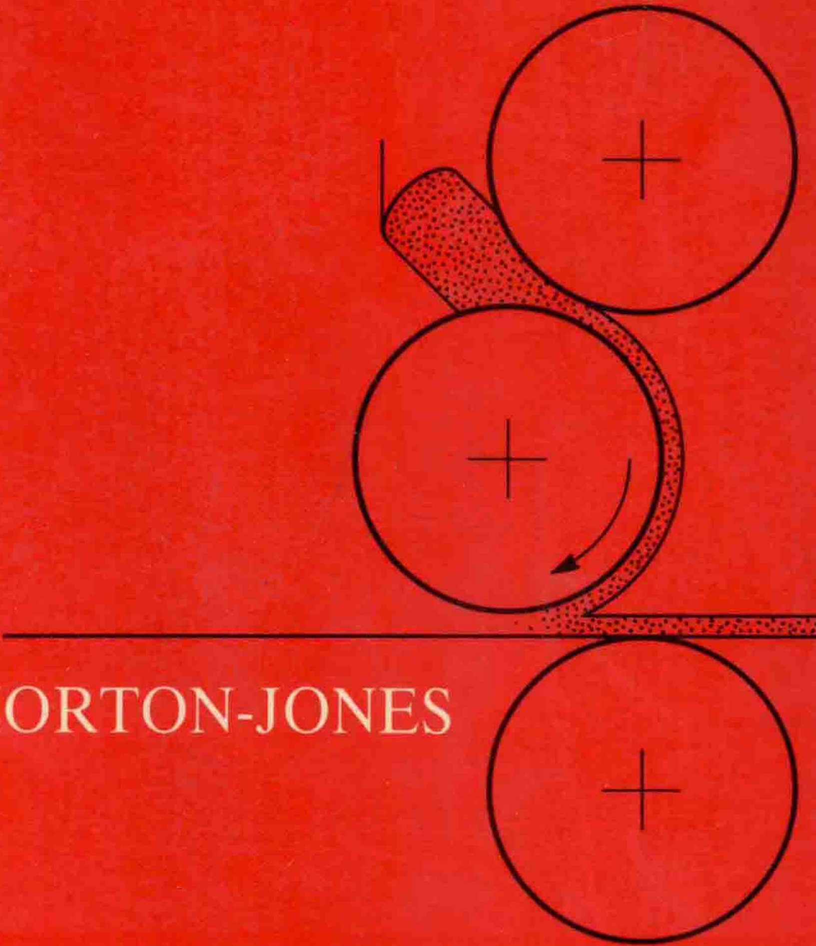
POLYMER PROCESSING



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CHAPMAN AND HALL

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Preface

It can be stated with some justification that polymers, because of their mainly synthetic origins, are important because of their applications, perhaps more than in the case of more familiar and conventional materials such as metals and wood, which would exist apart from their use in human activities. The majority of polymers have been synthesized under the impetus of requirements for new and improved properties. The preparative routes to new polymers and blends, and the exploration of their structures and properties constitute absorbing subjects for study, but it is the final application of these materials in real, commercial products that provides the driving force for such developments.

In recent years a number of excellent books have appeared which deal with the chemistry, structure, properties and engineering aspects of polymers. The processing of polymers, as products of the chemical industry, into engineering and consumer goods has received much less attention. There are some valuable texts for individual processes, especially the extrusion and injection moulding of thermoplastics, but others are less well served. This book provided a review of all the important processing routes for transforming polymers into products.

The custom of using the opening chapter of a polymer book to tell the reader what a polymer is has been continued. However, the approach here is rather less chemical than usual. The reader may be an established or student engineer, who will not require detailed chemistry, or may be a chemist, in which case he or she will already possess the necessary knowledge or have ready access to it. More relevant is the characteristic morphology of polymer structures and its influence on their physical behaviour. This has its roots, of course, in the underlying chemistry, and to this extent some chemical understanding is inescapable. Nevertheless, the emphasis is on morphology and the dependence of physical properties upon it.

