

AN INTRODUCTION TO POLYMER MECHANICS

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Taylor & Francis
London and Philadelphia
1985

UK

Taylor & Francis Ltd, 4 John St, London WC1N 2ET

USA

Taylor & Francis Inc., 242 Cherry St, Philadelphia, PA 19106-1906

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British Library Cataloguing in Publication Data

Arridge, R.G.C.

An introduction to polymer mechanics.

1. Polymers and polymerization—Mechanical properties

I. Title

620.1'92 TA455.P58

ISBN 0-85066-284-2

Library of Congress Cataloging in Publication Data

Arridge, R. G. C.

An introduction to polymer mechanics.

Bibliography: p.

Includes index.

1. Polymers and polymerization. I. Title.

TA455.P58A77 1985 620.1'92 85-4634

ISBN 0-85066-284-2

*Typeset by Mid-County Press, 2a Merivale Road, London
Printed in Great Britain by Taylor & Francis (Printers) Ltd,
Basingstoke, Hants.*

PREFACE

the purpose of research into materials

The student about to undertake research in materials science may be motivated by curiosity about the nature of common materials: why some are soft, some hard, some strong, and some brittle, and whether these differences can be explained satisfactorily in terms of their microstructure. Alternatively he may not wish to pursue the subject in great depth but, instead, may wish to use materials in new and imaginative ways, and therefore needs to understand their properties. In the last twenty years or so new materials have appeared which were hailed as the results of brave new technology, revolutionizing such fields of application as aerospace. While there have indeed been advances in our ability to invent new materials the principles upon which the properties of materials depend have not altered. The new materials, such as fibre composites, polymers, memory alloys and optical fibres have resulted from improved technology together with a more widespread understanding of the physical basis of the behaviour of materials. It should be stressed that the boundaries of one scientific discipline very often overlap those of another and advances are made at these boundaries rather than at the centre. A proper study of materials now requires a sound knowledge not only of metallurgy but also of crystal physics, ceramics, polymer physics, elasticity and continuum mechanics, as well as an understanding of practical mechanics. The computer, relevant in materials science as in all other spheres of modern science, enables analysis of structural and microstructural problems to be made by using, for example, the Finite Element method, while computer-controlled machines simplify the problems of data gathering so that reliable information on materials properties can be obtained rapidly. The practical user of solids as load-bearing materials requires information on, for example, displacement, load and time in order to design a useful structure—interpreting the term structure as anything from a bridge to a woven garment. For his purposes data sheets are ideal and standard tests laid down by the national standards institutions are the methods that he uses.

The materials scientist, however, seeks more fundamental information, attempting to answer the questions of the relation of structure to macroscopic

properties. Starting from the classical theories of elasticity such questions as the prediction of elastic moduli from the inter-atomic forces and the part played by crystal structure and crystal defects have been the subject of research for a great many years. We now understand many of the problems but there is still a great deal which is not properly understood. This is particularly, but by no means exclusively, the case in polymeric materials where great problems still exist in the proper description in terms of the microstructure.

One of the factors limiting our understanding is that, with few exceptions, we can never have a macroscopic single crystal to study as is the case with metals or ceramics. Polymers are multivariable systems. We cannot, as in the idealized experiment, vary only one quantity and assess its effect. For this reason, if for no other, the study of polymers is difficult and many techniques must be used.

In this monograph I deal mainly with the mechanical properties, showing, however, in the final chapter how some of these relate to other physical properties. I have further confined the text to the elastic and viscoelastic properties omitting the irreversible behaviour of yield and fracture. To have included the yield, crazing and fracture of polymers would have required another three chapters to do them justice. They should form the subject of a separate monograph by another hand.

The book is divided into seven chapters, each reasonably self-contained, and each designed to provide the serious student with a critical review of its subject-matter as a basis for further research. Since progress is still rapid I have chosen the title 'An Introduction to Polymer Mechanics' and have indicated in each chapter where further information may be sought and where current advances are being reported. Lastly, I have tried to show that the mechanical properties of many polymers may be described using the concepts and terminology of composites, so indicating the usefulness of what may be called a theory of materials. Using appropriate scaling factors, one can think of materials as structures and use the analysis appropriate, for example, to the description of the forces and displacements in a bridge or an aeroplane for describing the moduli of a semi-crystalline polymer. One such analytical method is that of Finite Element theory, much used in engineering and eminently suitable for modelling the microstructure of polymers and composite materials.

