21 Polymers – Macromolecules

Introduction

The purpose of this chapter is help those interested in the characterisation/identification of polymers. It is not the intention of this chapter to deal with the theoretical aspects of the vibrational spectroscopy of polymers (infrared or Raman) nor to deal with the sampling methods for the two techniques. There are many good books dealing with these aspects. However, as will be appreciated, it is not possible to deal with the characterisation of polymers without some mention of these aspects but this will be kept to a minimum. For example, in dealing with sampling techniques, the aim is merely to give an idea of what commonly-available techniques may be applied. It is also not the intention of this chapter to list recent developments in the field.

The vast majority of functional groups present in polymers give rise to bands in the infrared region. Hence, vibrational spectra can be used to identify polymers through the use of group frequencies or simply by attempting to compare the spectrum of an unknown with that of reference spectra. This latter approach can run into difficulties when dealing with copolymers or polymers that have been modified in one way or another – for example, by the addition of fillers or by being chemically modified, or where there are crystallinity differences between samples. In addition to providing data to enable the identification of polymers, vibrational spectroscopy can also yield valuable information on the microstructure of a polymer. This includes configurational and conformational information on the structure, how successive monomer units were added to the chain in both homo- and copolymers and the identification of end-groups and of defects.

It must be emphasised that infrared and Raman spectroscopy should not be used to the exclusion of other techniques such as ¹H and ¹³C nuclear magnetic resonance, which are particularly useful characterisation techniques. Other useful techniques are mass spectroscopy, ultraviolet-visible spectroscopy, chromatography, thermo-analytical techniques (such as differential scanning calorimetry (DSC), thermal gravimetry (TG) etc.), or combined techniques such as GC-MS (gas chromatography combined with mass spectrometry) or chromatography (liquid)combined with mass spectrometry etc. Such techniques may either yield additional information or provide the confirmation of a group or some other aspect that is required. As an example, nuclear magnetic resonance (NMR) and DSC may be used to distinguish between a blend or copolymer of two amorphous polymers, whereas this cannot easily be done using either infrared or Raman spectroscopy. Simple techniques should also not be ignored as they can save a great deal of time, for example, density, copper-wire flame test, etc.

A question often asked is, 'For polymer analysis, which is the better technique, infrared or Raman?' There is no simple answer since it depends on the task in hand. Even though great improvements have been made in laser Raman spectroscopy, the technique is still considered to be inferior to infrared spectroscopy for the characterisation and analysis of polymers. Some of the reasons for this are as follows:

1. Raman spectrometers tend to be more expensive than those of infrared and so are less common and therefore not readily available to the analyst. On the other hand, infrared is generally available in most laboratories for routine analysis and is a very versatile technique.
2. If good Raman spectra are to be obtained, more skill is required by the instrument operator and analyst than is the case for infrared, both in the experimental aspects and in the interpretation of the spectra obtained, although in many cases, sample preparation for Raman spectra is simpler than for infrared.
3. Infrared spectrometers and techniques and accessories are more established than those of Raman.
4. The acquisition of Raman spectral data has, in the past, been relatively slow, although in recent years great improvements have been made in this area.
5. One major advantage of the use of infrared spectra is that there is a vast base of reference spectra which can easily be referred to. In the case of Raman spectra, the reference libraries, although much better nowadays, still do not compare with those available for infrared.
6. Fluorescence has been a major source of difficulty for those using Raman spectra. Historically, this has led to the acquisition of poor spectra or
some cases no spectra at all. Of course, techniques are now available to minimize the effects of this problem. Techniques to burn out the fluorescence can be used in the case of some samples. In many cases, the use of near-infrared, Fourier-transform, Raman spectrometers has proved invaluable in overcoming the difficulties involved in obtaining the Raman spectra of many polymers. Removing or cleaning the surface layer of a polymer can reduce/remove the fluorescence observed.

7. If the sample absorbs the radiation used for excitation, this may result in poor Raman spectra being obtained. Localised heating may occur and this may result in numerous problems - phase changes, decomposition, etc. - if care is not taken. This heating effect may be a problem when using Raman techniques to examine coloured samples.

8. Quantitative measurements are a little more involved in Raman spectroscopy. In infrared spectroscopy, the concentration of a functional group is linearly dependent on the absorbance of its related band, absorbance being the logarithmic ratio of the intensities of the incident and transmitted radiation. This means that both short and long term fluctuations in the intensity of the radiation source are irrelevant. However, in the case of Raman spectroscopy, the intensity of a band is linearly dependent on the concentration of its related functional group. This means that direct measurements are required and this is not always possible, hence ratio techniques are commonly used and, in the case of solutions, an internal standard may be added to the solution.

On the other hand, it should be noted that:

1. Polymers usually contain a large number of additives, fillers, pigments, etc. Many of these substances may result in interference in the infrared spectrum or present other problems such as requiring prior removal or special sample preparation techniques, or other special techniques. Many of the pigments used in the polymer industry, with the exception of carbon black, are poor Raman scatterers, although some may exhibit fluorescence. Glass fibres are also poor Raman scatterers and hence samples containing these can often be examined without prior treatment. In general, sampling techniques are often not as involved as those for infrared since there may be no need to remove the additives, fillers, etc., before examination. However, despite this advantage, it may still not be possible to obtain a suitable Raman spectrum.

2. Over the years, both techniques have become more automated. However, since Raman frequently requires little or no sample preparation, pre-alignment sampling techniques have meant that often little operator skill is needed - the operator simply places the sample in its compartment and starts the scan. However, if the sample exhibits fluorescence or absorbs the radiation used or has certain other problems, no spectrum will be obtained.

It is fair to say that most organic substances exhibit fluorescence to some degree and it may be impurities in the polymer sample that are responsible for the observation of fluorescence.

3. These days it is possible, for a relatively small additional expenditure, to purchase dual purpose instruments - infrared/Raman spectrometers. However, the operation of such instruments is slightly more involved than for a straight infrared or Raman spectrometer. In addition, dual-purpose instruments do not have available the same high specifications as those using a single technique.

4. Raman has an advantage in the study of some samples in that glass cell and aqueous solutions may be used but then most soluble polymers require an organic solvent and infrared can easily be used.

5. Another point to bear in mind is that the infrared and Raman spectra of a given sample may differ considerably and hence each can be used to gain a different insight into the structure and properties of the sample. Often in the Raman spectra of polymers, the skeletal vibrations give characteristic bands which are usually very weak and of not much use for characterisation in the infrared. For example, the intensities and positions of the bands due to the skeletal vibrations are very characteristic of the different types of aliphatic nylon available and may be used for identification purposes.

6. Certain bands which are weak or inactive in the infrared, for example, those due to the stretching vibrations of C=C, C=C, C=N, C=S, S=S, N=N and O–O functional groups, exhibit strong bands when examined by Raman spectroscopy. Of course, the opposite is also true - certain vibrational motions of some groups which have weak bands in Raman may have strong bands in the infrared. However, the C=C, C=C, C=N, C=S, S=S, N=N and O–O functional groups, which, as mentioned, result in strong bands in Raman spectra, are to be found in many polymers and so, in this respect, Raman may sometimes have an advantage over infrared. Bands due to the following groups: OH, C=O, C–O, S=O, SO₂, P=O, PO₃, NO₂, etc. are strong in infrared. It should be pointed out that, for aromatics, the type of substitution present can normally be easily determined by infrared, the strong bands due to the CH out-of-plane vibrations and the overtone–combination bands being used. These vibrations result in weak (or no) bands in Raman spectra. However, other bands may be used in Raman spectroscopy to assist in the identification of the nature of the ring substitution. Although not always true, as a general rule, bands that are strong in infrared spectra are often weak in Raman spectra and bands that are strong in Raman spectra are often found to be weak in infrared spectra.

7. In some cases, in the infrared spectrum, bands occur in regions where they are overlapped by bands due to other groups making characterisation difficult/impossible (the same is true of Raman). By making use of Raman
spectroscopy, it is possible to examine bands which occur in relatively interference-free regions. For example, the alkene \( \text{C}=\text{C} \) stretching vibration band occurs near 1640 cm\(^{-1}\) (~6.10\(\mu\)m) where few other functional groups absorb. The \( \text{C}=\text{C} \) stretching vibration band is strong in Raman spectra. On the other hand, the alkene CH out-of-plane vibration bands are often overlapped in the infrared spectra of polymers, making assignments using these bands difficult/impossible.

8. In some cases, the infrared sample preparation techniques that may be required for the examination of a particular sample may destroy or modify the characteristics of interest. For Raman, very little, if any, sample preparation may be required.

9. Raman spectrometers are capable of covering lower wavenumbers (down to 100 cm\(^{-1}\) or lower) than those of infrared (400 or 200 cm\(^{-1}\)) and so can reveal information relating to polymer structure (see below) not easily available using other techniques.

Certainly for the routine analysis of polymers, infrared is by far the more popular but both techniques have their advantages and disadvantages.

### Pretreatment of Samples

Polymers are difficult to characterise, not because their infrared or Raman spectra are complicated, difficult to interpret or consist of broad overlapping bands, as, in general, they do not, but because so many different substances are added to polymers for one reason or another. For example, fillers may be added to modify the physical or chemical properties of the basic polymer or its appearance. Fillers may be added to alter the mechanical, thermal, electrical or magnetic properties of the final product. Of course, fillers may also be used simply to make the product cheaper by the addition of inexpensive substances such as chalk, glass, wood shavings, silica, or air (gas bubbles). In addition, other substances such as lubricants (to assist in the processing of the polymer), heat stabilisers (to prevent thermal degradation during processing), pigments (for colouring), plasticisers, antioxidants, UV stabilisers, fire retardants, etc., are added to polymers. The list is endless, basically, just about anything may be added to polymers. In some cases, it may be difficult to believe that two samples are based on the same polymer, for example, polyvinylchloride (PVC) plasticised and unplasticised.

It must also be remembered that, different preparative techniques may be used by different manufacturers with very different conditions. These may lead to the same polymer having similar but quite different characteristics. Different catalysts may be involved and, in some cases, the catalyst may still be bound/remain in the polymer. Different catalysts may be used to form stereo-regular polymers. Also, the basic polymer unit may be modified chemically eg. polyethylene and chlorinated polyethylene.

It must also be remembered that, unlike organic or inorganic compounds, the 'molecules' are not all identical, they do not all have the same relative mass (molecular weight) (ignoring isotopic variation). Copolymers are also commonly encountered in many everyday products. The proportions of the monomers and/or the sequencing employed may vary from manufacturer to manufacturer or be varied in order to obtain the properties required. The stereo-chemical nature of the polymer, its microstructure, crystallinity, may have a bearing on the spectrum obtained.

Polymers are very versatile materials and are used in many different products. For example, they are encountered in many different guises: fibres, paints, coatings, rubbers, adhesives, packaging, and are even used in food products, etc. Some products may appear to be a single polymer but are actually laminates or composed of mixtures of polymers. Composites may, for example, contain fibres or materials in another form and these substances may be organic or inorganic in nature.

Some polymers exist in equilibrium with water. In such polymers, there may be as much as 2% water so that additional bands due to water will normally be observed in their spectra. For example, for polyetherketones and polyethersulphones, bands near 3650 cm\(^{-1}\) (2.74\(\mu\)m) and 3550 cm\(^{-1}\) (2.82\(\mu\)m) may be observed. In order to avoid complications due to the presence of water, particularly if quantitative measurements are to be made, some polymers may need to be thoroughly dried before their spectrum is recorded.

It is seen that the spectrum of a sample may consist of the basic polymer spectrum on which are superimposed the spectra of the additives, fillers, lubricants, fire retardants, catalyst residues, contaminants, etc. in proportions relating to their concentrations in the sample. Hence, there are many reasons why difficulties may be encountered when examining polymeric samples. Obviously, there are advantages if the problem can be made simpler, perhaps by separation, eg. use of chromatography or solvent extraction etc. With certain polymeric samples, it may be possible to use selective solvent extraction but, in some of these samples, this may result in fine particles of carbon black remaining in suspension and being difficult to remove.