The second chapter deals with the relationship between processing routes and the rheology of polymers, and also with some aspects of heat transfer. The purpose of the chapter is to relate the behaviour of these materials to their processes in a simple manner which avoids the complexity of more mathematical and specialist texts.

The other twelve chapters are devoted to separate areas of processing technology. The processing methods for thermoplastics, thermosets, rubbers, fibre reinforced plastics and plastisols are described. Throughout, the processes are seen from the standpoint of the processor rather than that of the engineer; although the processing plant is described, the main interest is in how the plastics or rubber material behaves. The book is thus about polymer processing, and not about the construction of the processing plant. This treatment necessitates discussions of some of the materials, because of the way materials and processes interact; however the reader seeking comprehensive treatment of materials should refer to specialized texts.

Although the text is a review of the whole field of polymer processing, the specialist in a particular field should find the account of his own subject a useful summary, perhaps with helpful cross references to related or unfamiliar areas of processing. For example, the treatment of injection moulding in a general work of this length cannot hope to match that to be found in a book devoted entirely to that subject, but the inclusion of the derivative processes such as foam-cored moulding and RIM provides a concise summary of the whole field of injection moulding processes.

The aim has been to provide an outline account of all the major processing routes, for thermosets and rubbers as well as the more familiar thermoplastics. In some, a more quantitative approach has been adopted because the importance of the process has meant that such analysis has been developed, e.g. extrusion, which is seminal to most thermoplastics processes. In other processes a more descriptive account reflects the working practice to be found in the industry.

The book is aimed at undergraduate and postgraduate students who require a general overview of the field of polymer processing in a single easily assimilated volume. It will also be of value to the industrial processor and engineer seeking information about a variety of processes, and as a reference source for the general reader.

I have based this text on the course on processing which I taught as part of the MSc in Polymer Science and Technology (now superseded) at Lancaster University. In this course I was able to draw on the accumulated experience of 30 years' employment in the development of new and improved products in a variety of processing industries, supplemented by the production more recently of a series of intensive case studies of polymer applications. I have tried to pass on something of the endless appeal of these process industries. There is an infinite variety of detail to be tuned for each individual product; no two require exactly the same conditions. Research and Development in these industries requires the matching of the process to the properties of the material, often leading to a modified or even a new process. If this book helps to open the door to this fascinating world it will have succeeded in its purpose.

In conclusion, the acknowledgements: first to my daughter Gillian for her splendid artwork for all the figures, as original drawings; secondly to Mark Kimpton and Barry Statham of Trowbridge College for reading the manuscript and offering helpful suggestions for its improvement, and finally to my wife Jo for her patience through the seemingly endless evenings and weekends when I was hunched over the word processor.

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Lancaster
April 1989

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1

The nature and origins of polymers

1.1 Introduction

If we compare *polymers* like *polythene* and *nylon* with the more traditional materials used by engineers we find at once several important differences. A few simple tests soon show that polymers

- have lower strengths and stiffnesses
- often have temperature limitations in service – hot or cold
- mechanical tests, e.g. tensile tests, show that they 'creep' i.e., their properties are time-dependent, and this is their most significant mechanical characteristic.

The features listed above are drawbacks in comparison with metals, wood, ceramics, etc. Obviously, polymers must possess advantages in compensation because they are used in vast and increasing quantities, already exceeding and replacing more traditional materials in many key areas: thus by 1981, volume consumption of plastics exceeded that of steel at around 2000×10^3 m^3 p.a., and was increasing while steel consumption declined. What are the advantages offered by these remarkable materials which results in such a rapid expansion in their use? The most important attractions are:

- Polymer materials, both plastics and rubbers, are readily mouldable, which allows easy production of complex shapes with a minimum of fabrication and finishing;
- They have low densities, a property which leads to low weight products;
- They are resistant to corrosion and to chemical attack;
- They are usually electrical and thermal insulators;
- In many applications, the inherent flexibility of polymers is useful – this is especially true for rubbers;
- Although the absolute strength and modulus values of polymers are low, the specific values per unit weight or volume are often favourable. Hence the use made of speciality polymer materials in aerospace applications;
- The special properties of rubbers are elasticity and damping qualities which are applied in springs and energy-absorbing mountings.

