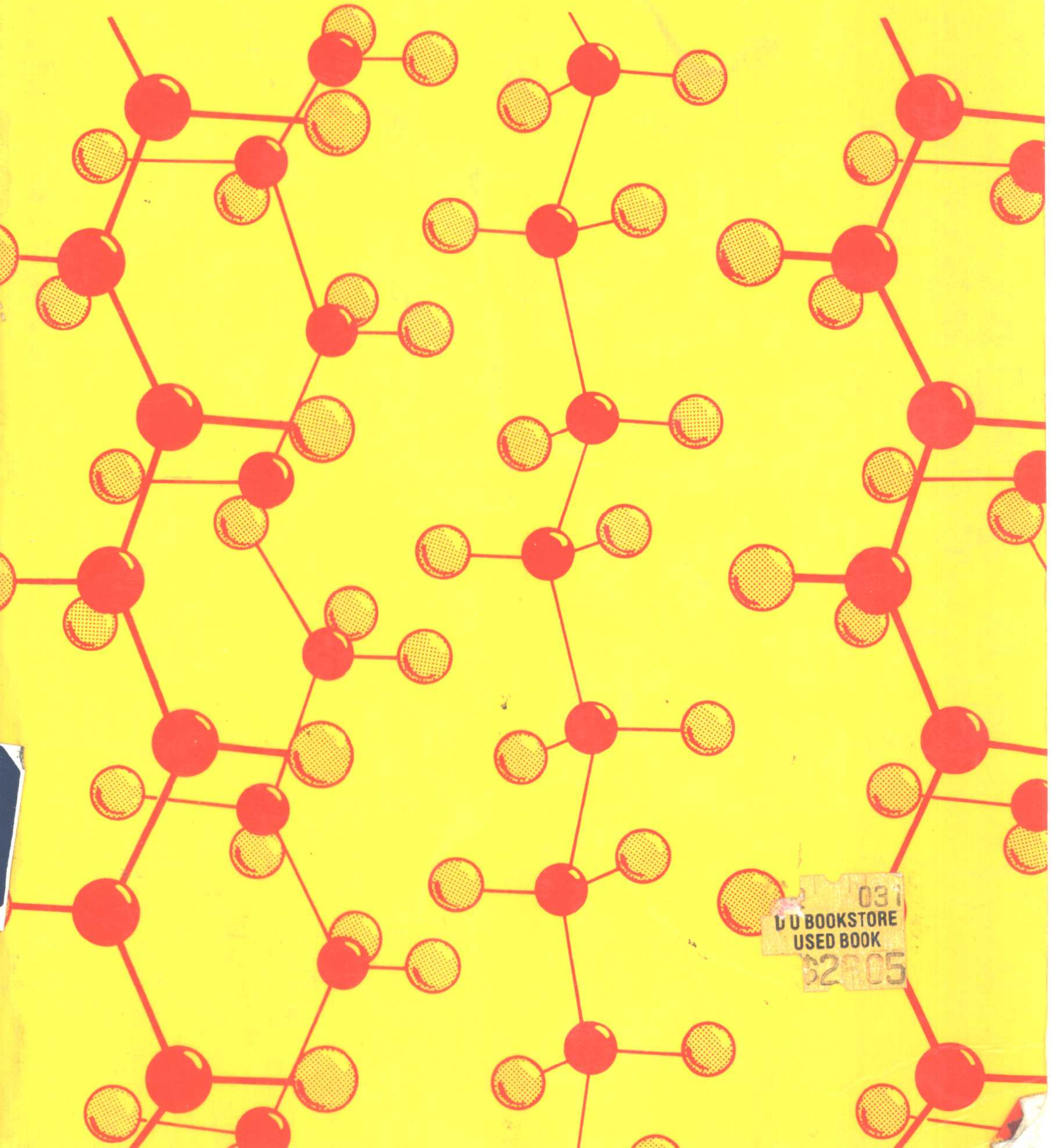
Introduction to POLYMERS

R. J. Young



Introduction to Polymers

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Preface

Polymers are a group of materials made up of long covalently-bonded molecules, which include plastics and rubbers. The use of polymeric materials is increasing rapidly year by year and in many applications they are replacing conventional materials such as metals, wood and natural fibres such as cotton and wool. The book is designed principally for undergraduate and postgraduate students of Chemistry, Physics, Materials Science and Engineering who are studying polymers. An increasing number of graduates in these disciplines go on to work in polymer-based industries, often with little grounding in Polymer Science and so the book should also be of use to scientists in industry and research who need to learn about the subject.