A simple technique used to determine the inorganic filler incorporated in a polymer is simply to burn the sample (place the sample in a furnace) and spectroscopically examine the residue. It may also be possible to determine the polymer by pyrolysing the sample and examining the pyrosylate.

In Raman spectroscopy, polymer samples often exhibit fluorescence due to contaminants on their surfaces. Wiping the sample with a solvent, eg. acetone or alcohol, can reduce this fluorescence. Alternatively, taking a thin slice off the surface of the sample can also be helpful.
Sample Preparation

Of course, as always, care must be taken not to contaminate samples or cells and not to use preparative techniques which affect the characteristics of the sample which are of interest.

Some polymeric samples can be examined directly without prior treatment. For example, thin polymeric films may be used for infrared transmission spectra and samples with glass-fibre fillers may be examined by Raman directly.

The sampling technique chosen is dependent not only on the availability of a spectrometer (infrared or Raman) and the facilities available on it, but also on the nature of the sample and the type of information required. In some instances, all that is required is confirmation that the sample is the same as that previously examined or is of a specific class of polymer, in which case a simple fingerprint may be sufficient to achieve this.

In many cases, the properties which make polymers attractive may actually make sampling difficult. For example, thermoplastics cannot easily be ground to form a powder for use in infrared, dispersive sampling techniques and many polymers exhibit fluorescence themselves (or the substances introduced to them are fluorescent) which can result in problems when attempting to obtain a Raman spectrum. Raman spectroscopy has two great advantages in that samples often need little, if any, preparation and samples of varying shapes and sizes can be examined.

Basic Techniques—Liquid, Solution, Dispersion

The techniques used in the study of low molecular weight organic and inorganic samples can, in many cases, be simply applied to polymers. For example, for infrared spectra, liquids may be examined in thin cells (small pathlength) having transparent windows over the frequency region of interest, or liquids (non-volatile) may be held by surface tension between transparent plates. Solids can be dissolved in suitable solvents and examined in the same way, perhaps also making use of compensating techniques. It should be noted that for polymeric fibres and powders, diffuse reflectance techniques, DRIFT, can be applied. In diffuse reflectance techniques, the radiation penetrates the sample and interacts with it, being partly scattered, reflected and absorbed. Hence, the emergent sample beam has the characteristic absorptions of the sample. Diffusion techniques can also be applied to many aspects of polymer spectroscopic studies. Reflection techniques, such multiple internal reflection, can be applied.

Dispersive Techniques

Polymeric samples, already in powder form, may, bearing in mind any particle size restrictions that might apply, also be examined by dispersive techniques, for example by preparing mulls or discs. Mulls may be prepared using liquid paraffin or polyfluorinated paraffin or some other suitable liquid. Discs may be prepared using potassium bromide or some other pure substance that is transparent over the spectral region of interest. If the polymeric specimen being examined is not already a powder then the solid may be ground to give a powder of the correct particle size. This may not be a problem if the material is brittle but if it is a thermoplastic or a rubber (elastomer) then it has to be cooled below its glass transition temperature before grinding can be successfully employed—low temperature grinding.

Films, Solvent Cast, Hot Press, Microtome

If the polymeric sample being examined is actually a sufficiently thin film, then it may be introduced directly into the sample compartment with no further preparation and examined by infrared transmission techniques, for example. It must be borne in mind that, with films examined by straight transmission, an interference pattern is often observed superimposed on the actual spectrum of the sample. Just as with low molecular weight organic substances, the variation in the band intensities observed for different functional groups mean that, in order to obtain the optimum spectrum, the pathlength may differ significantly from sample to sample. The thickness of the film may need to be adjusted in order to obtain the best spectrum.

If the polymeric specimen is a thermoplastic then it is possible to use a hot press (a temperature-controlled hydraulic press) to prepare a thin film which may then be directly examined. If the polymer is soluble in a suitable, relatively volatile solvent, then solvent casting may be used to prepare a film, this being similar to the technique of casting solid deposits on a transparent plate. Of course, with the latter technique, care must be taken to ensure that the solvent is completely removed or it will appear in the spectrum recorded. Special techniques may be required to remove the film from the base on which the film was cast. In some cases, it may be advantageous to cast the film on an infrared transparent plate. Thin films may also be prepared by using a microtome. Some thermoplastics may need a cryogenic microtome or, at least, to be cooled below their glass transition temperature so that they are sufficiently brittle to be sectioned. With some polymeric samples (e.g. rubbers), solvent swelling prior to the use of the microtome may be beneficial.
Attenuated Total Reflection, Multiple Internal Reflection and Other Reflection Techniques

If the sample has a smooth, planar surface so that good physical contact with an infrared-transparent, higher refractive index prism/plate may be achieved, it can be examined by an infrared reflection technique, for example, one using attenuated total reflection, multiple internal reflection. It should be borne in mind, when examining polymeric films, that the sample may be a laminate and hence examination may give very different spectra from reflection at the two surfaces and also from transmission techniques. A coating or paint may be directly applied to a transparent plate for transmission or reflection techniques.

Pyrolysis, Microscope, etc.

Different pyrolytic techniques may be used, the pyrosylates being examined by infrared, Raman spectroscopy or other techniques. Microscope techniques have improved over the last few years and this now means that very small regions of a sample may be successfully examined. The use of infrared microscopes has proved to be invaluable for the examination of laminates. It is often possible to microtome a thin cross-section from a laminate (for example, methylmethacrylate resin is sometimes used for this purpose) and then to examine individual layers in transmission using an infrared or Raman microscope system.

Other Techniques

It must not be forgotten that microscope techniques, infrared and Raman can be used to examine small samples or single fibres. For example, single fibres of the aromatic polyamide, Kevlar\textsuperscript{TM}, have been studied. In general, fibres have 'cylindrical' cross-sections. Synthetic polymer fibres are manufactured by extrusion from spinnerets. In some cases, the surface of the fibre may be treated and hence have an outer skin. The transmission spectra of fibres have three components: (1) stray light which has passed by the fibre without coming into contact with it, (2) radiation reflected from the surface of the fibre and (3) radiation transmitted through the fibre which has different pathlengths. Hence, strictly speaking the Beer–Lambert law does not hold in most cases, although the opposite is often assumed for certain bands in the spectra of fibres.

Glass fibres are often surface coated with an agent to help adhesion to the polymer matrix, for example, a silane coupling agent.

As a result of the manufacturing process, the molecules of synthetic polymer fibres are more or less oriented along the axis of the fibre. The degree of orientation affects the physical properties of the fibres. Just as in the case of drawn films etc., dichroism may be observed for fibres when they are examined using linearly polarised infrared radiation, an example where dichroic behaviour is observed being that of Kevlar\textsuperscript{TM}. Dichroism may also be measured by making use of Raman spectroscopy. The examination of fibres can often be made much simpler and more informative using Raman spectroscopy rather than infrared. Also, since often there is little required by way of sample preparation, the Raman technique can prove invaluable.

Theoretical Aspects – Simplified Explanations

General Introduction

In general, the infrared and Raman spectra of very large molecules are broad and so it is often difficult to identify the origins of particular bands. This is particularly true of large naturally-occurring substances such as proteins, carbohydrates, cell tissues. Even with these large molecules (biological), many advances have been made in both techniques and band identification.

Although it is helpful to have some basic understanding of the theoretical aspects of polymer vibrational spectroscopy, it is not absolutely essential in order to be able to identify or characterise polymers at a basic level. However, an understanding is useful in at least appreciating the origins of bands. The aspects covered below give the minimum required for a reasonable understanding, as applied to group frequency characterisation. The approaches given are relatively simple, so for a thorough understanding of the theory, the reader should turn to one of the many excellent texts available.

Consider a sample of a commercial polymer, such as polyethylene. Each of its chains will consist of a large number of atoms, on average 12 000 – at least. Hence, applying $3N - 6$ for a non-linear molecule, it can be seen that approximately 36 000 fundamental vibrations would be expected, which is a very large number. Therefore, it might be expected that, with many large, natural molecules, the spectra of synthetic polymers would consist of broad absorptions with few discernable features. However, in general, fortunately, the fundamental vibrations occur in relatively narrow ranges. Thus, unlike the spectra of many large, naturally-occurring molecules, the spectra of most synthetic polymers usually consist of sharp bands to which the normal group frequency approach may be applied. For some polymers, the spectra obtained are often very closely related to those of the monomers involved (with the addition of end-groups). Where this is the case, the bands in the polymer spectrum may be sharper than those in the spectra of the monomers. It is also true to say that, in other cases, the polymer spectrum observed bears little resemblance to the spectra of the starting materials.
In simple terms, it may be considered that the polymer chains are so long that the vast majority of functional groups experience very similar environments and interactions and therefore their vibrational motions are very similar so that they occur over narrow ranges.

Looked at another way, considering, say, polyethylene, the vast majority of \( \text{CH}_2 \) groups experience an averaged-out environment, so that the \( \text{CH}_2 \) groups in the middle of the chain will not experience environments very different from each other. In order to make such a statement, various assumptions/approximations are made, for example that chain folding does not have an influence on the vibrations of the group, that interactions between chains do not occur, etc. To simplify matters, consider that each polymer molecule is isolated from its neighbours or, alternatively, that all polymer molecules (and hence the repeat unit or functional groups) experience an averaged-out environment or interaction. The motions of each polymer functional group may be considered to be independent of its neighbours. Therefore, a change in the electric dipole or polarisability induced in one part of the polymer molecule may be cancelled by the opposite effect elsewhere in the chain. Hence, it is only when the vibrations of the functional groups are in phase that a net change in dipole or polarisability would occur and a band in the infrared or Raman spectra would be observed, that is, the vibration would be infrared or Raman active. As a result of this, the infrared and Raman spectra of polymers generally consist of sharp bands.

However, this would not be the situation when dealing with low molecular weight polymers or if a polymer is partly crystalline in nature but has numerous defects. For these situations, many functional groups within the molecule would differ from each other and therefore their vibrations would be infrared or Raman active. In fact, a similar effect is observed for long chain paraffins, where there is a general broadening of bands occurring as the chain length increases. For polymers, this broadening effect is not necessarily symmetrical about the central band position.

**Crystalline Polymers**

In general, it is true to say that the spectrum of a crystalline substance contains sharp discrete bands whereas that of non-crystalline materials contains broad, diffuse bands. In general, the vibrational spectra of crystalline polymers also exhibit a high degree of definition, since as mentioned previously, it is only the in-phase vibrational motions that result in active (infrared or Raman) spectral bands.

For theoretical purposes, just as with any other substances, the vibrational modes of crystalline polymers may be considered in terms of their unit cell and the symmetry associated with this cell. The number of atoms in the unit cell determines the maximum number of fundamental vibrations that may occur, rather than the number of atoms in the polymer repeat unit. Hence, since more than one polymer chain is often involved as part of the unit cell, the number of fundamental vibrations that may occur is almost always greater than that determined by considering the number of atoms in the isolated repeat unit. For example, two chains are involved in the unit cell of polyethylene and, for isotactic polypropylene, three chains are involved for each rotation of its helix.

The vibrational motions of a crystalline polymer may be considered as having two origins, internal and lattice. Lattice modes of vibration are those due to polymer chains moving relative to each other and occur at low wavenumbers, generally below 150 cm\(^{-1}\) (above 66.67 \(\mu\)m). Internal vibrational modes are those due to the motions of the atoms of a chain relative to each other and, in general, these occur in the region 4000–150 cm\(^{-1}\) (5.00–66.67 \(\mu\)m).