It is assumed that the reader is familiar with the elements of thermodynamics, statistical mechanics and elasticity to the level of an honours degree in physics or chemistry but since continuum mechanics and viscoelasticity are not commonly found in such courses a detailed account of them is given in Chaps 2 and 3. Chap. 4 is devoted to the consideration of polymers as *heterogeneous* materials, or composites since, except for amorphous polymers, most polymers which crystallize can be considered as at least two-phase materials. Many of the concepts developed, for example, in the field of fibre-reinforced composites are relevant to semi-crystalline polymers. Chap. 5 includes some detail on test methods which are peculiar to polymers and which have been specially developed for them. Chap. 6 gives an account of the classical statistical theories of rubber

elasticity and of polymer solutions and concludes with an introduction to the recent tube or tunnel theories of polymers associated with the names of de Gennes and of Edwards. Chap. 7, which is necessarily brief, shows the relationships between the mechanical and other properties of polymers. Its brevity reflects its purpose as a link with specialized treatises on, for example, optics, X-ray crystallography and infra-red spectroscopy, each one of which is a discipline in its own right.

I have drawn on my earlier book, Arridge (1975), referred to as (MP), for parts of the present book. It may sometimes serve as a companion to the present volume.

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CHAPTER 1

the polymeric state of matter

1.1. Introduction

For many purposes polymers can be thought of as entirely one-dimensional, that is, as mathematical lines. Thus in the theory of rubber elasticity the polymer chain is represented quite well by a random walk in three dimensions and from this the chain entropy and hence the free energy are deduced. Sometimes it is convenient to give the line some thickness and so what may be called the ‘cooked spaghetti’ model is used. For visualization this is, in fact, quite a useful model, since the sliding and bending of the cooked spaghetti as it traverses the mass of its neighbours models quite well the behaviour of real chains, particularly in the tunnel or tube models of polymers of de Gennes, Edwards and others (Figure 1.1).

The bulk modulus of polymers is determined almost entirely by the van der Waals’ forces between chains and so has values similar to those for the inert gases. Table 1.1 shows some comparisons.

The shear properties of polymers, however, are primarily determined by the wriggling, bending and twisting of the chains. The spaghetti model has uses here for visualization. In fact although the chemical structure of polymers, to be discussed below, does affect physical properties considerably it is not of prime importance for determination of the mechanical properties *when a particular state is being considered*. For example, in the glassy state all *unoriented* polymers have similar bulk and shear moduli. These will only be changed if the chemical composition is such as to ease crystallization or if the chains have been oriented by some means so that considerable *anisotropy* is present. Similarly, in the rubbery state the shear modulus of all polymers depends primarily upon the density of cross-links. This is why the simple random walk theories are so successful and why they apply to rubbers, gels and even to thermosets.

What the chemical structure of course does determine is the temperature at which the glassy state passes into the rubbery and, if the cross-linking is insufficient to prevent it, further passes from the rubbery to the liquid-like state. In addition the chemical translational symmetry, the symmetry along the chain,

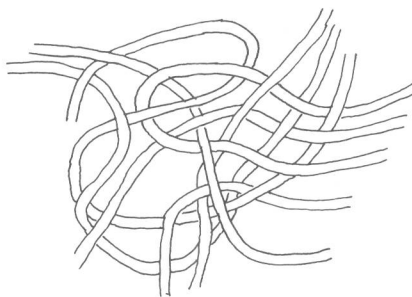


Figure 1.1. The 'cooked spaghetti' model of polymer chains.

Table 1.1. Bulk modulus, K , of some solids.

Material	K (GPa)
Solid argon	1.6
Solid neon	1.0
Solid krypton	1.8
Polyethylene	3.5
Polymethylmethacrylate	5–6
Polyvinylchloride	5
Epoxy resin	5
Polyisobutylene	2–5
Glycerol	5–7
Aluminium	73
Copper	138
Steel	180
Sodium chloride	30

determines whether or not the polymer is crystallizable and in what form. Thus if the polymer is *atactic*, that is, has no regular translational symmetry, it will form only an amorphous solid, whereas if stereo-regularity exists it can crystallize.