A basic knowledge of mathematics, chemistry and physics is assumed although it has been written to be, as far as is possible, self-contained with most equations fully derived and any assumptions stated. Previous books in this field have tended to be concerned primarily with either polymer chemistry, polymer structure or mechanical properties. An attempt has been made with this book to fuse together these different aspects into one volume so that the reader has these different areas included in one book and so can appreciate the relationships that exist between the different aspects of the subject. Problems have also been given at the end of each chapter so that the reader may be able to test his or her understanding of the subject and practise the manipulation of data.

The textbook approaches the subject of polymers from a Materials Science viewpoint, being principally concerned with the relationship between structure and properties. In order to keep it down to a manageable size there have been important and deliberate omissions. Two obvious areas are those of polymer processing (e.g. moulding and fabrication) and electrical properties. These are vast areas in their own right and it is hoped that this book will give the reader sufficient grounding to go on and study these topics elsewhere.

Several aspects of the subject of polymer science have been updated compared with the normal presentation in books at this level. For example, the mechanical properties of polymers are treated from a mechanistic viewpoint rather than in terms of viscoelasticity, reflecting modern developments in the subject. However, viscoelasticity being an important aspect of polymer properties is also covered but with rather less emphasis than it has been given in the past. The presentation of some theories and experimental results has been changed from the original approach for the sake of clarity and consistency of style.

I am grateful to Professor Bill Bonfield for originally suggesting the book and for his encouragement throughout the project. I am also grateful to my other colleagues at Queen Mary College for allowing me to use some of their material and problems and to many people in the field of Polymers who have contributed micrographs. A large part of the book was written during a period of study leave at the University of the Saarland in West Germany. I would like to thank the Alexander von Humboldt Stiftung for financial support during this period. The bulk of the manuscript was typed by Mrs Rosalie Hillman and I would like to thank her for her help. Finally, my gratitude must go to my wife and family for giving me their support during the preparation of the book.

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October 1980

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1 Introduction

1.1 Polymers as materials

Polymer Science is a relatively young discipline which developed rapidly following the recognition 30 or 40 years ago that polymers are made up of long molecules. Although it is now widely accepted that these materials contain macromolecules it was only with the pioneering work of people like Staudinger, Carothers and others that the chemical aspects of Polymer Science were established on a firm scientific footing.

Polymers have been around in a natural form since life began and naturally occurring biological polymers play an extremely important role in plant and animal life. Natural rubber has been known and used in practical applications for over 100 years and its unusual properties were studied by Scientists in the last century. This book is concerned mainly with synthetic polymers, the use of which has increased enormously over the past few decades. This has been due principally to their relative cheapness, ease of fabrication, low density, chemical inertness, and high electrical resistivity, but also to other factors. For example, polytetrafluoroethylene has a very low coefficient of friction and also very good 'non-stick' properties when used as a lining for cooking utensils. Poly(methyl methacrylate) has good optical clarity and superior mechanical properties to glass. It is therefore used in aeroplane windows where its lightness is an added bonus.

Polymers are now accepted as materials in their own right along with more conventional materials such as metals and ceramics. The study of the structure and properties of materials is known as *Materials Science*. This has developed relatively recently from metallurgy, which is only concerned with metals, to encompass now all materials used in practical or engineering situations. This book adopts a Materials Science approach to the study of polymers and is concerned principally with the relationship between structure and properties in these materials.

1.2 Basic definitions and nomenclature

In the discussion of the structure and properties of polymers there are several important words and concepts used which need to be defined. Most of these are discussed in detail when they are introduced, but at this stage there are several terms that must be defined.

A *polymer* is a long molecule which contains a chain of atoms held together by covalent bonds. It is produced through a process known as *polymerization* whereby *monomer* molecules react together chemically to form either linear chains or a three-dimensional network of polymer chains. The main characteristic of the chain is that the chemical bonding is strong and directional along the chains, but they are only bonded sideways by weak secondary van der Waals bonding or occasionally with hydrogen-bonding.