It is a simple matter to distinguish between the two modes of vibration. If the temperature of the sample is lowered then lattice vibrational frequencies increase since the distance between chains decreases, the force between the chains increases and this is directly related to the vibration frequency. On the other hand, internal vibrational modes are very little affected by temperature.

As mentioned earlier, in a crystalline polymer, more internal modes of vibration can occur than if a polymer molecule were considered as an isolated entity. The number is dependent on the structure of the unit cell, that is, it is dependent on the number chains involved in the unit cell. The internal modes of vibration of the chains in the unit cell may be in phase or out of phase with each other. Due to the intermolecular interactions of the chains, the in-phase and out-of-phase vibrations occur at different frequencies and so their associated internal vibrations occur at definite and fixed values. For example, for an isolated polyethylene chain, the \( \text{CH}_2 \) wagging vibration would be expected to occur at about 725 cm\(^{-1}\) (13.79 \(\mu\)m) but, in the crystalline phase, a doublet is observed in the infrared for this vibration, the bands occurring near 720 cm\(^{-1}\) (13.89 \(\mu\)m) and 730 cm\(^{-1}\) (13.70 \(\mu\)m). The components of this doublet are not necessarily of equal intensity since the absorptivities (infrared) or scattering cross-sections (Raman) may be different for the two vibrations. Another example is that of crystalline isotactic polypropylene where, due to the high degree of the symmetry of the unit cell, a number of additional bands, above those expected for an isolated chain, are observed.

Another approach to explain the observation that there are often more bands observed for crystalline polymers than expected by considering an isolated unit alone, is simply to consider that crystallinity results in a perturbation of the vibrational modes. Hence, using this approach, it may easily be appreciated that the intensity ratios of bands is related to the degree of crystallinity of the polymer.

As seen, the vibrational spectra of crystalline polymers have a high degree of definition. If the crystallinity of a particular sample is decreased, then...
various spectral changes are observed, the bands become broader and often new bands appear. These new bands are due to the vibrational motions of different conformations and/or rotational configurations of the parts of the polymer chains present in the disordered phases.

Heating a polymer sample will, in general, result in the broadening of bands as the crystalline arrangement is destroyed. The opposite is also true: as a polymer is cooled, and hence crystallises, its bands become narrower. It is very important to bear in mind, when examining the spectrum of a polymer, that a band should not be assigned as originating from the crystalline arrangement unless (a) it disappears on melting, (b) it is predicted by group theory and can be shown to depend on the presence of the crystal lattice. However, it is not always possible to ascertain that these conditions have been met. Hence, vibrational spectroscopy cannot always be thought of as a good method for determining the crystallinity of a polymer. It should also be borne in mind that conformational regularity may also be associated with amorphous regions and, for example, with orientated, but not necessarily crystalline, arrangements. When in doubt, either use another technique, such as X-ray diffraction or use such a technique to justify the infrared (or Raman) approach to be adopted. Even when it can be shown that bands are a result of the crystallinity of the polymer, their intensities cannot be relied on to be a good measure of the degree of crystallinity and a calibration plot must be made. In addition, different crystalline arrangements of a polymer may, in fact, have common absorption bands. Hence, if a polymer is polymorphic, care must be taken in making assignments and determinations.

If a polymer sample absorbs the exciting radiation significantly, it will become hotter and hence the bands will become broader. If no account is taken of the fact that radiation is strongly absorbed by the sample, it is possible to determine incorrectly the phase transition (crystalline–amorphous) temperature.

The degree of crystallinity and the amorphous content of polyethylene can be determined.1 The degree of crystallinity may be determined from the integrated intensity of the band near 1415 cm⁻¹ (7.07 μm) and the amorphous content from the intensities of the bands near 1300 cm⁻¹ (7.69 μm) and 1080 cm⁻¹ (9.26 μm). However, these days, the degree of crystallinity of a polymer is often determined by correlating whole spectra or spectral regions with X-ray or differential scanning calorimetry (DSC) measurements, using such techniques as partial least squares for calibration purposes.51-55 For example, the density of polyethylene may be determined by using a partial least-squares calibration employing micro-Raman spectroscopy.53 For the determination of the amorphous content of polytetrafluoroethylene, PTFE, a univariate method based on peak heights in the infrared region can be used.51,52 Fourier transform Raman spectroscopy may be used to measure the crystallinity of polyetheretherketone in isotropic and uniaxial samples using univariate and partial least-squares calibrations.54,55 Fourier transform Raman spectroscopy has been used to examine the crystallinity of polyethylene/teraphthalate.55

All crystalline polymers experience low-frequency vibrations along their chain—in effect, the chain is compressed and extended. The forces restraining this motion act along the axis of the chain and are very much smaller than those of the internal vibrations of groups. The frequencies of these vibrations are dependent on the Young's modulus of the crystal along the axis of the chain. Since these motions occur at very low frequencies, they are referred to as longitudinal acoustic vibrations.45 It should be pointed out that these motions can also occur along the transverse axes as well. In general, the frequencies of these motions are well below 200 cm⁻¹ and the bands are not really of any use in the identification or characterisation of polymers. However, these vibrations can yield information relating to the morphology of polymers. Normally Raman techniques are employed to observe these acoustic vibrations.

**Non-crystalline Polymers**

An individual, non-crystalline polymer chain may adopt a large number of rapidly interchanging rotational conformations relative to itself and its neighbours and hence the theoretical analysis of the polymer for spectroscopic purposes, using symmetry and fundamental vibrational modes, is impossible. The only approach which may be adopted for the analysis of such spectra is that based on the examination of the repeat unit, plus the end-groups, and treatment of the polymer as a liquid. As mentioned earlier, the spectra of non-crystalline polymers tend to involve bands that are broader than might be expected if the polymer had been crystalline.

If a vibration involves hydrogen bonding, or is affected by the conformational changes that occur, then the band may be very broad. On the other hand, if the band is relatively insensitive to external influences then the band may be quite sharp. For example, the spectrum of high density polyethylene (HDPE) has relatively sharp bands when compared with that of low density polyethylene (LDPE). The spectrum of non-crystalline, atactic polystyrene has bands due to the aromatic ring which are relatively sharp whereas other bands tend to be a little broader than for the crystalline, is tactic form.

It should be noted that, due to their lack of a uniform consistent structure, non-crystalline polymers do not exhibit lattice or acoustic bands.

**Band Intensities**

The intensities of bands are related to the concentrations of the functional groups producing them, allowing quantitative analysis if required. Provided
the normal precautions are taken and calibration is feasible, good results may be obtained. It must be borne in mind that, in general, for various reasons, using Raman for quantitative analysis is a little more difficult than using infrared which is quite straightforward. These days, it is fair to say that Raman excitation sources, lasers, are very much more stable and there is very little problem in making quantitative measurements provided the usual precautions are taken.

An oriented sample, such as a drawn polymer film, exhibits different vibrational spectra when the orientation of the sample relative to the direction of linear polarised electromagnetic radiation is altered. In other words, it should be borne in mind that, in the presence of polarised radiation, the relative intensities of bands may be affected. The interaction between the polarised electric field of the radiation and the dipole moment associated with the vibration becomes a maximum or minimum depending on the angle between these two vectors, 0° or 90°. Hence, in polarised light, the spectra of stretch-oriented polymers exhibit dichroism. Dichroism may also be observed in the stressed areas of a polymeric sample. The dichroic behaviour of a sample can provide information on (a) the direction of the vibrational modes, (b) the orientation of the functional group in the crystalline lattice and (c) the fraction of the perfect orientation in the oriented sample. The monitoring of the dichroism can be used to monitor the production of oriented polymeric films. This is commercially important as the physical properties of drawn samples are related to the degree of orientation.

As an example of dichroic behaviour, consider the infrared spectra of polyethylene. Polyethylene may be considered as a long chain of CH₂ units with its end groups, branching and any double bonds being ignored. Polyethylene molecules align themselves along the drawn axis and, as a result, the intensities of the bands due to the asymmetric and symmetric stretching vibrations reach a maximum when the electric field of the polarised radiation is perpendicular to the drawn axis, whereas the band associated with the wagging vibration reaches a maximum when these two are parallel. Other bands in the infrared spectra of polyethylene exhibit similar behaviour with regard to orientation and polarised light. It should be noted that polyacetylenes exhibit anomalous dichroic behaviour.

**Applications – Some Examples**

**Introduction**

There are so many polymers and copolymers and so many possible variations that the account given below can do no more than give selected examples in order to indicate the characterisation possibilities. When examining commercial products and artefacts, it must be borne in mind that, as already mentioned, the base polymers may contain numerous other products – stabilisers, fillers, etc. It should also be borne in mind that the relative intensities of bands in the spectra of copolymers are dependent on the proportions and sometimes the sequencing of the components present in the copolymer unless, of course, the bands are common to both units.

The difference in intensities observed for various compositions of a particular type of copolymer may be used to determine the composition of the copolymer, that is, the relative amounts of each monomer unit present. In the simplest case, where a particular band is due solely to one component of the copolymer, then either the absorptivity may be determined or a calibration graph constructed for this purpose. For systems where a band position free from the absorptions of other components of the copolymer cannot be found, a slightly lengthier approach is required. The absorptivities at various suitable locations in the spectrum must be determined for each component and then, by taking measurements for a variety of concentrations of the components in the copolymer at these different locations, equations can be constructed to determine the composition of an unknown copolymer. An example of this approach is the determination of the individual isomers of butadiene copolymers, cis-1,4-, trans-1,4- and 1,2-polybutadiene. From the solution spectra (using a suitable solvent such as carbon disulphide) of the individual components, which may be obtained separately, the absorptivities of each isomer may be determined at suitable points in the spectrum of the copolymer and hence used directly in the three equations required for the quantitative determination. In a similar manner, the isomer compositions of isoprene and chloroprene may be determined.

By making use of infrared, the pathlength of a liquid cell may be determined by measurement of the interference pattern observed. In the same way, the interference pattern often observed in the infrared spectra of thin polymeric films may be used to determine the thickness of the film. A knowledge of the refractive index of the polymer is required for this determination. If the incidence of the radiation is not normal then the angle of incidence is also required, see the equation below.

\[
d = \frac{N}{2(v_2 - v_1)(n^2 - \sin^2 \theta)^{1/2}},
\]

where \(d\) is the thickness measured in cm,
\(n\) is the refractive index of the film,
\(N\) is the number of peaks between the wavenumbers \(v_1\) and \(v_2\) measured in cm\(^{-1}\),
and \(\theta\) is the incident angle of the radiation.
The interference pattern in the infrared spectra of thin polymeric films may give rise to difficulties when attempting to observe weak bands. This problem can be overcome in several ways, the simplest being to place the film on an infrared transparent (in the region of interest) plate or simply, when casting a film, to leave it adhered to the transparent plate and to examine it directly allowing for compensation if necessary. It should be borne in mind that the infrared spectra of laminates may also exhibit an interference as a result of the interaction of reflections at boundaries and radiation transmitted directly.

Depending on the nature of the sample and the information required, it may be advantageous to use infrared, or Raman, or both techniques in a study. Remember that groups that have weak bands in Raman may have strong bands in the infrared, for example, OH, C=O, C=O, S=O, SO2, P=O, PO2, NO2, etc. are all strong in infrared. The C=C, C=C, C=N, C=S, S=S, N=N and O=O functional groups result in strong bands in Raman spectra and usually weak bands in infrared. All these groups are commonly found in many polymers.

