1   Introduction

1.1   Vibrational spectroscopy

1.1.1   *Molecular vibrations*

Molecules consist of atoms bound together by what are usually called *chemical bonds*. The nature of these bonds will be discussed more fully in chapter 2 and it is only necessary to note here that the bonds and the angles between them are not rigid. To a first approximation the force required to make a small change in the length of a bond, or a small change in the angle between two bonds, is proportional to the change produced; similarly, the torque required to twist one part of a molecule through a small angle with respect to the rest about a bond is approximately proportional to the angle of twist. The molecule thus consists of a set of coupled harmonic oscillators and if it is disturbed from its equilibrium state it will vibrate in such a way that the motion can be considered to be a superposition of a number of simple harmonic vibrations. In each of these so-called *normal modes* every atom in the molecule vibrates with the same frequency, and in the simplest molecules all atoms pass through their respective positions of zero displacement simultaneously.

There are three principal methods by which the vibrations may be studied: infrared and Raman spectroscopies and inelastic neutron scattering. The first two methods are available in very many laboratories, since the equipment required is relatively small and cheap. Neutron scattering is less readily available, since the technique requires a neutron source, which is usually a nuclear reactor, and relatively specialized and expensive equipment to analyse the energies of the neutrons scattered from the sample. In this book we shall not consider neutron scattering in any detail, although it will be mentioned occasionally. The main purpose of the book will be to explain what kinds of information infrared and Raman spectroscopies can provide about polymers and how the information may be obtained. Much of chapters 2 and 3 and parts of chapter 4 are, however, relevant to the study of the vibrations of molecules of any kind.

1.1.2   *Infrared and Raman spectroscopy*

A vibrating molecule may interact in two distinctly different ways with electromagnetic radiation of appropriate frequency. If the

1

radiation has the same frequency as one of the normal modes of vibration, and this usually means that it will be in the infrared region of the electromagnetic spectrum, it may be possible for the molecule to *absorb* the radiation. The energy absorbed will later be lost by the molecule either by re-radiation or, more usually, by transfer to other molecules of the material in the form of heat energy. An *infrared absorption spectrum* of a material is obtained simply by allowing infrared radiation to pass through the sample and determining what fraction is absorbed at each frequency within some particular range. The frequency at which any peak in the absorption spectrum appears is equal to the frequency of one of the normal modes of vibration of the molecules of the sample.

The second way in which electromagnetic radiation may interact with a molecule is by being *scattered*, with or without a change of frequency. If light is allowed to fall on a sample which is homogeneous on a scale large compared with the wavelength of light both types of scattering will in general take place. The scattering without change of frequency may be thought of as scattering from the equilibrium states of the molecules and is called *Rayleigh scattering*. The scattering with change of frequency is called *Raman scattering* and the change in frequency is equal to the frequency of one of the normal modes of vibration of the molecules. The strongest scattering is at frequencies lower than that of the incident light and this is called the *Stokes Raman scattering*.

In general, some but not all of the modes of vibration of a particular type of molecule can be observed by means of infrared spectroscopy and these are said to be *infrared-active* modes. Similarly, some but not all modes are *Raman active*. Which modes are active for which process depends on the symmetry of the molecule. Chapters 2 and 3 are largely devoted to a discussion of molecular symmetry and how it affects the nature of the normal modes of molecules, polymer chains and polymer crystals. Chapter 4 considers the *selection rules* which determine whether each mode is infrared or Raman active and how observed spectral features can be *assigned* to normal modes.