Chemical structure determines also, of course, the chemical properties of the polymer such as solubility, reactivity, the optical and electrical properties and, most basic of all, whether the polymer can be made at all from the small molecules which constitute the monomer.

No attempt will be made here to discuss the chemistry of polymers but certain terms used by the chemists must be defined if the simple physicist's view of the polymeric state of matter is to be understood.

Monomers are the raw material of polymers and there are several ways in which a monomer is polymerized, that is, joined end-to-end as in linear polymers or in multidimensional ways as in three-dimensional polymers or *thermosets*. One monomer may be *added* to another or to itself in so-called *addition reactions*. Examples are: polyethylene, polypropylene and polyvinylchloride—to name

three familiar polymers. Another way to form a polymer is by a *condensation reaction* where the reaction of two monomers results in a composite molecule together with a product of the reaction. A common example is the reaction of diacid and di-amine to form nylon with water as a by-product. (Molten nylon held under pressure in an atmosphere of steam in fact *depolymerizes* in a reversal of this condensation reaction.) Other examples of polymers obtained by condensation reactions are the saturated polyesters, polyurethane, and the old-established phenol- and urea-formaldehyde (which form three-dimensional networks). Three-dimensional networks can also be formed with polyesters if they are *unsaturated* and mixed with an unsaturated monomer, such as styrene, which polymerizes by addition, cross-linking to the points of unsaturation of the polyester.

These polymers are extensively used for structures made with glass-fibre reinforcement. Another important class of three-dimensional networks forming polymers is the group of polyethers termed epoxy resins or epoxides.

Many polymerizations proceed best in the presence of catalysts and in consequence the resulting material often contains catalyst residues. It is also important to remember that in commercial plastics the basic polymer is not the only constituent. Apart from the catalyst residues referred to above a commercial plastic will contain many additives such as anti-oxidants, colouring agents, plasticizer molecules (small molecular weight additives which affect the mechanical properties) as well as components required by the chemist to stop the chain growing. The details of the composition of a commercial plastic are commonly kept secret but they may nevertheless play a vital part in determining its properties. Examples are to be found in, for example, the textile industry, where commercial acrylic fibres differ considerably from one another although they are all nominally polyacrylonitrile.

Nature herself feels free to impose secrecy as regards the composition of some of her polymers and one of the most interesting fields of polymer research today is that of bio-polymers, where the techniques of the explorer are as important for the researcher as those of the polymer chemist. Such familiar materials as hair, leather, skin and bone are by no means fully understood.

1.2. The main chain

When a monomer polymerizes it will only yield a useful polymer if it does so in the form of a long chain. Ring compounds of low molecular weight exist but we are here mainly concerned with the properties of long-chain polymers—ones in which there are hundreds or thousands of repeat units before the end of the chain, a branch or a cross-link occurs. In linear polyethylene, for example, the molecular weight may be as high as 1 000 000, that is, the chain consists of some 70 000 CH_2 repeat units. Where the polymer cross-links to itself or, as in polyester resins, to another polymer, the term *molecular weight between cross-links* is used. It is self-

explanatory. In branched polymers such as the older, high-pressure, polyethylene the molecular-weight between side chains is relevant. It may be as low as 500 (3 branches per 100 carbon atoms) in high-pressure polyethylene, which in consequence has a lower density than its linear brother—high-density polyethylene, which has a molecular weight between branches approaching 3000. In cross-linked thermosets like epoxy resins the molecular weight between cross-links is about 500, while in rubbers it is very much greater (of the order of 10 000).

The value of molecular weight determined for any given polymer depends upon the method used. We cannot in fact count the number of monomer units in a chain and we must remember that, even if we could, this number would be very unlikely to be the same for all chains. The term used for this is *polydispersity* and it is described by parameters derived from the statistics of the method used for molecular weight determination.