If only one type of monomer is employed to form the polymer the resulting molecule is called a *homopolymer.* Often superior properties are obtained by using different types of monomer species. In this case the polymer is termed a *copolymer.*

The naming of polymers or envisaging the chemical structure of a polymer from a knowledge of its name is an area which often gives students a great deal of difficulty. This problem is compounded by the variety of trade-names which are also used to describe particular polymers. In the case of addition polymers or in other cases where a single monomer species is used the prefix 'poly-' is added to the name of the monomer. So that ethylene polymerizes to give polyethylene, styrene to give polystyrene and methyl methacrylate forms poly(methyl methacrylate). In the last case brackets are used because the monomer name consists of two words. Some condensation polymers are made by reacting two types of monomer together which form an alternating sequence in the polymer chain. The polymer formed from the reaction between ethylene glycol and terephthalic acid is then termed poly(ethylene terephthalate). Attempts have been made to unify the nomenclature of polymers rather than using these trivial names. However, the trivial names are still widely used especially for simple polymers. The number of polymers in this book referred to by their chemical name has been kept as small as possible and it is hoped that the student will be able to recognize the more important polymers very quickly without being confused by a large number of different names.

1.3 Molecular architecture and classification of polymers

The main feature which sets polymers apart from other materials is that polymer samples are made up of long molecules. A typical sample of polyethylene may have molecules which contain an average 50 000 atoms and would be 25 000Å long. The presence of these macromolecules has a dominant effect upon the properties of the polymeric material. There can be a considerable variation in the architecture of the individual molecules in different polymer samples. Although by definition polymer molecules are long they can be linear, branched or even in the form of a three-dimensional network as shown in Fig. 1.1. The particular type of architecture the molecules possess controls the properties of the material.

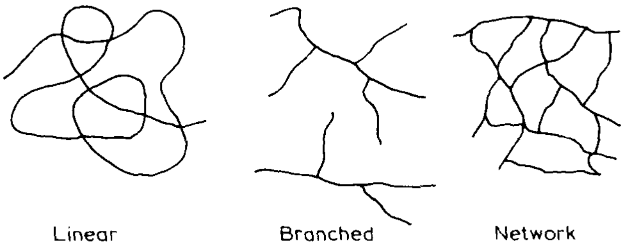


Fig. 1.1 *Schematic representation of different types of polymer molecules.*

Any attempts to classify polymers into different categories tend to be somewhat arbitrary. One useful way is to put them into groups displaying similar properties which also has the advantage reflecting the underlying molecular structure. This classification is outlined in Fig. 1.2 where they are separated into three groups; *thermoplastics*, *rubbers* and *thermosets*. In addition thermoplastics are separated into those which are either crystalline or non-crystalline (amorphous).

Thermoplastics, which are often referred to just as 'plastics' are linear or branched polymers which can be melted upon the application of heat. They can be moulded and remoulded using conventional techniques and now make up the largest bulk of polymers used. Thermoplastics can be sub-divided into those which crystallize on cooling and those which do not and are normally used as polymer glasses. The ability of the polymers to crystallize depends upon many factors such as the degree of branching and the regularity of the molecules. However, crystalline thermoplastics are invariably only partly (semi-) crystalline and do not crystallize completely when cooled from the melt.

Rubbers are materials which display elastomeric properties, i.e. they can be stretched easily to high extensions and will spring back rapidly when the stress is released. This extremely important and useful property is a reflection of the molecular structure of the polymer which consists of a lightly cross-linked macromolecular network. The molecules slide past each other on deformation, but the cross-links prevent permanent flow and the molecules spring back to their original position on removal of the

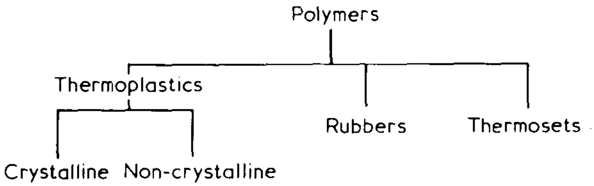


Fig. 1.2 *Classification of polymers.*

stress. The presence of the cross-links means that it is impossible to melt a rubber once it has undergone cross-linking.

Thermosets are heavily cross-linked polymers which are normally rigid and intractable. They consist of a dense three-dimensional molecular network and, like rubbers, degrade rather than melt on the application of heat. Common thermosetting polymers include phenol–formaldehyde or urea–formaldehyde resins and high-performance adhesives such as epoxy resins.

The chemical structure and uses of a variety of common thermoplastic polymers are listed in Table 1.1.