1.2   **Fundamentals of polymers**

In this book the term *polymer* is used to mean a particular class of macromolecules which consist, at least to a first approximation, of a set of regularly repeated chemical units of the same type, or possibly of a very limited number of different types (usually only two), joined end to end to form a chain molecule. If there is only one type of chemical unit the corresponding polymer is a *homopolymer* and otherwise it is a *copolymer*. The synthetic polymers will form the main examples in this

book although much of what is said applies equally to certain classes of biological macromolecules, or *biopolymers*. In this section we consider briefly the main types of chemical structural repeat units present in synthetic polymers, together with the kinds of structural regularities and irregularities that may occur. Further details of the structures of individual polymers will be given in later sections of the book. It should be noted that the term *monomer* or *monomer unit* is often used to mean either the chemical repeat unit or the small molecule which polymerizes to give the polymer. These are not always the same in atomic composition, as will be clear from what follows, and the chemical bonding must of course be different even when they are.

1.2.1   *Addition polymers*

The sequential addition of monomer units to a growing chain is a process which is easy to visualize and is the mechanism for the production of an important class of polymers. For the most common forms of this process to occur, the monomer must contain a double (or triple) bond. The process of addition polymerization occurs in three stages. In the *initiation* step an activated species, such as a free radical from an initiator added to the system, attacks and opens the double bond of a molecule of the monomer, producing a new activated species. In the *propagation* step this activated species adds on a monomer unit which becomes the new site of activation and adds on another monomer unit in turn. Although this process may continue until thousands of monomer units have been added sequentially, it always terminates when the chain is still of finite length. The *termination* process normally occurs by one of a variety of specific chain terminating reactions, which lead to a corresponding variety of end groups.The propagation process is normally very much more probable than the termination process, so that macromolecules containing thousands or tens of thousands of repeat units are formed.

The simplest type of addition reaction is the formation of polyethylene from ethylene monomer:

$$\ce{+CH_2+_{\it n}CH_2-CH_2^{\bullet} + CH_2=CH_2 \to +CH_2+_{\overline{\it n+2}}CH_2-CH_2^{\bullet}}$$
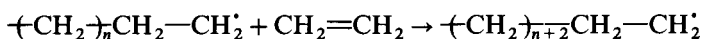
Polyethylene is a special example of a generic class that includes many of the industrially important macromolecules, the *vinyl* and *vinylidene* polymers. The chemical repeat unit of a vinylidene polymer is $-CH_2-CXY-$, where X and Y represent single atoms or chemical groups. For a vinyl polymer Y is H and for polyethylene both X and Y are H. If X is $-CH_3$, Cl, $-CN$, $-\langle\bigcirc\rangle$ or $-O\,.\,CO\,.\,CH_3$ and Y is H,
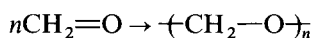
4   *Introduction*

the well-known materials polypropylene, poly(vinyl chloride) (PVC), polyacrylonitrile, polystyrene or poly(vinyl acetate), respectively, are obtained. When Y is not H, X and Y may be the same type of atom or group, as with poly(vinylidene chloride) (X and Y are Cl), or they may differ, as in poly(methyl methacrylate)(X is $-CH_3$, Y is $-COOCH_3$) and poly(α-methyl styrene) (X is $-CH_3$, Y is $-\langle\bigcirc\rangle$). When the substituents are small, polymerization of a tetra-substituted monomer is possible, to produce a polymer such as polytetrafluoroethylene (PTFE), $+CF_2-CF_2+_n$, but if large substituents are present on both carbon atoms of the double bond there is usually steric hindrance to polymerization.

Polydienes are a second important group within the class of addition polymers. The monomers have two double bonds and one of these is retained in the polymeric structure, to give one double bond per chemical repeat unit of the chain. This bond may be in the backbone of the chain or in a side group. If it is always in a side group the polymer is of the vinyl or vinylidene type. The two most important examples of polydienes are polybutadiene, containing 1,4-linked units of type $-CH_2-CH=CH-CH_2-$ or 1,2-linked units of type $-CH_2-CH(CH=CH_2)-$, and polyisoprene, containing corresponding units of type $-CH_2-C(CH_3)=CH-CH_2-$ or $-CH_2-C(CH_3)(CH=CH_2)-$. Polymers containing both types of unit are not uncommon, but special conditions may lead to polymers consisting largely of one type. Acetylene, $CH\equiv CH$, polymerizes by an analogous reaction in which the triple bond is converted into a double bond to give the chemical repeat unit $+CH=CH+$.