Stereoregularity, Configurations and Conformations

These days catalysts exist for the preparation of many stereoregular polymers. The mechanical properties and spectra of the different stereoregular isomers of a particular polymer and also its atactic form may differ significantly. In general, it is obvious that stereoregular polymers may easily form crystals when they solidify. From the commercial point of view, since the different configurations of a polymer have different properties, it is essential to know the isomeric composition of a sample bearing in mind its intended application. When compared with the vibrational spectrum of the atactic form, the spectra of stereoregular isomers appear to have more bands and many of the bands are sharper. For example, the spectrum of isotactic polypropylene has numerous additional sharp bands in the region 1350-800 cm\(^{-1}\) (7.41-12.50 \text{um}). The spectrum of isotactic polystyrene differs significantly from that of the atactic form, which has broader bands. The same is true of the syndiotactic forms. Hence, in general, the spectra of stereoregular isomers have additional sharp bands when compared with spectra of the atactic form.

For some polymers, different conformers may be possible, for example, polyethylene terephthalate has two conformational isomers gauche and trans. For the gauche isomer, the -O-CH2-O- group has its oxygen atoms slightly displaced from each other, whereas in the case of the trans form, the oxygen atoms are opposite each other. The spectra of both forms are quite different, additional bands being observed for each form. Two characteristic bands for the gauche form occur near 1140 cm\(^{-1}\) (\sim 8.77 \text{um}) and 890 cm\(^{-1}\) (\sim 11.24 \text{um}). Two characteristic bands for the trans form occur near 970 cm\(^{-1}\) (\sim 10.31 \text{um}) and 840 cm\(^{-1}\) (\sim 11.90 \text{um}).

Some polymers, in addition to having different conformers, may also have configurational isomers associated with some of the conformers. These different arrangements may all be observed in their vibrational spectra. Polyvinylchloride is an example where bands originating from different isomers are commonly observed. In its infrared spectrum, a broad absorption is observed in the region 750-550 cm\(^{-1}\) (13.33-18.18 \text{um}), this being due to a number of overlapping bands some of which can be quite distinct.

Morphology - Lamellae and Spherulites

Some polymers, when they solidify from a melt, form crystals which have the appearance of being composed of thin, flat platelets, lamellae which are about 0.1nm thick and many micrometres wide. In some cases, the polymer crystallites may be arranged in groups with their axes arranged radially. These groups form features known as spherulites. Spherulites are often many times larger than crystallites and can sometimes be seen by the naked eye. The morphology of a polymer has a great bearing on its mechanical strength and stability and hence is of great interest. Infrared and Raman spectroscopy may be used to study the morphology of polymers.

The frequency bands due to longitudinal acoustic vibrations which, as mentioned previously, are not observed in infrared spectra but occur in Raman spectra, are inversely proportional to lamella thickness. These bands are usually difficult to observe. For example, a low frequency band due to a longitudinal acoustic vibration has been found in the Raman spectra of polyethylene and polypropylene which is related to the chain length and the lamellar thickness. The longitudinal acoustic vibration is dependent on the force constant (dependent on the chain's longitudinal Young's modulus), the interlamellar forces, structure of the chain folding sequence, the proportions of the amorphous and crystalline components and the density of the polymer.

C=C Stretching Band

An advantage of using Raman spectroscopy is that the C=C group, which is commonly found in many polymers, has a stretching vibration resulting in a strong band (in infrared this band is, generally, weak or in inactive) and hence can often be used to determine polymer conformations in which it occurs, determine the extent of curing or cross-linking, or follow the chemical kinetics of polymerisation. For example, the different isomers of butadiene may be distinguished by using Raman and examining the band due to the C=C stretching vibration. Bearing in mind that in certain instances
fluorescence may present problems, polymers containing aromatic groups may also be easily examined by the use of Raman techniques. Of course, the same is true of polymers which are similar, such as isoprene and chloroprene.

Thermal and Photochemical Degradation

As a result of thermal degradation, both polyethylene and polypropylene form hydroperoxide groups. These groups are not easy to detect by infrared, especially as the O–O stretching vibrations result in a very weak band and, in addition, the concentration of the hydroperoxide is low, although it should be borne in mind that peroxides give a strong Raman band. The OH stretching band may also be difficult to observe as it only results in a medium intensity band. Fortunately for infrared analysts, hydroperoxide groups react to form a variety of carbonyl-containing compounds. It is usually possible to detect bands due to ketones which absorb near 1720 cm⁻¹ (~5.81 μm), aldehydes, near 1735 cm⁻¹ (~5.76 μm) and carboxylic acids, near 1710 cm⁻¹ (~5.85 μm). In a given sample, these bands are often observed to overlap one another. The carboxylic acid band near 1710 cm⁻¹ (~5.85 μm) may be removed by converting the acid into a salt by treating the sample with a relatively strong alkali. The band due to the salt CO₂⁻ group, occurs near 1610 cm⁻¹ (~6.21 μm). In the case of photochemically decomposed samples, in addition to bands due to the various carbonyl groups, bands due to the vinyl group are also observed, occurring near 910 cm⁻¹ (~10.99 μm) and 990 cm⁻¹ (~10.10 μm). By making use of an infrared microscope, it is possible, for example, to monitor the effects of weathering on a polymeric sheet by examining a cross-section of the polymer sample at positions relating to various depths.

Due to the sensitivity of Raman spectroscopy to the –C=C– vibrational motion, a strong signal being observed, the degradation of polyvinylchloride, PVC, may be studied by making use of resonance Raman techniques. The degradation of PVC results in the loss of hydrogen chloride gas and the production of carbon–carbon double bonds, leading eventually to sequences of conjugated polyenes.

Polyethylene and Polypropylene

Polyethylene has strong bands in its infrared spectrum near 2950 cm⁻¹ (~3.39 μm) and 1460 cm⁻¹ (~6.85 μm) and a band of medium intensity, which is often a doublet, near 725 cm⁻¹ (~13.79 μm). These bands are due to the CH stretching, deformation and rocking vibrations. If the polymer has significant branching then additional weak bands near 1380 cm⁻¹ (~7.25 μm) and 1365 cm⁻¹ (~7.33 μm) are observed. These bands are usually observed in the spectra of samples of low density polyethylene, LDPE.

The methyl groups of chain-branched polyethylene have, as mentioned above, a weak band near 1380 cm⁻¹ (~7.25 μm). On the other hand, methyl groups have a stronger band at 1365 cm⁻¹ (~7.33 μm) which overlaps this methyl band. By making use of the spectra of linear polyethylene and deconvolution techniques, it is possible to determine the degree of branching.

Linear low density polyethylenes (LLDPE), are low-concentration α-olefin modified polyethylenes. The olefines usually used are propylene, butene, hexene, octene, 4-methyl pentene-1. Due to the relatively high concentration of methyl groups in linear low density polyethylenes, greater intensities are normally observed for the bands associated with the CH₃ group than are observed for high density polyethylenes (HDPE) so care must be exercised when making assignments.

As a result of its commercial preparation, the chemical structure of polyethylene may also contain double bonds. The percentage of double bonds may be estimated by making use, in the infrared, of the band due to the vinyl CH out-of-plane deformation vibration which occurs near 910 cm⁻¹ (~10.99 μm) and, in the Raman, of the C=C stretching band near 1640 cm⁻¹ (~6.10 μm) and determining the ratio of the intensities of these bands compared with other bands in the polyethylene spectrum. Some commercial low-density polyethylene, prepared using high pressures, contains vinylidene groups which, in the infrared, absorb near 890 cm⁻¹ (~11.24 μm) due to the CH₂ out-of-plane deformation vibration. Polyethylene prepared using Ziegler catalysts often contains defects resulting in the presence of vinyl, vinylidene and trans-vinylene groups. The positions of the CH out-of-plane deformation vibration bands for vinyl and vinylidene have been mentioned above, that for trans-vinylene is near 965 cm⁻¹ (~10.36 μm).

It is often true that the infrared and Raman spectra of samples have few similarities. In the Raman spectrum of polyethylene, the C–H stretching vibration bands are very strong and those due to rocking vibrations, near 725 cm⁻¹ (~13.79 μm), are very weak or absent. In addition, in Raman spectra, the skeletal vibrations give characteristic bands near 1300 cm⁻¹ (~7.69 μm), 1130 cm⁻¹ (~8.85 μm) and 1070 cm⁻¹ (~9.35 μm).

The infrared spectrum of polypropylene has strong bands near 2950 cm⁻¹ (~3.39 μm), 1460 cm⁻¹ (~6.85 μm) and 1380 cm⁻¹ (~7.25 μm). In addition, bands of medium intensity are observed near 1155 cm⁻¹ (~8.66 μm) and 970 cm⁻¹ (~10.31 μm). For isotactic polypropylene, a number of sharp bands of medium intensity are observed in the region 1250–835 cm⁻¹ (8.00–11.98 μm). In the spectra of the molten, or atactic form, of polypropylene, most of these sharp bands disappear, except for the bands near 1155 cm⁻¹ (~8.66 μm) and 970 cm⁻¹ (~10.31 μm). For some samples of
polypropylene, a band near 885 cm\(^{-1}\) (~11.30 \(\mu\)m) is observed which may be due to the CH out-of-plane motions of an end group, \((-\text{CH}_3\text{)}\text{C}=\text{CH}_2\).

Some ionomers are based on polyethylene with carboxyl groups located along the carbon chain. These carboxyl groups allow for the cross-linking of chains to occur by means of ionic bonds. Metal ions, such as sodium, potassium, magnesium and zinc, form the cationic link. The infrared spectra of ionomers are composed of the bands due to polyethylene mentioned above. In addition, bands are observed for the carboxylate portion near 1640 cm\(^{-1}\) (~6.10 \(\mu\)m), 1560 cm\(^{-1}\) (~6.41 \(\mu\)m) and 1400 cm\(^{-1}\) (~7.14 \(\mu\)m). Bands are also observed in the region 1350–1100 cm\(^{-1}\) (7.41–9.09 \(\mu\)m) which have their origin in the CH\(_2\)-acid salt structure.

Polystyrenes

In its vibrational spectra, polystyrene has a strong band due to the \(-\text{C}=\text{H}\) stretching vibration between 3100 and 3000 cm\(^{-1}\) (3.23–3.33 \(\mu\)m). In general, this band may be observed for aromatic or olefinic components (or both). Its presence in the polystyrene spectrum, together with that of a medium intensity band at 1600 cm\(^{-1}\) (~6.25 \(\mu\)m), indicates aromatic, rather than olefinic, components. This band is due to one of the aromatic ring-stretching vibrations which occur in the region 1600–1430 cm\(^{-1}\) (6.25–6.99 \(\mu\)m).

The very strong bands observed in the infrared spectrum near 760 cm\(^{-1}\) (~13.16 \(\mu\)m) and 690 cm\(^{-1}\) (~14.49 \(\mu\)m) confirm the presence of a monosubstituted aromatic group. These bands are due to the CH out-of-plane vibration and a ring out-of-plane deformation respectively. The overtone and combination bands which occur in the region 2000–1660 cm\(^{-1}\) (5.00–6.02 \(\mu\)m) also indicate the presence of a monosubstituted aromatic. The positions of these bands are approximately 1940 cm\(^{-1}\) (~5.15 \(\mu\)m), 1870 cm\(^{-1}\) (~5.35 \(\mu\)m), 1800 cm\(^{-1}\) (~5.56 \(\mu\)m), 1740 cm\(^{-1}\) (~5.75 \(\mu\)m) and 1670 cm\(^{-1}\) (~5.99 \(\mu\)m). The band due to the \(-\text{C}=\text{H}\) stretching vibration of the aliphatic group occurs between 3000–2800 cm\(^{-1}\) (3.33–3.57 \(\mu\)m). The bands due to the aliphatic CH deformation vibrations are in their typical positions.