1.4 **Molar mass and degree of polymerization**

Since the characteristic properties of polymers depend intimately upon the size of the macromolecules present in the sample it is essential to have a method of describing their dimensions. This is normally done by quoting the *molar mass (M)* of the polymer which is simply the 'mass of one mole of the polymer' and so has units of g mol^{-1} or kg mol^{-1}. A *mole* of a substance being defined as 'the amount of that substance containing as many particles (i.e. polymer molecules) as there are atoms in 0.012 kg of carbon 12'. The term 'molecular weight' is often still used instead of molar mass, but this is not preferred because it can be somewhat misleading. It is really a dimensionless quantity, the relative molecular mass, rather than the weight of an individual molecule, which is of course a very small quantity ($\sim 10^{-20}$g).

An associated parameter which is often used to describe the size of a polymer molecule is the *degree of polymerization* (x) which is simply 'the number of chemical repeat units in the polymer chain'. It can be readily determined since

$$x = M/M_0 \tag{1.1}$$

where M_0 is the molar mass of the polymer repeat unit which can usually be taken as the molar mass of the monomer.

1.4.1 *Distribution of molar mass*

A normal polymer sample contains molecules with a variety of lengths and it is only possible to quote an average value of the molar mass. A typical distribution of molar mass is shown in Fig. 1.3. Often the exact form of the distribution is not known and it is conventional to describe it in terms of either a number average molar mass, $\bar{M}_n$ or a weight average molar mass, $\bar{M}_w$. Both of these parameters can be measured experimentally. In the definition of $\bar{M}_n$ and $\bar{M}_w$ it is envisaged that the distribution of molar mass

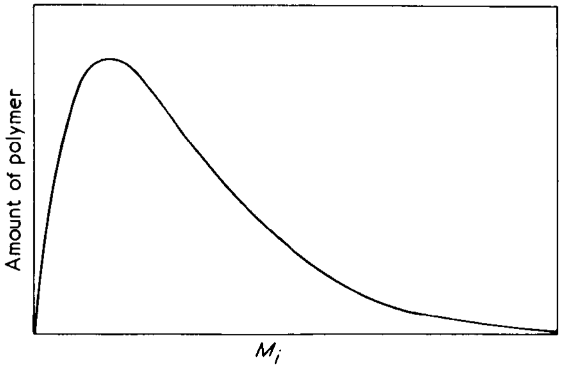


Fig. 1.3 *Typical molar mass distribution curve.*

can be split up into discrete fractions of molar mass M_i made up only of molecules which contain a discrete number of i repeat units.

(i) *The number average molar mass,* $\bar{M}_n$ is defined as 'the sum of the products of the molar mass of each fraction multiplied by its mole fraction'

$$\text{i.e.} \quad \bar{M}_n = \sum X_i M_i \tag{1.2}$$

where X_i is the mole fraction of molecules of length i, the ratio of the number of molecules of length i, N_i, to the total number of molecules, N. It follows therefore that

$$\bar{M}_n = \sum N_i M_i / N$$

$$\text{or} \quad \bar{M}_n = \sum N_i M_i \Big/ \sum N_i \tag{1.3}$$

It is often more convenient to deal in terms of mass fractions w_i rather than the numbers of molecules, the mass fraction w_i being defined as the mass of molecules of length i divided by the total mass of all molecules.

$$\text{i.e.} \quad w_i = N_i M_i \Big/ \sum N_i M_i \tag{1.4}$$

which can be written as

$$\sum (w_i/M_i) = \sum N_i \Big/ \sum N_i M_i \tag{1.5}$$

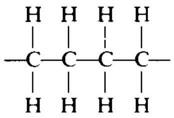
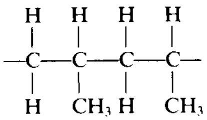
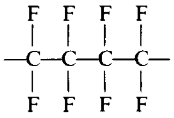
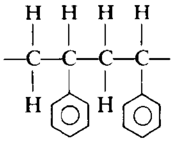
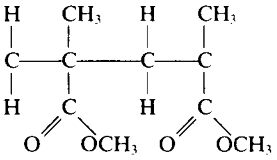
Combining Equations (1.3) and (1.5) gives $\bar{M}_n$ in terms of mass fractions as

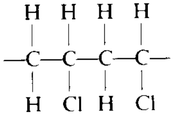
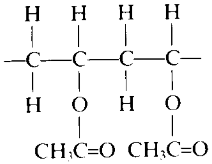
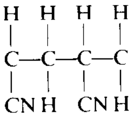
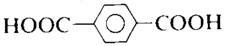
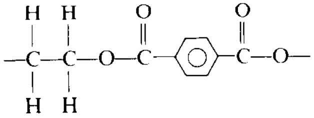
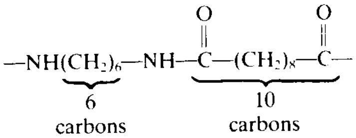
$$\bar{M}_n = 1 \Big/ \sum (w_i/M_i) \tag{1.6}$$