Ring-opening polymerizations, such as those in which cyclic ethers polymerize to give polyethers, may also be considered to be addition polymerizations:

$$n\overline{CH_2-(CH_2)_{m-1}-O} \rightarrow [+(CH_2)_{m}O]_n$$
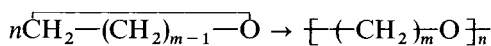
The simplest type of polyether, polyoxymethylene, is obtained by the similar polymerization of formaldehyde in the presence of water:

$$nCH_2=O \rightarrow +CH_2-O+_n$$
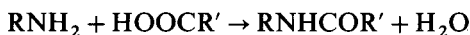
1.2.2   *Step growth polymers*

Step growth polymers are obtained by the repeated process of joining together smaller molecules, which are usually of two different kinds at the beginning of the polymerization process. For the production of linear (unbranched) chains it is necessary and sufficient

that the number of reactive groups on each of the initial 'building brick' molecules is two and that the molecule formed by the joining together of two of these molecules also retains two appropriate reactive groups. There is usually no specific initiation step so that any appropriate pair of molecules present anywhere in the reaction volume can join together. Many short chains are thus produced initially and the length of the chains increases both by the addition of monomer to either end of any chain and by the joining together of chains.
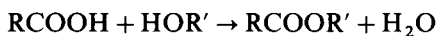
Condensation polymers are an important class of step growth polymers formed by the common condensation reactions of organic chemistry. These involve the elimination of a small molecule, often water, when two molecules join, as in *amidation*:
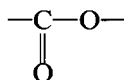
$$RNH_2 + HOOCR' \rightarrow RNHCOR' + H_2O$$

which produces the *amide linkage*

$$\begin{array}{cc} -N- & C- \\ | & \| \\ H & O \end{array}$$
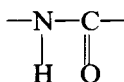
and *esterification*:

$$RCOOH + HOR' \rightarrow RCOOR' + H_2O$$

which produces the *ester linkage*

$$\begin{array}{cc} -C- & O- \\ \| \\ O \end{array}$$
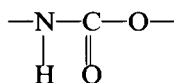
An important example of a reaction employed in step growth polymerization which does not involve the elimination of a small molecule is the reaction of an isocyanate and an alcohol

$$RNCO + HOR' \rightarrow RNHCOOR'$$
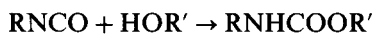
which produces the *urethane linkage*

$$\begin{array}{ccc} -N- & C- & O- \\ | & \| \\ H & O \end{array}$$

In all these reactions R and R' may be any chemical group.

The amidation reaction is the basis for the production of the *polyamides* or *Nylons*. For example, Nylon 6,6, which has the structural repeat unit $-HN(CH_2)_6NHCO(CH_2)_4CO-$, is made by the condensation of hexamethylene diamine, $H_2N(CH_2)_6NH_2$, and adipic acid, $HOOC(CH_2)_4COOH$, and Nylon 6,10 results from the

6   *Introduction*

comparable reaction between hexamethylene diamine and sebacic acid, $HOOC(CH_2)_8COOH$. In the labelling of these Nylons the first number is the number of carbon atoms in the amine residue and the second the number of carbon atoms in the acid residue. Two Nylons of somewhat simpler structure, Nylon 6 and Nylon 11, are obtained, respectively, from the ring-opening polymerization of the cyclic compound ε-caprolactam:

$$n\overline{OC(CH_2)_5N}H \rightarrow \left(OC(CH_2)_5NH\right)_n$$
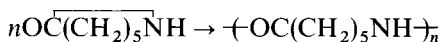
and from the self-condensation of ω-amino-undecanoic acid:

$$nHOOC(CH_2)_{10}NH_2 \rightarrow \left(OC(CH_2)_{10}NH\right)_n + nH_2O$$
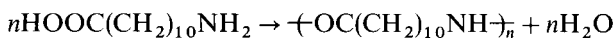
The most important *polyester* is poly(ethylene terephthalate), $\left(CH_2\right)_2OOC-\bigcirc-COO\right)_n$, which is made by the condensation of ethylene glycol, $HO(CH_2)_2OH$, and terephthalic acid, $HOOC-\bigcirc-COOH$, or dimethyl terephthalate, $CH_3OOC-\bigcirc-COOCH_3$. There is also a large group of unsaturated polyesters that are structurally very complex because they are made by multi-component condensation reactions, e.g. a mixture of ethylene glycol and propylene glycol, $CH_3CH(OH)CH_2OH$, with maleic and phthalic anhydrides (see fig. 1.1).

One of the most complex types of step growth reactions is that between a glycol, $HOROH$, and a di-isocyanate, $O=C=NR'N=C=O$, to produce a polyurethane, which contains the structural unit $-ORO.CO.NHR'NH.CO-$. Several subsidiary reactions can also take place and although all of the possible reaction products are unlikely to be present simultaneously, polyurethanes usually have complex structures. Thermoplastic polyurethanes are copolymers which usually incorporate sequences of polyester or polyether segments and they are considered in more detail in subsections 5.3.5 and 6.6.3.

Fig. 1.1. (*a*) maleic anhydride; (*b*) phthalic anhydride.
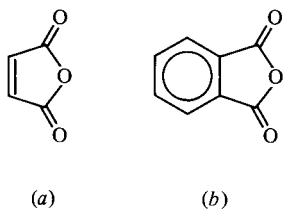
(*a*)   (*b*)

Formaldehyde, $CH_2{=}O$, provides a very reactive building block for step growth reactions. For example, in polycondensation reactions with phenol, ⟨◯⟩—OH, or its homologues with more than one OH group, it yields the *phenolic resins* and with urea, $CO(NH_2)_2$, or melamine (see fig. 1.2*a*) it yields the *amino resins*. The products of such condensation reactions depend on the conditions employed but they are usually highly cross-linked. Acid conditions lead to the formation of methylene bridged polymers of the type shown in fig. 1.2*b* and *c*, whereas alkaline conditions give structures containing the methylol group, $-CH_2OH$, which may condense further to give structures containing ether bridges, of the form $R-O-R'$ (fig. 1.2*d*).

In general, step growth polymers are likely to produce rather complex spectra because of the size of the building blocks, even when only one type of unit is present, as for example in poly(ethylene terephthalate). When more than one type of reaction occurs to an appreciable extent, as with phenolic resins and polyurethanes, the additional complexity resulting from the two- or multi-component mixture will lead to still more marked difficulties of interpretation.

1.2.3 *Regular chains and defect structures*

A perfectly regular polymer chain would consist of the repetition of identical structural units at equal intervals and with the same orientation along the direction of the chain: sets of corresponding