Any frequency distribution such as that schematically shown in Figure 1.2 can be described by the moments $\bar{\mu}_p = \sum x^p f(x)$, the first four of which are commonly used in statistics. In the language of polymers the first moment \bar{M}_n , the

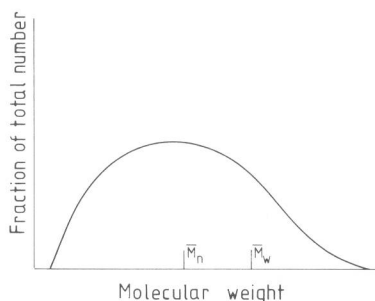


Figure 1.2. A schematic molecular weight distribution, showing the relation between M_n and M_w .

mean, is denoted by $\bar{M}_n = \sum M_i N_i / \sum N_i$, where N_i is the number of molecules of molecular weight M_i . Such averages are found from techniques which effectively count the *number* of molecules in a given mass or volume, such as end group analysis or studies of osmotic pressure. Other methods such as light scattering give weight averages, defined as $\bar{M}_w = \sum N_i M_i^2 / \sum N_i M_i$. This average is related to the second moment \bar{M}^2 of the distribution by the equation $\bar{M}^2 = \bar{M}_w \bar{M}_n$. The ratio \bar{M}_w / \bar{M}_n is commonly used as a measure of the dispersity of the molecular weight distribution. It must be greater than unity unless all the molecules are of equal length, as is easily seen. For $\bar{M}_w = \bar{M}^2 / \bar{M}_n$, and $\bar{M}^2 - (\bar{M}_n)^2$ is the variance $= \sigma^2$, where σ is the standard deviation. This is zero only if the distribution is monodisperse, that is, all molecules are of the same size, and we have $\bar{M}_w / \bar{M}_n = \bar{M}^2 / (\bar{M}_n)^2 = 1 + (\sigma / \bar{M}_n)^2$, which is ≥ 1 .

For example, the two types of linear polyethylene Rigidex 50 and Rigidex 25 (in the USA, Marlex) have widely differing M_n and M_w :

Polymer	M_n	M_w	M_w/M_n
Rigidex 50	6990	113 000	16.2
Rigidex 25	12950	98 800	7.6

Flory (1953) defines higher averages \bar{M}_z and \bar{M}_{z+1} as $\sum N_i M_i^3 / \sum N_i M_i^2$ and $\sum N_i M_i^4 / \sum N_i M_i^3$ respectively. These are related to the third and fourth moments of the distribution by the equation $\bar{M}^3 = \bar{M}_z \bar{M}_w \bar{M}_n$ and $\bar{M}^4 = \bar{M}_{z+1} \bar{M}_z \bar{M}_w \bar{M}_n$ respectively. (Statistical terms such as variance, skewness and kurtosis, though easily defined in terms of the above molecular weight averages, are not usually employed in polymer science.)

The viscosity average molecular weight is defined (Flory) as

$$\bar{M}_v = \left(\frac{\sum N_i M_i^{1+a}}{\sum N_i M_i} \right)^{1/a}$$

where $0.5 < a < 1$, and a is the coefficient in the expression for intrinsic viscosity, $[\eta]$, defined in Chap. 6. $[\eta] = KM^a$.

The full amount of information contained in the molecular weight distribution is of course not to be described by one or two averages, the complete set of moments being required. In practice \bar{M}_w and \bar{M}_n are usually sufficient except where details of the tails of the distribution are needed. Examples of this are in studies of crystallization and the deformation behaviour of polymers.

When this is the case methods which give the entire distribution rather than some of the averages referred to above must be used. A device in common use is the gel permeation chromatograph (GPC), although any technique which employs a measure that is dependent upon molecular weight, such as viscosity, will give information. Recent studies on extensional flow suggest that measurement of the viscosity in such flows may contain information on the molecular weight distribution not easily obtained by other means.

Modification of the GPC to allow preparation of well defined molecular weight fractions is a refinement of value, for example in studies of crystallization. Further details of the GPC can be found in the review by Johnson & Porter (1970).