In addition to the bands due to polystyrene, the spectrum of styrene-butadiene copolymer contains bands which may be associated with the butadiene component. A band near 1640 cm\(^{-1}\) (~6.10 \(\mu\)m), due to the \(-\text{C}=\text{C}\) stretching vibration, and strong bands near 965 cm\(^{-1}\) (~10.36 \(\mu\)m) and 910 cm\(^{-1}\) (~10.99 \(\mu\)m), due to the CH out-of-plane vibrations, are observed in the infrared spectra of this copolymer. Bands due to the different isomers of butadiene may also be observed. The cis-1,4-butadiene isomer which absorbs weakly near 730 cm\(^{-1}\) (~13.70 \(\mu\)m) is often overlooked due to the presence of the strong bands of styrene. The 1,2-isomer and the trans-1,4-isomer absorb strongly near 965 cm\(^{-1}\) (~10.36 \(\mu\)m) and 910 cm\(^{-1}\) (~10.99 \(\mu\)m). Hence, the relative proportions of the 1,2- and the trans-1,4-isomers present in the sample affect the spectral region 1000–900 cm\(^{-1}\) (10.00–11.11 \(\mu\)m).

In addition to the bands mentioned in the previous paragraph, the infrared spectra of acrylonitrile-butadiene-styrene copolymers will contain bands due to the acrylonitrile component. The additional presence of the characteristic band due to the nitrile group, which occurs near 2240 cm\(^{-1}\) (~4.46 \(\mu\)m), in a relatively band-free region of the infrared range, is a good indicator for this copolymer. It should be noted that the nitrile group gives a strong band in Raman spectra. Conformers of polycrylonitrile\(^{37}\) have been studied.

Polyvinylchloride, Polyvinylidenechloride, Polyvinylfluoride, and Polytetrafluoroethylene

The infrared spectrum of polyvinylchloride contains the bands typical of aliphatic CH groups, except that the band due to the CH\(_2\) deformation vibration is shifted by about 30 cm\(^{-1}\) to lower wavenumbers, to near 1430 cm\(^{-1}\) (~6.99 \(\mu\)m). In addition to the aliphatic CH bands, the spectra of PVC contain contributions due to the C–Cl vibrations.\(^{31}\) For example, a broad, strong band is observed in the region 710–590 cm\(^{-1}\) (14.08–16.95 \(\mu\)m) due to the C–Cl stretching vibration. Since there are a very large number of additives possible, great care needs to be taken in the analysis of PVC samples. A band near 1720 cm\(^{-1}\) (~5.81 \(\mu\)m) is often observed in the infrared spectra of commercial samples of PVC. This band may be assigned to a carbonyl group present in the plasticiser employed and hence is assigned to the C=O stretching vibration.

Polyvinylidenechloride has a strong doublet in its infrared spectrum near 1060 cm\(^{-1}\) (~9.43 \(\mu\)m) and strong bands due to the \(-\text{C}=\text{Cl}\) stretching vibrations near 660 cm\(^{-1}\) (~15.15 \(\mu\)m) and 600 cm\(^{-1}\) (~16.67 \(\mu\)m). A band of medium intensity is also observed near 1420 cm\(^{-1}\) (~7.04 \(\mu\)m) due to CH deformation vibrations.

Polyvinylfluoride has a strong band near 1085 cm\(^{-1}\) (~9.22 \(\mu\)m) due to the C=O stretching vibration. The bands near 2940 cm\(^{-1}\) (~3.40 \(\mu\)m) and 1430 cm\(^{-1}\) (~6.99 \(\mu\)m) are due to CH stretching and deformation vibrations respectively. Polytetrafluoroethylene\(^{31}\) has a strong absorption in the region 1250–1100 cm\(^{-1}\) (8.00–9.09 \(\mu\)m) apart from which the region above 650 cm\(^{-1}\) (below 15.38 \(\mu\)m) is relatively free of absorptions. The weak band near 2330 cm\(^{-1}\) (~4.29 \(\mu\)m) is due to the overtone of the CF\(_2\) stretching vibration. Polyvinylidenefluoride has a relatively weak band near 2940 cm\(^{-1}\) (~3.40 \(\mu\)m) due to the CH stretching vibration. However, the CH\(_2\) deformation vibration is stronger than might be expected. The spectrum of polyvinylidenefluoride is greatly affected by the sample preparation techniques used.
Polyesters. Polyvinylacetate

In general, the infrared spectra of all polyesters contain bands due to the ester group, that is, bands which may be associated with the carbonyl, C=O, and C–O functional groups. The positions of these bands are characteristic of the basic nature of the particular polyester. Hence, strong bands in the region 1800–1700 cm⁻¹ (5.56–5.88 μm) due to the carbonyl group and also in the region 1300–1000 cm⁻¹ (7.69–10.00 μm) are expected.

The spectrum of polyvinylacetate contains bands typical of ester groups and in particular of the acetate group. Strong bands are observed near 1740 cm⁻¹ (~5.75 μm) due to the C=O stretching vibration and 1250 cm⁻¹ (~8.00 μm) due to the asymmetric stretching of the acetate C–O–C group. Of course, bands due to the aliphatic portion of the polymer are also present in the spectrum at their typical positions. It should be noted that carbonates also have bands at the two positions mentioned above but do not have the strong band found near 1020 cm⁻¹ (~9.80 μm).

The spectra of copolymers of vinylacetate with other monomers will, of course, contain the bands of the spectra of both components superimposed in the proportions in which they are present in the copolymer.

Acrylates have two characteristic strong bands due to the C–O stretching vibration, one near 1260 cm⁻¹ (~7.94 μm) and the other near 1170 cm⁻¹ (~8.55 μm), this latter band being the stronger of the two. Polymethylmethacrylate also has an additional band near 1200 cm⁻¹ (~8.33 μm) which, together with a band near 835 cm⁻¹ (~11.98 μm), can be used to identify it. The ratio of the intensities of the CH deformation bands, which appear in the region 1470–1370 cm⁻¹ (6.80–7.30 μm), may be used to distinguish polymethylmethacrylate from polyvinylacetate (the CH₂O group may be distinguished from the CH₃ group in that the former absorbs in the region 1475–1440 cm⁻¹ (6.78–6.94 μm)). Other features which may be of assistance in this task are that polymethylmethacrylate usually has a doublet of medium intensity in the region 1500–1425 cm⁻¹ (6.67–7.02 μm), a medium-to-strong band near 1150 cm⁻¹ (~8.70 μm) and a medium-intensity band at 750–725 cm⁻¹ (~13.33–13.79 μm), which are not normally evident in spectra of polyvinylacetate. Polymethylmethacrylate has a sharp Raman band at 800 cm⁻¹ (~12.50 μm) whereas polyvinylacetate absorbs near 650 cm⁻¹ (~15.38 μm). The spectrum of polyvinylacetate is very similar to that of cellulose acetate but these two polymers may be distinguished by examination of the region below 1000 cm⁻¹ (above 10.00 μm). Polymethylmethacrylate has strong bands near 1025 cm⁻¹ (~9.76 μm) and 850 cm⁻¹ (~11.76 μm).

The infrared spectrum of polyethylene terephthalate contains a band due to the carbonyl group near 1740 cm⁻¹ (~5.75 μm) and two strong bands, typical of aromatic esters, near 1260 cm⁻¹ (~7.94 μm) and 1130 cm⁻¹ (~8.85 μm), due to the asymmetric and symmetric stretching vibrations of the C–O–C functional group. In addition, bands due to the aliphatic and aromatic portions of the polymer are present in the spectrum, most of which are in their normal positions. The strong band due to the aromatic ring out-of-plane deformation is not in its normal position for para-substituted aromatics instead it is found at slightly higher wavenumbers, 730 cm⁻¹ (~13.70 μm). This shift is attributed to an interaction of the ester group with the aromatic ring. The vibrational spectra of polyethylene terephthalate are greatly influenced by both the crystallinity and molecular orientation of the polymer. If it is not thoroughly dried, bands due to water may be observed and these may make any quantitative measurements of the end-groups, hydroxyl and carboxyl groups (~OH and –COOH) difficult. The OH and COOH groups absorb near 3450 cm⁻¹ (~2.90 μm) and 3260 cm⁻¹ (~3.07 μm) respectively. In Raman spectra, polyethylene terephthalate has a very strong band due to the aromatic component near 1000 cm⁻¹ (~10.00 μm).

Polyamides and Polyimides

The infrared spectra of polyamides have a number of bands due to the amide group. The amide I, II and III bands occur near 1640 cm⁻¹ (~6.10 μm), 1540 cm⁻¹ (~6.49 μm) and 1280 cm⁻¹ (~7.81 μm) respectively. In addition, bands of medium-to-weak intensity, due to the secondary NH group, may be observed near 3310 cm⁻¹ (~3.02 μm) and 3070 cm⁻¹ (~3.26 μm). These bands are generally broad due to the presence of hydrogen bonding. Individual aliphatic polyamides, nylons, may be identified by the careful examination of the relatively weak bands in the region 1500–900 cm⁻¹ (6.67–11.11 μm), although care is needed as the crystallinity of the polymer affects its spectrum.

Hence, for a series of aliphatic polyamides where the number of methylene groups is increased, differences in their vibrational spectra may be observed in the region 1500–900 cm⁻¹ (6.67–11.11 μm). These differences are mainly due to bands resulting from CH₂ bending, twisting and wagging vibrations and the skeletal motions of the C–C backbone. It is possible to identify particular polyamides, as with any polymer, by simply comparing a spectrum with the spectra of known examples. It is also possible to identify particular polyamides by measuring the relative intensities of bands. The bands normally used are those due to the CH₂ bending vibration at approximately 1440 cm⁻¹ (~6.94 μm) and that of the amide I band at 1640 cm⁻¹ (~6.10 μm). These two bands are used since there is a linear dependence of the ratio on the number of methylene groups present in the polyamide.

As seen, there are several types of polyamide which have different chemical structures. In addition, crystalline isomers, α-form, β-form and γ-forms, may result in slightly different spectra for a given polyamide. Hence, the identification of polyamides requires great care. It has been suggested that to identify certain simple polyamides the following band positions may be used:
polyamide-6: 1465 cm⁻¹ (≈6.83 μm), 1265 cm⁻¹ (≈7.91 μm), 960 cm⁻¹ (≈10.42 μm), 925 cm⁻¹ (≈10.81 μm)
polyamide-66: 1480 cm⁻¹ (≈6.76 μm), 1280 cm⁻¹ (≈7.81 μm), 935 cm⁻¹ (≈10.70 μm)
polyamide-610: 1480 cm⁻¹ (≈6.76 μm), 1245 cm⁻¹ (≈8.03 μm), 940 cm⁻¹ (≈10.64 μm)
polyamide-11: 1475 cm⁻¹ (≈6.78 μm), 940 cm⁻¹ (≈10.64 μm), 720 cm⁻¹ (≈13.89 μm)

In addition to the bands mentioned above, the spectra of aromatic polyamides, such as Kevlar™ and Nomex™, contain bands due to the aromatic components.

Polyimides have a characteristic doublet near 1780 cm⁻¹ (≈5.61 μm) and 1720 cm⁻¹ (≈5.81 μm) which is due to the carbonyl group of the imide ring, the latter band being broader and stronger than the former band which tends to be relatively sharp. Due to their aromatic ring nature, polyimides have a number of sharp absorptions which may be associated with CH and CC vibrations. The Raman spectra of polyimides have been studied.29

Polyvinyl Alcohol

The infrared spectra of polyvinyl alcohols contain characteristic bands due to the OH stretching vibrations near 3400 cm⁻¹ (≈2.94 μm) which is of strong intensity and due to the C=O stretching vibration near 1100 cm⁻¹ (≈9.09 μm) which is of medium-to-strong intensity. Bands are also observed due to the CH stretching and deformation vibrations near 2940 cm⁻¹ (≈3.40 μm) and 1420 cm⁻¹ (≈7.04 μm) respectively.