Fig. 1.2. (*a*) melamine; (*b*), (*c*) and (*d*) various bridging structures in phenolic resins.
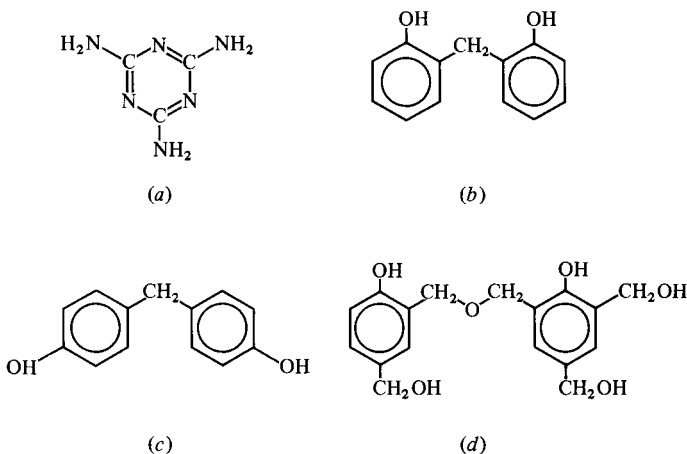
points in all structural units would lie on parallel straight lines. The term *defect structure* will be used to denote a chain-terminating group, a chain branch or a stereochemical imperfection in an otherwise regularly repeating polymer chain, i.e. a region in which either the internal bonding of a structural unit or its orientation with respect to the adjacent unit on one or both sides causes the chain to depart from regularity. This definition excludes the alternative types of chemical structural units that are frequently formed during condensation reactions. Polymers containing the latter structures may be regarded as copolymers. All real polymer chains contain defect structures, even those in the most perfect of polymer single crystals (see section 1.2.4).

Irregularities of addition, leading to defect structures, can occur during addition polymerization for several reasons. In polymers of the vinyl or vinylidene class, sequence isomerism may occur. The two carbon atoms of $-CH_2-CHX-$ or $-CH_2-CXY-$ bear different substituents. The units usually add *head-to-tail*, to give the regular structure $+CH_2-CHX+_n$ or $+CH_2-CXY+_n$, but they may add *head-to-head* or *tail-to-tail*, to give units of type $+CH_2-CHX-CHX-CH_2+$ or $+CHX-CH_2-CH_2-CHX+$, respectively, for a vinyl polymer. Most substituents are sufficiently bulky to cause some degree of steric hindrance in the head-to-head arrangement and this structure is usually of sufficiently higher energy that it is formed in very low concentration. The van der Waals radius of the fluorine atom is comparatively small and an appreciable degree of head-to-head addition occurs during the polymerization of vinyl fluoride and vinylidene fluoride, with a corresponding amount of tail-to-tail addition, necessarily.

The most important type of structural irregularity in polymers of the vinyl or vinylidene type occurs because the four bonds to each carbon atom are arranged approximately tetrahedrally in space, and this means that for vinyl polymers of the type $+CH_2-CHX+_n$ two regular types of spatial disposition of the substituent X with respect to the polymer backbone of carbon atoms are possible. The simplest types of structure that may be envisaged are those in which the carbon atoms form a planar zig-zag structure. If we look edge-on to the plane of this zig-zag, three distinct types of placing of the X atoms are possible (fig. 1.3). In the *isotactic* chain all the X atoms or groups are on the same side of the plane of the zig-zag, whereas in the *syndiotactic* chain they are alternately on opposite sides. These two structures are said to be *stereoregular*. In the *atactic* chain the X atoms or groups are randomly placed on the two sides of the plane. None of these three types of arrangement can be converted into any of the others without breaking and reforming

chemical bonds and they are said to differ in *configuration*, or to be different *configurational isomers*. The term *tacticity* is used to refer to the type or degree of configurational regularity of vinyl chains. If the configuration is largely of one regular type, either syndiotactic or isotactic, but contains a small proportion of the other type, this latter may be regarded as a defect structure.

It is possible for a vinyl or vinylidene chain to take up the regular planar zig-zag structure referred to above, whatever its configurational structure, provided that the groups X (or X and Y) are small enough. Rotations about the C—C bond may occur, however, to give non-planar *conformational isomers* (or *conformers*). These structures may be of lower or higher energy depending on the size of the groups X (or X and Y). In the remainder of this book the terms *configurational* and *conformational* isomerism will be used strictly in accordance with the definitions just given, but the reader is warned that although this distinction is now made by most authors, passages will often be found in the literature in which the two types of isomerism are not clearly distinguished. The important distinction is that a new configurational

Fig. 1.3. Planar zig-zag conformations of vinyl polymers: (*a*) carbon backbone; (*b*) regular isotactic configuration; (*c*) regular syndiotactic configuration; (*d*) random atactic configuration.