It is possible to define a number average degree of polymerization as

$$\bar{x}_n = \bar{M}_n / M_0 \tag{1.7}$$

TABLE 1.1 *Some common thermoplastic polymers*

Monomer	Polymer	Comments
Ethylene $CH_2{=}CH_2$	polyethylene (PE) 	Moulded objects, tubing, film, electrical insulation, e.g. 'Alkathene'.
Propylene $CH_2{=}CH(CH_3)$	polypropylene (PP) 	Similar uses to PE; lighter, stiffer, e.g. 'Propathene'.
Tetrafluoroethylene $CF_2{=}CF_2$	polytetrafluoroethylene (PFTE) 	Mouldings or film. High-temperature polymer. Excellent electrical insulator. Low coefficient of sliding friction. Expensive, e.g. 'Teflon', 'Fluon'.
Styrene $CH_2{=}CH(C_6H_5)$	polystyrene (PS) 	Cheap moulded objects. Polymerized with butadiene to make high impact polystyrene (HIPS). Expanded with pentane to make plastic foam.
Methyl methacrylate $CH_2{=}C(CH_3)COOCH_3$	poly(methyl methacrylate) (PMMA) 	Transparent sheets and tubing. More expensive than PS. Aeroplane windows, e.g. 'Perspex', 'Lucite'. Low-molecular-weight grade 'Diakon for transparent mouldings.

Vinyl chloride $CH_2=CHCl$	poly(vinyl chloride) (PVC)  $-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\overset{\text{H}}{\underset{\text{Cl}}{\text{C}}}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\overset{\text{H}}{\underset{\text{Cl}}{\text{C}}}-$	Gramophone records, water pipes, gutters etc. plasticised to make raincoats, garden hoses and orange squash bottles, e.g. 'Darvic', 'Welvic'.
Vinyl acetate $CH_3COOCH=CH_2$	poly(vinyl acetate) (PVA)  $-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\overset{\text{H}}{\underset{\substack{\text{O}\\ \text{CH}_3\text{C=O}}}{\text{C}}}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\overset{\text{H}}{\underset{\substack{\text{O}\\ \text{CH}_3\text{C=O}}}{\text{C}}}-$	Chewing gum, adhesives, surface coatings.
Acrylonitrile $CH_2=CHCN$	polyacrylonitrile (PAN)  $\overset{\text{H}}{\underset{\text{CN}}{\text{C}}}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}-\overset{\text{H}}{\underset{\text{CN}}{\text{C}}}-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}$	Textile fibres, e.g. 'Orlon', 'Acrilan'.
Ethylene glycol $HOCH_2-CH_2OH$ and terephthalic acid 	polyethylene terephthalate (PET) 	Textile fibres, e.g. 'Terylene'. Thin drawn film, e.g. 'Mylar', 'Melinex'
Hexamethylene diamine $H_2N-(CH_2)_6-NH_2$ and sebacic acid $HOOC-(CH_2)_8-COOH$	nylon 6.10  $-NH\underbrace{(CH_2)_6}_{\substack{6\\ \text{carbons}}}-NH-\underbrace{\overset{\text{O}}{\overset{\Vert}{\text{C}}}-(CH_2)_8-\overset{\text{O}}{\overset{\Vert}{\text{C}}}}_{\substack{10\\ \text{carbons}}}-$	Textile fibres, also moulded objects. Bearing and gear wheels.

(ii) *The weight average molar mass*, $\bar{M}_w$ is defined as 'the sum of the products of the molar mass of each fraction multiplied by its weight fraction, w_i'

$$\text{i.e.}\quad \bar{M}_w = \sum w_i M_i \tag{1.8}$$

and combining this equation with Equation (1.4) gives

$$\bar{M}_w = \sum N_i M_i^2 \Big/ \sum N_i M_i \tag{1.9}$$

which is an expression for $\bar{M}_w$ in terms of the numbers of molecules. As before, a weight average degree of polymerization can be given as

$$\bar{x}_w = \bar{M}_w / M_0 \tag{1.10}$$

The breadth of the molar mass distribution or dispersivity is often described in terms of the *heterogeneity index*, $\bar{M}_w/\bar{M}_n$. Some types of polymerization lead to a value of $\bar{M}_w/\bar{M}_n = 2$ whereas a *homodisperse* polymer would have a value of $\bar{M}_w/\bar{M}_n = 1$. The value of the index gives an idea of the spread of the distribution for a *polydisperse* sample in which there is a range of molar mass.