1.3. Main chain bond energies

There are three quantities of significance to the understanding of mechanical properties. One is the potential energy and stiffness of the primary main chain bond, that is, its behaviour under a direct pull when the chain is fully extended. The second is the size and shape of the potential energy well that determines bond

rotation, for without rotation the polymer chains would behave as rigid rods and rubbers, for example, would not exist. The first property, the resistance to direct pull, determines of course the ultimate strength of the polymer in extended chain form. Failure of the chain links is called *scission* and it can be caused not only by strain but also by chemical means.

The third property of a polymer which affects its mechanical behaviour is the between-chain potential energy. This is some orders of magnitude less than the primary bond energy and, as mentioned above, is responsible for the bulk modulus and bulk cohesion of the polymer.

The interactions involved in bond-length and bond-angle deformation are usually small, and details of the deformation mechanism are ignored in favour of a simple Hookean spring model with a force constant k derived from infra-red and Raman spectra. Typical values of the force constants are given in Table 1.2.

Table 1.2. Force constant k in the expression $V = \frac{1}{2}k(\Delta s)^2$.

Mode	k (N m ⁻¹)
C-H stretch	479
C-C stretch	450
C-C-C bend	100
H-C-H bend	46
Rotation around C-C bond	9

After McCullough (1974)

These figures in Table 1.2 are derived from spectroscopic studies except for the last, which is discussed later.

Many calculations have been made of what is termed the chain modulus from the force constants such as those in Table 1.2. Results have been derived for the modulus of the polyethylene chain (which, because of the smallness of the unit cell, should be the largest chain modulus available) varying from 256 GPa to as high as 380 GPa. Measured values at present indicate that the chain modulus of polyethylene is certainly higher than 280 GPa. If we compare this modulus with the typical bulk modulus of a polymer—about 5 GPa—it is clear that the forces opposing extension, whether by bond stretching or bond bending, in any one chain are considerably greater than the forces which hold one chain to the next. It is quite justifiable therefore to picture polymers as made up from stiff but flexible chains freely sliding among their neighbours and constrained only by cross-links or entanglements—unless, of course, strong lateral forces also exist, such as the hydrogen bonds in polypeptides or polyamides, which tend to hold neighbouring chains together.

1.4. Rotation about bonds

In the calculation of moduli, whether the 'chain' modulus or the bulk modulus, it has been assumed that the displacements are small enough for a Hookean spring to be the model for the interaction. The Hookean spring model is, however, inappropriate for description of the rotation of molecular groups about bonds (Figure 1.3). Such rotations are commonly described in terms of a potential energy function possessing a number of minima (Figure 1.4).

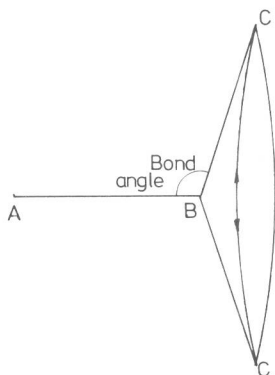


Figure 1.3. The bond-angle cone: atom C may move over the cone centred on atom B.

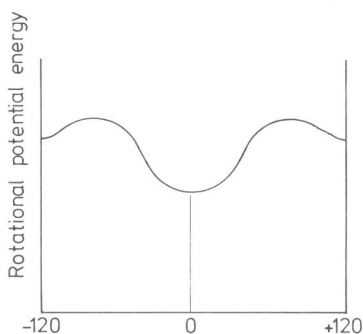


Figure 1.4. The potential 'wells' available to bonds in rotation.

The deepest 'energy well' in a symmetrical polymer such as polyethylene corresponds to the chain configuration in which the atoms of the side groups are as far apart from each other as possible. This gives the *planar zigzag* chain configuration and this is termed the *trans* form. Subsidiary minima which occur at angles of rotation $\pm 120^\circ$ from the *trans* form are called *gauche*. This of course implies that the minimum energy configuration of an isolated chain is the