In the early days of plastics and rubbers, the special properties of these materials were ill understood and many early failures occurred because designers did not recognize the significance (or even, often, the existence) of the time-dependent nature of these properties. Nowadays, these properties are well defined and are applied in the design of components to ensure good performance and a long service life. Also, many new types of high-performance polymers have been developed in recent years, which overcome the deficiencies of early types. These are the *engineering polymers*, which offer superior physical properties and enhanced temperature tolerance. Thus, the ready mouldability and insulating and corrosion resistant qualities of polymers can be utilized in more demanding applications.

In this chapter, we shall see how the special and characteristic properties of polymers result from their *chemical* and *morphological* structures; we shall also see the main petrochemical routes in the manufacture of polymers themselves. These then are the raw materials for our main concern, which is the processing of polymer materials into products for engineering or consumer use.

1.2 Nature of polymers

1.2.1 *What is a polymer?*

Essentially, a polymer is a substance whose molecules form long chains, usually several thousand atoms long (Fig. 1.1). The word 'polymer' means 'many units'. Polymers are characterized, and differ from one another, through the chemical and physical nature of the *repeating units* in the chains. The main interest today is in synthetic polymers such as polyethylene, nylon, synthetic rubbers, melamine laminates, etc. However, there are important naturally-occurring polymers which give a clue to some of the special features of polymeric materials. For example, cellulose is a polymer made by plants in which the long chain-like molecules are linearly aligned to give the plant skeleton linear strength combined with lateral flexibility. This allows the plant to grow tall but to yield without snapping to lateral forces, such as bending in the wind.

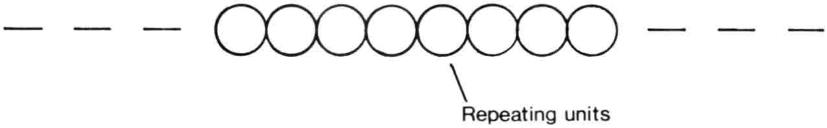
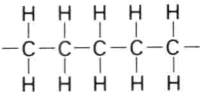


Fig. 1.1 Polymer molecules form long chains.

1.2.2 *Some polymer dimensions*

What are the actual dimensions of, for example, a polyethylene long-chain molecule of, say, 1000 units (i.e., there are 1000 carbon atoms joined in a continuous chain)? The chemical formula is shown in Fig. 1.2. In fact, this depiction, though useful to the chemist, does not accurately display the structure of a polyethylene molecule. In reality, the molecule exists, of course, in three dimensions, and the four bonds connecting each carbon to its neighbours are angled symmetrically towards the corners of a tetrahedron, at 109.5°. This can be represented in a three-dimensional drawing (Fig. 1.3).



$$-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-$$

Fig. 1.2 Chemical formula for polyethylene.

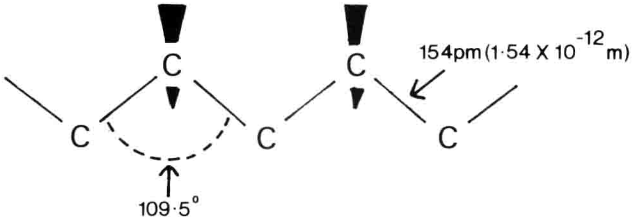


Fig. 1.3 Three-dimensional structure of a polyethylene molecule.