2 Synthesis

2.1 **Step-growth polymerization**

It is conventional to divide the synthesis of polymers into two main categories. One is step-growth polymerization which is often also called *condensation polymerization* since it is almost exclusively concerned with condensation reactions taking place between multifunctional monomer molecules. The other category is *addition polymerization* where the monomer molecules add on to a growing chain one at a time and no small molecules are eliminated during the reaction. Step-growth polymerization is characterized by the gradual formation of polymer chains through successive reactions coupling monomers to each other to form dimers which can also react with other dimers or unreacted monomer molecules.

2.1.1 *Condensation reactions*

Since step-growth polymerization is mainly concerned with condensation reactions it will be useful first of all to look at what is meant by a condensation reaction. In simple terms it is a reaction between an organic base (such as an alcohol or amine) with an organic acid (such as a carboxylic acid or acid chloride) in which a small molecule like water is eliminated (condensed out).

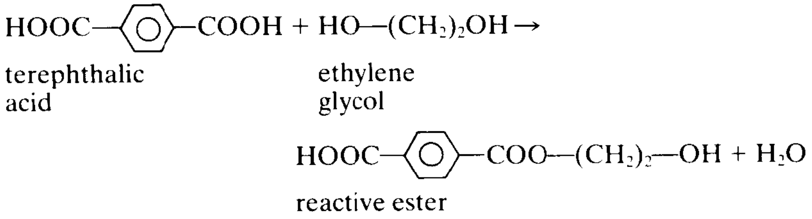
A typical condensation reaction is the reaction between acetic acid and ethyl alcohol

$$\underset{\text{acetic acid}}{CH_3COOH} + \underset{\text{ethyl alcohol}}{C_2H_5OH} \rightarrow \underset{\text{ethyl acetate}}{CH_3COOC_2H_5} + H_2O$$

Two important points to note are that a small molecule, water, is produced by the reaction. Also the product ethyl acetate is known as an *ester*. There are many examples of condensation reactions in organic chemistry and other products as well as esters are produced. For example, amides can be produced by reactions between organic acids and amines.

2.1.2 *Functionality and polycondensation reaction*

In order to produce polymer molecules by step-growth polymerization it is essential that the monomer molecules must be able to react at two or more sites. In the condensation reaction shown in Section 2.1.1 each of the two reactants can only react at one point. Because of this once the initial reaction has taken place the ester produced is incapable of taking part in any further reactions. Now, if reactants are used which are capable of reacting at two sites polymerization can start to take place. A reaction between a diacid and a diol (di-alcohol) yields an ester which still has unreacted end groups.



This reaction can be written in a general form,

$$\mathrm{HOOC{-}R_1{-}COOH + HO{-}R_2{-}OH \rightarrow}$$

diacid monomer — diol monomer

$$\mathrm{HOOC{-}R_1{-}COO{-}R_2{-}OH + H_2O}$$

Dimer

where R_1 and R_2 are general groups. The ester produced has an acid (COOH) group at one end and a hydroxyl (OH) group at the other and so can react with other monomer or dimer molecules to form a trimer or tetramer and go on through further condensation reactions to form long polymer molecules. The number of sites at which a monomer molecule is able to react is called its *functionality* and this is a concept which is of prime importance in step-growth polymerization. In order to form linear molecules it is necessary that the monomer molecules are bi-functional. If the monomers have a functionality of greater than two it is sometimes possible to form network polymers rather than linear molecules.

The general reaction for the production of a polyester from a diacid and a diol is

$$n\mathrm{HOOC{-}R_1{-}COOH} + n\mathrm{HO{-}R_2{-}OH} \rightarrow \mathrm{HO[{-}OCR_1COOR_2{-}O]_{\mathit{n}}H} + (2n-1)\mathrm{H_2O}$$

In the initial stages of the reaction diol monomer molecules react with diacid molecules. However, as the supply of monomer molecules is used up it is more likely that growing polyester molecules will also react with others of their own type.

e.g. $$\mathrm{HO[{-}OCR_1COOR_2O{-}]_{\mathit{i}}H + HO[{-}OCR_1COOR_2O{-}]_{\mathit{j}}H \rightarrow HO[{-}OCR_1COOR_2O{-}]_{(\mathit{i+j})}H + H_2O}$$