Polycarbonates

The infrared spectra of polycarbonates have strong characteristic bands near 1785 cm⁻¹ (≈5.60 μm) and 1250 cm⁻¹ (≈8.00 μm) due to the C=O and C–O–C stretching vibrations respectively. Aromatic polycarbonates also contain a band of medium-to-strong intensity due to CH out-of-plane vibrations indicating the presence of a p-substituted aromatic, near 860 cm⁻¹ (≈11.63 μm). Often, different aromatic polycarbonates may be identified by careful examination of the region 1100–900 cm⁻¹ (9.09–11.11 μm).

Polyethers

The spectra of aromatic and aliphatic polyethers contain bands that may be associated with the ether linkage, C–O–C. There is a strong absorption in the infrared spectra of aliphatic polyethers in the region 1150–1060 cm⁻¹ (8.70–9.43 μm) and for aromatic polyethers, 1270–1230 cm⁻¹ (7.87–8.13 μm) due to the C–O–C asymmetric stretching vibration. In Raman spectra, the aliphatic polyethers absorb strongly at 1140–820 cm⁻¹ (8.77–12.20 μm) and aromatic polyethers at 1120–1020 cm⁻¹ (8.93–9.80 μm). Of course, bands associated with the other components of the polymer, aliphatic and aromatic, are also present.

Polyetherketone and Polyetheretherketone

The chemical structure of polyetherketones is such that the functional groups, the ether and ketone, are separated in the chain by an aryl group and should properly be named poly (aryl ether ketones) and poly (aryl ether ether ketones). Polyetherketones may exist in equilibrium with water – as much as 2% water may be present in a sample – so bands due to water will normally also be observed in the spectra of polyetherketones and polyetheretherketones. For example, bands near 3650 cm⁻¹ (2.74 μm) and 3550 cm⁻¹ (2.82 μm) may be observed.

The crystallinity of polyetherketone may be determined by measurement of the relative intensities of the doublet observed due to the C=C stretching vibration24 in the Raman spectrum of the polymer. The relative intensity of the band near 1595 cm⁻¹ (≈6.27 μm) increases compared with that of the band near 1605 cm⁻¹ (≈6.23 μm) as the crystallinity of the polymer increases. The relationship of the ratio of the intensities to crystallinity appears to be linear. However, it has been found that for uniaxially-oriented polyetheretherketone, this intensity ratio is also dependent on the alignment of the sample to the laser beam.25 Other bands in the spectra of these types of polymer may be used for the determination of crystallinity.

Polyethersulphone and Polyetherethersulphone

The chemical structure of polyethersulphones is such that the functional groups, the ether and ketone, are separated in the chain by an aryl group and should properly be named poly (aryl ether sulphones) and poly (aryl ether ether sulphones).36

Polyethersulphones may exist in equilibrium with water – as much as 2% water may be present in a sample – so bands due to water will normally also be observed in the spectra of polyethersulphones and polyetherethersulphones. For example, bands near 3650 cm⁻¹ (2.74 μm) and 3550 cm⁻¹ (2.82 μm) may be observed.

The relative compositions of copolymers of polyethersulphone and polyetherethersulphone can be determined.28 Polysulphones are amorphous
and hence there are no changes due to crystallinity to result in problems determining relative compositions. In Raman spectra, the intensity ratio of the components of the doublet near 1600 cm\(^{-1}\) (\(~6.25\mu m\)) is related to the composition of the copolymer. The ratio of the intensities of bands near 1200 cm\(^{-1}\) (\(~8.33\mu m\)) and 1070 cm\(^{-1}\) (\(~9.35\mu m\)) may be used in a similar way.

**Polyconjugated Molecules**

Polyconjugated systems have been studied in undoped, doped (with electron donors or acceptors) and photoexcited states. The spectra obtained for a particular polymer in these three different states are quite different. Some of the spectral features observed are common to all polyconjugated polymers in these different states. Some of the features are related to the existence of a network of delocalised \(\pi\) electrons which can be considered to be along a one-dimensional lattice. An important parameter which affects the spectral features observed is the conjugation length. As might be expected for polyconjugated polymers, as with most polymers, stretch-oriented samples in the different states exhibit dichroism. Various polyconjugated systems have been studied – polyacetylene, polythiophene, phenylpolyene, etc.

The infrared spectra of undoped polymers do not show unusual features. Their spectra may be interpreted in the normal way by using group frequency correlations or vibrational analysis. In general, the vibrational frequencies of groups are independent of the number of mers in an oligomer. As the number of mers is increased, the spectra become simpler, since the relative intensity of the bands due to the end-groups decreases compared with those due to the majority of units in the chain ‘core’. The chain length may be determined by measuring the ratio of the intensities of bands due to vibrations from these two types of group – end and core. Doped and photoexcited systems exhibit dichroism.

The Raman spectra\(^6\) of undoped polyconjugated polymers, such as polyacetylenes, are simple – in general, only a few bands are observed. These bands are due to the C=C stretching vibration, which occurs in the region 1500–1400 cm\(^{-1}\) (6.67–7.14 \(\mu m\)), and have a relatively strong intensity, and bands due to C=C and CH wagging vibrations, which are observed in the approximate region 1200–900 cm\(^{-1}\) (8.33–11.11 \(\mu m\)). In general, the strongest bands in the Raman spectra exhibit some degree of dispersion.\(^{11}\) For polyconjugated systems, the Raman scattering cross-sections of some groups have been observed to increase rapidly with increase in the number of conjugated units.\(^{5}\) For polyconjugated systems, the Raman scattering cross-sections of some groups have been observed to increase rapidly with increase in the number of conjugated units.\(^{10}\)

The infrared and Raman spectra of doped or photoexcited polyconjugated systems are very different from those of the equivalent undoped material.\(^{6,7}\) New bands which are extremely strong and complex are observed. These new bands result in a broad, poorly-defined pattern in the region 1600–700 cm\(^{-1}\) (6.25–14.29 \(\mu m\)). The position (frequency) of the bands in the infrared spectra of doped samples appears to be independent of the doping species,\(^{13}\) although band intensities may decrease with increased doping level. The frequencies of vibrations do not appear to alter with concentration of the doping species.\(^{13}\) In a few oligomers, the frequency of some bands observed in the spectra of doped species and photoexcited species decrease with increase in the number of conjugated units.

In general, it has been found that the infrared spectra of photoexcited and doped materials are very similar. It has been found that for some samples, for example \(\text{trans-polyacetylene}\), bands in the spectrum of the photoexcited species experience a red-shift with respect to the doped material. In general, however, the spectra of the two are almost identical. Very slightly doped materials usually have very similar Raman spectra to those of the equivalent undoped system. The Raman spectra of doped and photoexcited species usually have broad, weak bands and are often not observed unless resonance enhancement conditions can be achieved. For example, for polyacetylene,\(^{15}\) at large doping levels, new bands appear near 1600 (\(~6.25\mu m\)) and 1270 cm\(^{-1}\) (\(~7.87\mu m\)). At very high doping levels, some characteristic bands of undoped polyacetylene become weak and Raman scattering becomes weak.

The vibrational spectra of polyconjugated systems can only be interpreted by taking both the molecular structure and the electronic structure (\(\pi\) electrons) into account.

Polyacetylene in the \(\text{cis}\)-form undergoes a solid state thermal isomerisation to give the \(\text{trans}\)-isomer. The infrared spectra of the \(\text{cis-}\) and \(\text{trans}\)-isomers are quite different.\(^{6}\) The out-of-plane CH vibration of the \(\text{cis}\)-isomer results in a strong band which occurs near 735 cm\(^{-1}\) (\(~13.61\mu m\)) at room temperature. When time-dependent spectroscopy is used to examine the \(\text{cis}\)-isomer at an elevated temperature, this band is observed to decrease in intensity with time and move to slightly higher wavenumbers, approximately +7 cm\(^{-1}\). Similarly, the \(\text{trans}\)-isomer, which has its out-of-plane CH vibration near 1015 cm\(^{-1}\) (\(~9.85\mu m\)), when examined at elevated temperature, increases in intensity and moves to lower wavenumbers, approximately −5 cm\(^{-1}\). Other bands in the spectra of these \(\text{cis-}\) and \(\text{trans}\)-isomers are also observed to change position slightly.

**Resins**

The infrared spectra of phenol formaldehyde resins have a broad, strong band at about 3350 cm\(^{-1}\) (\(~2.99\mu m\)) due to the OH stretching vibration of the phenolic group. Another strong band is observed near 1230 cm\(^{-1}\) (\(~8.13\mu m\)) due to the C-O stretching vibration. A doublet is usually observed at 1600 cm\(^{-1}\) (\(~6.25\mu m\)) due to a stretching vibration of the aromatic ring. Strong bands are also observed in the infrared spectra of phenol formaldehyde...
resins at about 760 cm⁻¹ (~13.16 μm) and 820 cm⁻¹ (~12.20 μm) due to the aromatic CH out-of-plane vibrations. These last two bands indicate that the aromatic ring has formed both ortho and para bonds. Novolak resins have only one strong band in their infrared spectra in the region 900–730 cm⁻¹ (11.11–13.70 μm), this occurring at about 760 cm⁻¹ (~13.16 μm).

Uncured resole resins have a strong band near 1010 cm⁻¹ (~9.90 μm) due to the CO stretching vibration of the methyol group. As curing takes place, the intensity of this band decreases. Care needs to be exercised, as hexamine, which is often used as the cross-linking agent, has a weak absorption in the same region.

The infrared spectra of melamine–formaldehyde resins contain a band due to the OH stretching vibration near 3350 cm⁻¹ (~2.99 μm), a strong, broad band near 1560 cm⁻¹ (~6.41 μm), principally due to the stretching motions of the triazine ring, a broad, medium-strong band near 1040 cm⁻¹ (~9.62 μm), due to the C–O stretching vibration, and a band near 820 cm⁻¹ (~6.41 μm), again due to the triazine ring. The infrared spectra of urea–formaldehyde have a broad, strong band at about 3350 cm⁻¹ (~2.99 μm) due to the OH stretching vibration, a broad, strong band near 1570 cm⁻¹ (~6.32 μm), a strong band near 1040 cm⁻¹ (~9.62 μm), due to the C–O stretching vibration and a broad band near 625 cm⁻¹ (~16.00 μm).

Coatings and Alkyd Resins

For environmental and other reasons, these days, many coatings/paints are water based. This means that coatings must either be first dried or cells with water-stable windows must be used if infrared spectra are required. In addition, large regions in which water absorbs strongly may obscure sample bands that need to be observed. Heavy water can be used to expose the regions in which the water bands cause concern but this, in general, is not helpful if commercial samples need to be examined. On the other hand, water is not a problem if Raman spectra can suffice. Polymerisation and curing reactions may be followed spectroscopically.

With dried coatings, reflection techniques can be employed to obtain infrared spectra. An emulsion or latex can be examined by similar techniques to those described above. Solvent-based coatings can be examined either directly in liquid cells or as dried films. Usually the evaporation of the solvent can be monitored spectroscopically. Alkyd resins which are solvent based still form a substantial part of the commercially available coatings. The band due to the C=C stretching vibration may be used to follow the curing process.

Elastomers

Elastomers³⁰,³⁶,⁵⁶ present numerous problems with regard to the acquisition of vibrational spectra. For infrared spectra, special techniques must be used for sample preparation. In the past, using Raman, fluorescence has restricted the number of elastomers and the manner in which they could be studied. It was only for pure, unvulcanized elastomers that spectra could be obtained. Certainly, near infrared Fourier transform Raman spectrometers have helped resolve these difficulties. Of course, samples containing high proportions of carbon black can still present problems, especially with regard to Raman spectra. In the case of Raman spectroscopy, the absorption of the laser excitation source by the carbon can lead to rapid heating of the sample and degradation of the elastomer or, when a spectrum is obtained, a high baseline is observed, resulting in a poor spectrum where weak bands are lost.