Let us see how large this 1000-unit molecule is. The length of the C—H bonds is 154 pm (1.54×10^{-12} m). If the chain is fully extended linearly, this gives a molecular length of

$$999 \times 154 \times \frac{\sin 109.5}{2}$$

$$= 0.13 \times 10^{6} \text{ pm}$$
$$= 0.13\ \mu\text{m}$$
$$= 1.3 \times 10^{-5} \text{ m}.$$

It is difficult to imagine the physical reality of these dimensions. We know the molecules are elongated, but how can we describe their 'aspect ratio'? A useful analogy is that their *L*/*D* (or aspect) ratio is similar to that of a piece of ordinary string about 2 m long. Thus, they are very long and thin. The C—H bond is fixed in length and angle, but it can rotate. The result is that the long, thin chains are flexible. They readily become convoluted and entangled with one another, and as we shall see shortly, their basic physical properties derive from this entangled mass. To continue the string analogy, a mass of polymer resembles an entangled ball or web made up of many pieces of string, rather than a box of matches. Such a ball of string would contain pieces of different lengths, and analogously the polymer mass has molecules containing different numbers of units.

1.2.3 *Molar mass of polymers*

In simple materials like salt or phenol or alcohol, all the molecules are the same and have a characteristic *molar mass* (sometimes called by the old name *molecular weight*).

Because a polymer sample contains molecules of different sizes we have to use average values for molecular weight. There is a distribution of molecular sizes and statistical methods are used to express average molar mass. The two most important averages are the *number average molar mass*, M_n and the *weight average molar mass*, M_w.

The number average compares the *total length of polymer chain* with the *number* of individual chains present. The weight average compares the *total length of chain* with the mass fraction of individual chains. Figure 1.4 shows where these two values lie for a polymer with a normal distribution of molar mass. Often, the distribution is asymmetric, and may be broader than shown in Fig. 1.4. Figure 1.5 shows some other common forms of distribution.

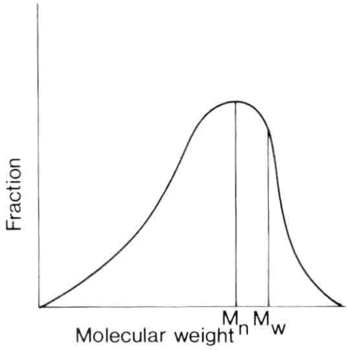


Fig. 1.4 Typical normal distribution of molar mass.

The molar mass (or molecular weight, which is the more traditional term) of a particular grade of polymer is an important consideration for processing and performance in service. To define this properly, we need to know not only its value, i.e. whether it is a high or low molecular weight grade, but also the molecular weight spread.

The number average and weight average molar masses can be expressed

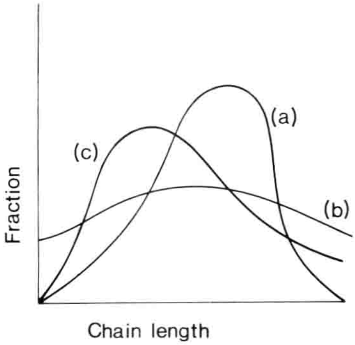


Fig. 1.5 Examples of molar mass distributions: (a) normal distribution; (b) symmetric, broad distribution; (c) asymmetric distribution, a common type.

algebraically as follows. For the *number average molar mass* M_n we find the total mass of polymer chain present and divide this by the number of chains present. Consider an individual chain of length i. Its molar mass is M_i and chains of this size make up a fraction X_i of the total chains present. If we now allow for all values of i, the sum of their masses and their fractions is M_n

$$M_n = \Sigma\, M_i\, X_i.$$

But the fraction X_i is also the number of i-sized chains related to N, the total number of chains. If there are N_i chains of size i

$$X_i = N_i/N$$

and therefore $$M_n = \Sigma\, \frac{M_i N_i}{N}.$$

But $N = \Sigma\, N_i$, i.e. the sum for all values of i, and so

$$M_n = \Sigma\, \frac{M_i N_i}{\Sigma\, N_i}.$$

The number average molar mass thus takes account of the *number* of chains, without regard to their various sizes.

Weight average molar mass, M_w, also uses the total mass (or weight) of the chains, but now, for each individual chain, the fractional *mass*, w_i is used.

$$M_w = \Sigma\, M_i\, w_i.$$

The ratio M_w/M_n is the *dispersivity*, and is a measure of the molecular weight spread. It is unity only when all the polymer chains are the same length, i.e., the polymer is said to be monodisperse. Normal commercial grades of polymer are never monodisperse, but show a spread of molecular weight which varies according to method of manufacture and finished product and processing needs. The dispersivity of so-called 'living polymers', made by anionic polymerization, is often nearly 1, and these polymers are important as speciality products.