○ , H; ● , C; ⊘ , Cl or other group
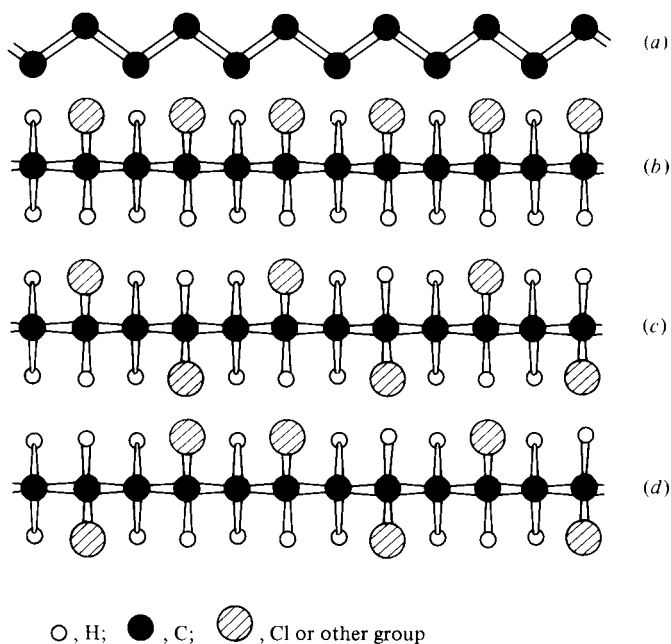
isomer can only be formed by breaking and reforming one or more bonds, whereas a change of conformational isomer can be achieved simply by the rotation of parts of the molecule around single bonds.

In many vinyl polymers the X atom or group is rather large and the planar conformation is a high energy one for the isotactic configuration, because of the small mutual separation of those atoms or groups in that structure, and a different conformational isomer may result. Isotactic sequences in PVC are a good example of this. The equilibrium proportions of such conformers present at a particular temperature are determined by the differences between their Gibbs free energies. In isotactic vinyl polymers with bulky side groups a helical structure often occurs. This may be imagined to be formed from the planar zig-zag by rotating the part of the molecule on one side of a backbone C—C bond through 120° around the bond with respect to the rest of the molecule and repeating the operation for alternate C—C bonds, the rotation being always in the same direction.

The helical structure just considered illustrates two important conformational features which can occur in many polymers. In the planar zig-zag structure every backbone C—C bond may be considered to be the central member of a group of three C—C bonds which are coplanar, and in which the outer two bonds are on opposite sides of the projected line of the central bond (see fig. 1.4). The central bond of any such group is said to be a *trans* bond. In the helical structure alternate bonds are trans, but those about which the rotation has taken place, and which are parallel to the axis of the helix, are said to be *gauche* even though the rotation may be to the right. Left and right gauche bonds correspond to anticlockwise and clockwise rotations, respectively, of the third bond by 120° from the plane formed by the first two of the group of three, and a helix may be a regular right-handed or left-handed structure or it may have kinks where the handedness changes.

Polydienes which retain the double bond in the main polymer chain (1,4-polydienes) show a different type of isomerism from that of the vinyl polymers. This isomerism is called *cis/trans* isomerism and is illustrated in fig. 1.5. It must be stressed that unlike trans/gauche isomerism this is configurational rather than conformational isomerism, since rotation cannot take place about the double bond, and the properties of the all-cis and all-trans forms of the same polymer are often very different. An important example is polyisoprene, which occurs naturally in both forms; the cis form is natural rubber and the trans form is gutta percha, which is hard and inelastic at room temperature. In certain polymer structures three single bonds take up a cis or nearly cis conformation and a cis/trans isomerism that is conformational rather than