It should be borne in mind that the cooling or stretching of certain elastomers can lead to crystallisation. Hence, the morphology of such samples can be studied using vibrational spectroscopy.

When spectra can be obtained by Raman, the bands due to the groups C=C and S=S, which occur in many elastomers, are strong and easy to observe. The band due to the C=C stretching vibration occurs near 1600 cm⁻¹ (~20.83 μm) and that due to the S=S stretching vibration occurs near 480 cm⁻¹ (~20.83 μm). By making use of Raman spectroscopy, it is possible to study vulcanisation and identify different types of sulphur linkage, for example disulphide, polysulphide, thioalkane and thioalkene.

Polyisobutylene⁵⁸ has a strong, sharp band near 1220 cm⁻¹ (~9.20 μm) and a characteristic absorption due to the two CH₃ groups, near 1385 cm⁻¹ (~9.20 μm) and 1365 cm⁻¹ (~7.33 μm).

Silicone rubbers have a very strong, broad absorption in their infrared spectra at 1100–1000 cm⁻¹ (9.09–10.00 μm) due to the Si–O–Si stretching vibration. The band may be split into two broad peaks. The symmetric CH₃Si deformation vibration occurs at 1265 cm⁻¹ (~7.91 μm) and, because it is strong and sharp, it is easily identified even in the presence of other functional groups/substances. Another useful band occurs near 810 cm⁻¹ (~12.35 μm) and is due to the Si–C stretching vibration and CH₃ deformation vibration. The OH group, which is found in some silicone rubbers, absorbs near 3340 cm⁻¹ (~2.99 μm) due to the O–H stretching vibration. The Si–O stretching vibration results in a broad band in the region 900–835 cm⁻¹ (11.11–11.98 μm). However, this band may be obscured by bands associated with the SiCH₃ group.

Plasticisers

Strongest Band(s) in the Infrared Spectrum

In this section, the characteristics bands are given for various common polymer plasticisers.
Observed throughout the spectrum will be dependent on the composition of the copolymer. These days, the hazardous nature of certain chlorinated aromatic hydrocarbons is known.

Characteristic Absorption Patterns of Functional Groups Present in Plasticisers The characteristic absorption patterns of some common functional groups that appear in plasticisers are discussed below.

Carbonyl groups Carbonyl groups in one chemical form or another are commonly found in many plasticisers. Plasticisers containing carbonyl groups are discussed below.

Carboxylic acids Ether extracts often contain carboxylic acids either as free acids or as salts. The carboxyl group absorbs strongly near 1700 cm\(^{-1}\) (~5.88 \(\mu\)m) and has a broad band due to the OH stretching vibration. In addition, as most plasticisers are long chain aliphatic acids, a band is observed near 2940 cm\(^{-1}\) (~3.40 \(\mu\)m), due to CH stretching. In the case of high molecular weight aliphatic acids which are obtained in a reasonably pure state, their spectra are quite distinctive. The principal differences occur in the region 1280–1180 cm\(^{-1}\) (7.81–8.47 \(\mu\)m), where they have weak absorptions, and these differences may be used for identification purposes. For example, the infrared spectrum of lauric acid has three weak, clear, sharp bands in this region whereas that of stearic acid has five weak bands in this region.

Carboxylic acid salts In their infrared spectra, carboxylic acid salts have two relatively strong bands near 1590 cm\(^{-1}\) (~6.29 \(\mu\)m) and 1410 cm\(^{-1}\) (~7.09 \(\mu\)m). The position and shape of the band near 1590 cm\(^{-1}\) (~6.29 \(\mu\)m) is dependent on the anion but there is little to recommend infrared as a means of identifying the metal anion by this method as there are simpler and more positive methods, such as atomic emission spectroscopy.

Care should be exercised with o-hydroxyl benzophenone, as it has a strong, broad absorption in its infrared spectrum near 1590 cm\(^{-1}\) (~6.29 \(\mu\)m) but no strong absorption near 1410 cm\(^{-1}\) (~7.09 \(\mu\)m), with a hydroxyl band near 3340 cm\(^{-1}\) (~2.99 \(\mu\)m) also being observed, in addition to the aromatic bands.

Ortho-Phthalates Phthalates absorb at the positions give in the table below, Table 21.1. It should be borne in mind that some solvent extracts from polymeric samples may be due to the presence of o-phthalate resins rather than plasticisers.

Since o-phthalates have a very distinctive infrared spectrum, they are easily recognised. If, in the infrared spectrum of a sample, there are no additional bands having a significant intensity in the region 1500–600 cm\(^{-1}\) (6.67–16.67 \(\mu\)m) then the substance is a simple alkyl phthalate. In a relatively
pure state, the lower members of the alkyl series can be distinguished by careful examination of the weak bands in the region 1000–835 cm\(^{-1}\) (10.00–11.11 \(\mu\)m). Examples of these simple alkyl phthalates are dimethyl, diethyl, di-\(n\)-butyl, ... di-sec-octyl etc. The higher alkyl esters are difficult to identify unambiguously unless they possess some significant structural feature. For example, phthalates containing a gem-dimethyl group have a doublet due to the \(CH_2\) deformation vibrations at 1385–1365 cm\(^{-1}\) (7.22–7.25 \(\mu\)m). Hence, in general, the esters of higher members of the alkyl series are more difficult to identify by infrared alone. They usually have a single broad band in the region 950 cm\(^{-1}\) (~10.53 \(\mu\)m).

In addition to the usual bands in the region 1000–900 cm\(^{-1}\) (10.00–11.11 \(\mu\)m), di-alkyl phthalate has a sharp band near 1650 cm\(^{-1}\) (~6.06 \(\mu\)m) due to the \(C=O\) stretching vibration.

The infrared spectra of samples exhibiting the normal distinctive \(\alpha\)-phthalate pattern but, in addition, possessing sharp weak bands in the region 1110–835 cm\(^{-1}\) (9.01–11.98 \(\mu\)m) may be associated with the alicyclic esters. For example, the spectra of cyclohexyl esters possess a number of sharp bands of medium intensity in the region 1430–715 cm\(^{-1}\) (6.99–13.99 \(\mu\)m).

Phthalates derived from aromatic alcohols or phenols, such as diphenyl phthalate and dibenzyl phthalate, are relatively easy to distinguish. In addition to the \(\alpha\)-phthalate pattern, their infrared spectra also contain bands due to the aromatic substitution pattern in the region 835–670 cm\(^{-1}\) (11.98–14.93 \(\mu\)m) and the band due to \(CH\) stretching vibration near 2940 cm\(^{-1}\) (~3.40 \(\mu\)m) is very weak, especially when compared with the relative band intensity at this position for the alkyl phthalates. However, the possibility of mixed alkyl–aryl esters should be borne in mind when considering the band near 2940 cm\(^{-1}\) (~3.40 \(\mu\)m) – for example, butyl benzyl phthalate has a band of medium intensity due to the \(CH\) stretching vibration. In the case of this phthalate, the region, 1000–900 cm\(^{-1}\) (10.00–11.11 \(\mu\)m) may be examined for bands characteristic of the butyl group.

The infrared spectra of complex phthalates possess the characteristic \(\alpha\)-phthalate bands but, in addition, usually have strong bands in the region 1430–1000 cm\(^{-1}\) (6.99–10.00 \(\mu\)m). For example, the spectra of alkyl phthalyl alkyl glycollates, such as methyl phthalyl methyl glycollate, have a strong near 1200 cm\(^{-1}\) (~8.33 \(\mu\)m) due to the \(C=O\) stretching vibration. It should be noted that this band appears near 1160 cm\(^{-1}\) (~8.62 \(\mu\)m) for simple mixtures of phthalates with aliphatic esters. In the case of some glycol phthalates, one hydroxyl group is esterified with phthalic acid and the other hydroxyl group is condensed with an aliphatic alcohol to form an ether, for example di-methoxy ethyl phthalate. The \(C=O\)--\(C=O\) stretching vibration results in an additional band of medium-to-strong intensity near 1125 cm\(^{-1}\) (~8.62 \(\mu\)m). This band is, generally, narrower and at higher wavenumbers than those of simple alkyl ethers.

**Aliphatic esters** Although the infrared spectra of aliphatic esters allow them to be distinguished from other carbonyl-containing compounds, it is often difficult to differentiate between esters which are similar in chemical structure. It is not sufficient to compare the spectrum of an unknown with that of a reference and thus to conclude, because the spectra are similar, even after careful attention to the positions and relative intensities of bands, that an identification has been positively made. It is often necessary to carry out hydrolysis of the sample and to examine the alcohol and acid fragments separately, or, alternatively, another spectroscopic technique may be used to identify the ester directly.

All long chain aliphatic esters have a band near 725 cm\(^{-1}\) (~13.79 \(\mu\)m) which may, in some samples, appear as doublet. Typical compounds are ethyl palmitate and glyceryl di-stearate. Both of these substances exhibit a band near 3340 cm\(^{-1}\) (~2.99 \(\mu\)m) due to the presence of hydroxyl groups. The observation of this band is useful in that esters derived from poly-functional alcohols generally exhibit this absorption.

Plasticisers containing the acetyl group, such as glyceryl triacetate, have a strong band in their infrared spectra near 1230 cm\(^{-1}\) (~8.13 \(\mu\)m). Esters containing the epoxy group have a band, often a doublet, of weak-to-medium intensity near 835 cm\(^{-1}\) (~11.98 \(\mu\)m).

The spectra of different esters based on the same dibasic, such as alkyl adipates or sebacates, are very similar. Replacing the alcohol, in the case of simple low molecular weight alcohols, has a greater effect on the infrared spectrum than changing the acid.

As mentioned above, \(\alpha\)-phthalate esters also containing an ether linkage normally exhibit a medium-to-strong band near 1125 cm\(^{-1}\) (~8.89 \(\mu\)m). Other plasticisers containing the aliphatic ester group and the ether group, for
Infrared and Raman Characteristic Group Frequencies

example those based on di- and tri-ethylene glycol and monocarboxylic acids, have a broad absorption due to the ether C–O–C stretching vibration near 1110 cm⁻¹ (~9.01 μm). In this latter case, the absorption is similar to that observed for polyethylene oxide derivatives.

Some plasticisers based on dicarboxylic acids may not only be esters but also salts. The infrared spectra of these plasticisers obviously contain the bands associated with both esters and carboxylic acid salts. This means that it is difficult to distinguish between a compound and a mixture of an ester and salt. In a similar fashion, it is difficult to distinguish between plasticisers based on dicarboxylic acids and diols and polyesters based on similar compounds. There are no easily recognisable spectral features to distinguish between monomeric esters and an equivalent polyester.

Aromatic esters

The most common plasticisers based on aromatic esters are benzoates of one type or another. The infrared spectra of benzoates all have a strong band near 715 cm⁻¹ (~13.99 μm). Another reasonably common type of aromatic ester is that based on salicylic acid. The spectra of salicylates, in common with other aromatic compounds which have a hydroxyl group adjacent to a carbonyl group (i.e. at the ortho position), do not have the band near 3340 cm⁻¹ (~2.99 μm).

Sulphonamides, sulphones and sulphonates

Sulphonamides are easily recognised by the strong bands in their infrared spectra near 1315 cm⁻¹ (~7.60 μm) and 1165 cm⁻¹ (~8.58 μm). Different sulphonamides may be distinguished by the number bands, positions and intensities, in the region 850–650 cm⁻¹ (11.76–15.38 μm). In addition, N-substituted sulphonamides have bands associated with NH rather than NH₂, the band-structure of the former being simpler (see the chapter dealing with amines).