extended planar zigzag if the polymer is a symmetric one, for example polyethylene, polyvinylchloride or polytetrafluoroethylene. The actual configuration taken up in a solvent, in the liquid or in the solid, will, however, depend upon the sum total of all the interactions whether intrachain or interchain rather than upon the nearest neighbours only. It will also depend upon the temperature. The equilibrium *trans* form may not therefore always occur and, as the temperature is raised, so the other configurations become more probable; so also does the difference between rotational energy levels become small enough in comparison with thermal energy for the rotation to be considered as free on the surface of the bond angle cone and even, in the limit, to be considered as random or Gaussian. This change of properties of a chain from the restricted rotations imposed by energy barriers to the freedom of unrestricted rotation is reflected in the mass by the phenomenon of the glass-to-rubber transition or glass transition as it is commonly termed. This is discussed more fully in Chap. 3. The temperature at which this freedom of the chains to take up any configuration allowed by the bond angle cone occurs will depend upon the chemical composition of the polymer, which, in turn, determines the depth and shape of the energy wells governing the probability of any configuration through a Boltzmann factor. Restriction of the rotation to the surface of the bond angle cone (Figure 1.3) does not in fact alter the 'Gaussian' chain model appreciably since an 'equivalent random link' may always be found, whatever the restrictions on bond angle. This may be done by defining $n_r = R_m^2 / \overline{r_m^2}$ and $l_r = \overline{r_m^2} / R_m$, where n_r is the number of links of length l_r in the equivalent random chain and R_m and $\overline{r_m^2}$ are, respectively, the fully extended and the mean square length of the real chain. The meaning of these terms will be made clearer in Chap. 6.

Detailed analysis of the local bond structure is required when defects are being considered, such as jogs, folds and kinks in the solid polymer. These are defined in the following way (Figure 1.5).

Jogs occur when, over a small number of monomer units, the linear chain is displaced laterally but continues in the same direction as before. If the direction is reversed the defect is called a *fold*, while if the defect causes neither displacement nor reversal of direction but only a local disordering of the zigzag configuration it is called a *kink*.

There have been many studies of the energetics of such chain defects both analytically and experimentally. Some of them are held to be responsible for relaxation phenomena at low temperatures while folds are of great importance in the crystallization of polymers.

Finally, the energy barriers to rotation about primary main chain bonds must play a part in determining the freedom of chains to slide relative to each other, both in the crystalline state and in the amorphous. Chains are not really cylinders of uniform diameter and material, and so in longitudinal motion relative to another chain (as in a crystal) a combination of oscillation and translation must occur. Similarly, where bending takes place, the restrictions on rotation of one chain link relative to its neighbour imply a coupling of bending

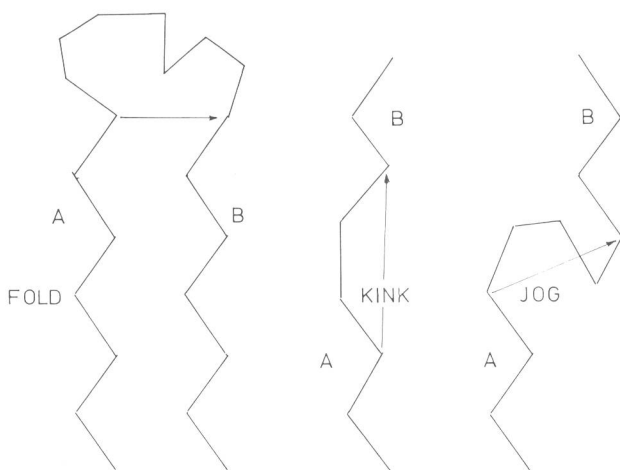


Figure 1.5. Definitions of 'fold', 'kink', and 'jog' illustrated for a simply polymer chain.

and rotation at the level of the chain link. The above effects are likely to be important only at or below the glass transition temperature but they do not seem to have been analysed to date, nor is there yet a molecular interpretation of the frictional forces between chains arising from these and other causes.

Further reading

A good general introduction to polymers is the book by Young (1981) but the most comprehensive account is still to be found in Flory (1953).

Aspects of polymer science such as viscoelasticity and the statistical mechanics of long-chain molecules are discussed in Chaps 3 and 6 and references for further reading given there.

There are several journals devoted to polymer science. Some, such as *Advances in Polymer Science* (Springer) and *Progress in Polymer Science* (Pergamon) consist of review articles on various aspects of the subject. Some of these reviews will be referred to in later chapters.