly and in large distances distributed along the chains, thus producing an irregular network of areas with high molecular cohesion. Still another method is to distribute very small particles with high adsorption power (active fillers) in the polymer, which provide for fix points by adsorbing parts of the mobile chains irreversibly on their active surfaces. If a rubber crystallises upon stretching, the areas of crystallisation themselves act like strong cross-links between the individual chains.

In all these cases, the localized and infrequent strong links between the individual flexible chains suppress the external Brownian movement sufficiently to prevent permanent flow of the sample as a whole, while they leave the internal Brownian movement sufficiently unaffected to allow rapid extension and contraction to be possible.

This discussion shows that a polymer can exist not in two but in *three condensed states*: the *solid*, the *rubbery* and the *liquid*. In the solid state (crystal or glass) *both* Brownian movements are *frozen* in; in the *rubbery* state the *internal* Brownian motion is *activated* while the *external* Brownian movement is still *frozen* in; and finally, in the *liquid* state of a polymer (in the melt or in a highly swollen sample) *both* Brownian movements are *activated*. Under the influence of an external force the solid state exhibits only short range, high modulus elasticity, the rubbery state possesses long range, low modulus elasticity, whereas the liquid state provides for flow. An ordinary organic substance has only two condensed states, the solid and the liquid; there exists only one type of Brownian motion, which is activated in the latter and frozen in the former state. These two phases, solid and liquid, are in equilibrium with each other at the freezing (or melting) temperature. In the case of polymers there are two characteristic temperatures (or temperature ranges): the *brittle temperature*, which separates the solid from the rubbery state, and the *flow*

temperature, which separates the latter from the liquid. Table III attempts to give a schematic picture of this situation.

Considering the facts as discussed in the preceding section, it becomes clear that, in order to produce a polymer for practical purposes, one has to synthesise chain molecules with a D.P. around or above 1000, having a certain degree of internal flexibility. This material has then to be brought into the proper physical state or mixture of states. And here we realise that we have at our disposal three different phases: the *solid*, the *rubbery* and the *liquid*. The task of bringing the polymer into the best physical state is similar to that of a metallurgist, who attempts to find the best properties of his alloy in the phase diagram of his system, with the difference that this organic chemical "metallurgy" puts one more state at his disposal, namely, the rubbery. This is because of the presence of the long chain molecules.

It is now obvious that, if the desire is to produce a strong and resilient fibre, one will have to accentuate the solid crystalline state in order to get stiffness and tenacity and will have to provide for only as much rubberiness as will give a sufficient resiliency. Any liquid constituent in such a fibre would be unwelcome because of the permanent set to which it leads under prolonged external stress. If one aims at the production of a typical rubber, it will be necessary to have the bulk of the material in the rubbery state, with perhaps some crystalline domains in order to provide for a sufficiently strong fix-point system. Finally, in producing a plastic, one will have to provide for an appropriate mixture of solid and liquid material with as little rubberiness as possible in order to guarantee smooth extruding, casting or moulding without recovery after the desired shape has been obtained.

In this sense it can be said that fibres, plastics and rubbers are not intrinsically different materials: they are merely different combinations of three fundamental states in which organic high polymers can appear; and there exists, obviously, a continuous range of systems, starting with extreme fibre properties and ending with extreme rubber qualities, depending essentially upon the degree to which the solid, rubbery and liquid state are represented in the sample.

Hence, there are two independent ways to arrive at new polymers with novel and interesting mechanical properties: (i) to prepare chemically new monomers and produce long chain molecules of them with a high D.P. and a favourable molecular weight distribution, and (ii) to bring these substances into the proper physical state by adjusting the proportions of these solid, rubbery and liquid constituents such that they incorporate to the best degree the desired properties. Along both lines a large number of research chemists and physicists are active, and there can be little doubt that their work will lead to an ever-increasing number of new materials with valuable and surprising properties.

Résumé.

Les différents systèmes chimiques employés dans la préparation des hauts polymères—dérivés du silicium inclus—sont ici classés et brièvement passés en revue. L'influence de la structure chimique des molécules et de la texture physique de l'échantillon macroscopique sur le comportement ultime du polymère est discutée sous l'angle de la configuration des molécules, de leur arrangement dans la chaîne et des mouvements browniens interne et externe.

Zusammenfassung.

Die verschiedenen chemischen Systeme, die zur Darstellung hochpolymerer Substanzen Verwendung finden, darunter Siliziumverbindungen, werden klassifiziert und kurz besprochen. Die Beziehung zwischen der chemischen Struktur und makroskopischen physikalischen Textur einerseits und dem allgemeinen Verhalten der polymeren Substanz andererseits wird auf Basis der Kettenstruktur, Anordnung der Kettenmoleküle und der internen und externen Brownschen Bewegung erörtert.