1.2.4 *Determination of molar mass*

Many methods exist for determining one of the average values for molar mass. It is not our purpose to deal with them in detail here, but one which is widely used is outlined below, because it illustrates how simple determinations can be used to find a fundamental polymer property. The method uses *solution viscosity*. When a polymer is dissolved in a solvent, there is a noticeable increase in the viscosity of the solvent. The viscosities of pure solvent and solutions of known concentration can be measured by timing flow through a capillary tube. If the flow time for the solvent is t_o and for a solution of concentration C is t, a number of values can be calculated.

Relative viscosity $$\eta_r = \frac{\eta_{\text{solution}}}{\eta_{\text{solvent}}} = \frac{t}{t_o}.$$

Specific viscosity $$\eta_{sp} = \eta_r - 1 = \frac{t - t_o}{t_o}.$$

Reduced viscosity
(viscosity number) $$\eta_{red} = \frac{\eta_{sp}}{C}.$$

Inherent viscosity
(log viscosity number) $$\eta_{inh} = \frac{\ln \eta_r}{C}.$$

Intrinsic viscosity
(limiting viscosity number) $$[\eta] = \left[\frac{\eta_{sp}}{C}\right]_{C\to 0} = \left[\frac{\ln \eta_r}{C}\right]_{C\to 0}$$

The intrinsic viscosity is found by plotting η_{red}/C against C and extrapolating to zero concentration.

The molecular weight M is then found from the Mark–Houwink equation

$$[\eta] = KM^a.$$

K and a are experimentally determined constants which can be looked up in the literature and M is the *viscosity average* molecular weight, which lies between M_n and M_w.

1.3 Basic chemical types

Many chemical routes exist for the manufacture of polymers, and it is not our purpose here to describe them in detail. Instead the reader is referred to several excellent accounts in the bibliography at the end of the chapter. However, as an introduction for the non-chemical reader especially, the two most widely used manufacturing routes are outlined. These are *addition polymerization* and *step growth* (or *condensation*) *polymerization*.

1.3.1 *Addition polymerization*

The addition method for making polymers uses as starting material the monomer. As the name implies (one part), this is the small-molecule chemical which will eventually form the polymer by joining up into long molecular chains. The characteristic shared by all small molecules capable of forming polymers in this way is that they are chemically *unsaturated*. This means that they possess a *double bond* between two of their carbon atoms, as shown for ethylene in Fig. 1.6. Although this depiction might suggest that two carbons joined thus are more strongly bonded than a pair joined by a single bond, the opposite is in fact the case. The electronic configuration in a double bond is less favourable and is at a higher energy level than it is in a single bond, with the consequence that a double bond in a molecule is a point vulnerable to chemical attack. This is what happens when an unsaturated monomer is converted to a polymer. The mechanism of the attack involves *homolytic scission* of the double bond to form *free radicals*, i.e., the electron pair comprising the bond divides. The overall effect is for the double bond to be replaced by a single one and the molecule to extend itself, eventually to form a polymer. Figure 1.7 shows the overall result.

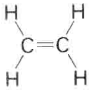


Fig. 1.6 Chemical structure of ethylene, showing double bond.

$$H_2C{=}CH_2 \longrightarrow -CH_2{-}CH_2-$$

Fig. 1.7 Polyethylene forms from ethylene monomer by opening of the double bond.

Ethylene is chemically the simplest of a range of addition polymers. As we have seen, its chemical formula is $CH_2{=}CH_2$. If one of the hydrogen atoms is replaced by another chemical group a different polymer results. We can use the symbol R to represent the replacement group, and the general formula becomes $CH_2{=}CHR$. Some examples are given in Table 1.1.

One or two slightly more complex cases may be mentioned here, to show the great versatility of this method for producing polymers. For instance, if the original monomer molecule contains two double bonds, the resulting