Sulphonic acid esters

Alkyl aryl sulphonic acid esters, such as ethyl p-toluene sulphonate, have two strong characteristic bands near 1350 cm⁻¹ (~7.41 μm) and 1180 cm⁻¹ (~8.47 μm) in their infrared spectra. Aryl esters of alkyl sulphonic acids normally have a strong absorption near 865–650 cm⁻¹ (11.56–15.38 μm) due to aromatic CH out-of-plane deformation vibrations and in this respect their spectra are similar to those of ary1 sulphonamides but, of course, sulphonamides have additional bands due to their NH stretching vibrations.

Characteristic Bands of Other Commonly Found Substances

The solvent extracts of resins may contain antioxidants, some of which may be based on aromatic amines, examples of antioxidants being derivatives of diphenyl amine and p-phenylene diamine. These substances have spectra which are similar to those of sulphonamides. They have one or two bands due to NH or NH₂ stretching vibrations respectively near 3340 cm⁻¹ (~2.99 μm) and a strong band near 1300 cm⁻¹ (~7.69 μm). However, since these compounds do not have the second strong band near 1165 cm⁻¹ (~8.58 μm), this is a reliable way of distinguishing between them and sulphonamides.

Sulphates and sulphonates have strong absorptions in their infrared spectra between 1250 and 1110 cm⁻¹ (8.00–9.01 μm).

A strong band near 3340 cm⁻¹ (~2.99 μm), with one or more strong bands near 1250 cm⁻¹ (~8.00 μm), indicates a possible phenolic constituent. It should be borne in mind that epoxy compounds, which are often extracted from resins, have spectra similar to those of phenols. Since they are usually of low molecular weight and have only terminal hydroxyl groups, the O–H stretching vibration band near 3340 cm⁻¹ (~2.99 μm) is usually of moderate intensity. In addition, it should be noted that p-aromatic epoxy compounds have a prominent band near 835 cm⁻¹ (~11.98 μm).

Common Inorganic Additives and Fillers

The inorganic chapter of this book, and some earlier chapters, should also be studied for relevant information concerning many of the inorganic additives and fillers commonly found in polymers. The chapters dealing with silicon, boron and phosphorus may also contain information relevant to the inorganic compounds found in a particular polymer of interest. As mentioned earlier and in the Inorganic chapter, Raman spectroscopy is particularly useful in the characterisation of inorganic compounds that are commonly found in commercial polymer samples.

Carbonates

The infrared spectra of inorganic carbonates consist of a strong broad band at 1530–1320 cm⁻¹ (6.54–7.58 μm) (which in Raman is of weak-to-medium intensity and is often found near 1450 cm⁻¹ (~6.90 μm)), a band of medium intensity near 1160 cm⁻¹ (~9.62 μm), a weak band at 1100–1040 cm⁻¹ (9.09–9.62 μm) (which is of strong-to-medium intensity in Raman), a band of medium intensity at 890–800 cm⁻¹ (11.24–12.50 μm) and a band of variable intensity at 745–670 cm⁻¹ (13.42–14.93 μm) (which is of weak intensity in Raman). For calcium carbonate, a strong Raman band is observed near 1085 cm⁻¹ (~9.26 μm).
Table 21.2 Calcium carbonate

<table>
<thead>
<tr>
<th>Functional Groups</th>
<th>Region cm⁻¹</th>
<th>Intensity μm</th>
<th>IR</th>
<th>Raman</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCO₃</td>
<td>2530-2500</td>
<td>3.95-4.00</td>
<td>w</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1815-1770</td>
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<td>vs</td>
<td>m-s</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1495-1410</td>
<td>6.69-7.09</td>
<td>m</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>~1160</td>
<td>~8.62</td>
<td>m</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>1090-1080</td>
<td>9.17-9.26</td>
<td>w</td>
<td>s</td>
<td>May be absent</td>
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<tr>
<td></td>
<td>885-870</td>
<td>11.30-11.49</td>
<td>m-s</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>860-845</td>
<td>11.63-11.83</td>
<td>m</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>~715</td>
<td>~13.99</td>
<td>m-w</td>
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<tr>
<td></td>
<td>705-695</td>
<td>14.18-14.39</td>
<td>m-w</td>
<td></td>
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<tr>
<td></td>
<td>~330</td>
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<tr>
<td></td>
<td>~230</td>
<td>~43.48</td>
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<td>Sharp</td>
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</table>

**Sulphates**

In the infrared, sulphates have medium-intensity bands at 1200-1140 cm⁻¹ (8.33-8.77 μm) and 680-580 cm⁻¹ (14.71-17.42 μm) (these bands are of medium-to-strong intensity in Raman). A strong band at 1130-1080 cm⁻¹ (8.85-9.26 μm) (which is of medium-to-strong intensity in Raman) and weak bands at 1065-955 cm⁻¹ (9.39-10.47 μm) and 530-405 cm⁻¹ (18.87-22.49 μm) (in Raman these bands are both of strong intensity). The Raman spectrum of barium sulphate has a strong band near 985 cm⁻¹ (~10.15 μm) and weak bands near 1160 cm⁻¹ (~8.62 μm), 1135 cm⁻¹ (~8.81 μm), 645 cm⁻¹ (~15.50 μm), 615 cm⁻¹ (~16.26 μm), 460 cm⁻¹ (~21.74 μm) and 450 cm⁻¹ (~22.22 μm).

Table 21.3 Barium sulphate

<table>
<thead>
<tr>
<th>Functional Groups</th>
<th>Region cm⁻¹</th>
<th>Intensity μm</th>
<th>IR</th>
<th>Raman</th>
<th>Comments</th>
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<td>~6.06</td>
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<td>~6.80</td>
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<td></td>
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<td>m-s</td>
<td>Sharp</td>
</tr>
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<td>8.85-9.01</td>
<td>vs</td>
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<td></td>
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<td>m-w</td>
<td>s</td>
<td>Doublet</td>
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<td>640-630</td>
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<td>615-605</td>
<td>16.26-16.53</td>
<td>m-w</td>
<td>m-s</td>
<td></td>
</tr>
<tr>
<td></td>
<td>~460</td>
<td>~21.74</td>
<td>w</td>
<td>w</td>
<td></td>
</tr>
<tr>
<td></td>
<td>~415</td>
<td>~24.10</td>
<td>w</td>
<td>w</td>
<td></td>
</tr>
</tbody>
</table>

**Talc**

Talc has strong bands at 1030-1005 cm⁻¹ (9.71-9.95 μm), 675-665 cm⁻¹ (14.81-15.04 μm), 540-530 cm⁻¹ (18.52-18.87 μm) and 455-445 cm⁻¹ (21.98-22.47 μm).

**Clays**

Most clays usually have strong bands in the region 3670-3600 cm⁻¹ (2.72-2.78 μm), 3450-3400 cm⁻¹ (2.90-2.94 μm) and 500-450 cm⁻¹ (20.00-22.22 μm), a very strong band at 1075-1050 cm⁻¹ (9.30-9.52 μm), a band of medium-to-weak intensity near 1640 cm⁻¹ (~6.10 μm), a band at 945-905 cm⁻¹ (10.58-11.05 μm), a weak band at 885-800 cm⁻¹ (11.30-12.50 μm) and a band of variable intensity at 440-420 cm⁻¹ (22.73-23.81 μm).

Kaolin normally contains water of crystallisation and as a result has a distinctive absorption pattern in the infrared near 3600 cm⁻¹ (~2.78 μm).

Table 21.4 Talc

<table>
<thead>
<tr>
<th>Functional Groups</th>
<th>Region cm⁻¹</th>
<th>Intensity μm</th>
<th>IR</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Talc</td>
<td>~3685</td>
<td>~2.71</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>~3675</td>
<td>~2.72</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>~3660</td>
<td>~2.73</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1640-1620</td>
<td>6.10-6.17</td>
<td>w</td>
<td>Sharp</td>
</tr>
<tr>
<td></td>
<td>1050-1040</td>
<td>9.52-9.61</td>
<td>vs</td>
<td>Broad</td>
</tr>
<tr>
<td></td>
<td>1030-1005</td>
<td>9.71-9.95</td>
<td>vs</td>
<td>Broad</td>
</tr>
<tr>
<td></td>
<td>785-760</td>
<td>12.74-12.99</td>
<td>w</td>
<td></td>
</tr>
<tr>
<td></td>
<td>~740</td>
<td>~13.51</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>760-740</td>
<td>14.29-14.49</td>
<td></td>
<td>Sharp</td>
</tr>
<tr>
<td></td>
<td>675-665</td>
<td>14.81-15.04</td>
<td>s</td>
<td></td>
</tr>
<tr>
<td></td>
<td>540-530</td>
<td>18.52-18.87</td>
<td>s</td>
<td></td>
</tr>
<tr>
<td></td>
<td>~500</td>
<td>~20.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>475-455</td>
<td>21.05-21.98</td>
<td>m</td>
<td>Sharp</td>
</tr>
<tr>
<td></td>
<td>455-445</td>
<td>21.98-22.47</td>
<td>vs</td>
<td></td>
</tr>
<tr>
<td></td>
<td>~440</td>
<td>~22.73</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>~425</td>
<td>~23.53</td>
<td>m</td>
<td>Sharp</td>
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Table 21.5 Kaolin

<table>
<thead>
<tr>
<th>Functional Groups</th>
<th>Region cm⁻¹</th>
<th>Intensity μm</th>
<th>IR</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaolin</td>
<td>3710-3695</td>
<td>2.69-2.71</td>
<td>s</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3670-3650</td>
<td>2.72-2.74</td>
<td>m-s</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3655-3645</td>
<td>2.74-2.74</td>
<td>v</td>
<td>Usually s</td>
</tr>
<tr>
<td></td>
<td>3630-3620</td>
<td>2.75-2.76</td>
<td>m-s</td>
<td></td>
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<tr>
<td></td>
<td>1650-1640</td>
<td>6.06-6.10</td>
<td>w</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1120-1090</td>
<td>8.93-9.17</td>
<td>s</td>
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<tr>
<td></td>
<td>1050-1000</td>
<td>9.52-10.00</td>
<td>s</td>
<td></td>
</tr>
<tr>
<td></td>
<td>960-935</td>
<td>10.42-10.70</td>
<td>m</td>
<td>Sharp</td>
</tr>
<tr>
<td></td>
<td>920-905</td>
<td>10.87-11.05</td>
<td>s</td>
<td>Sharp</td>
</tr>
<tr>
<td></td>
<td>800-780</td>
<td>12.50-12.82</td>
<td>w</td>
<td></td>
</tr>
<tr>
<td></td>
<td>760-745</td>
<td>13.16-13.42</td>
<td>w</td>
<td></td>
</tr>
<tr>
<td></td>
<td>700-685</td>
<td>14.29-14.60</td>
<td>m</td>
<td></td>
</tr>
<tr>
<td></td>
<td>~605</td>
<td>~16.53</td>
<td>w</td>
<td></td>
</tr>
<tr>
<td></td>
<td>550-515</td>
<td>18.18-19.42</td>
<td>s</td>
<td></td>
</tr>
<tr>
<td></td>
<td>475-460</td>
<td>21.05-21.74</td>
<td>s</td>
<td></td>
</tr>
<tr>
<td></td>
<td>435-415</td>
<td>22.99-24.10</td>
<td>s</td>
<td></td>
</tr>
<tr>
<td></td>
<td>~345</td>
<td>~28.99</td>
<td>w</td>
<td></td>
</tr>
<tr>
<td></td>
<td>~275</td>
<td>~36.36</td>
<td>w</td>
<td></td>
</tr>
<tr>
<td></td>
<td>~200</td>
<td>~50.00</td>
<td>w</td>
<td></td>
</tr>
<tr>
<td></td>
<td>~190</td>
<td>52.63</td>
<td>w</td>
<td></td>
</tr>
</tbody>
</table>

**Titanium Dioxide**

Titanium dioxide has strong absorptions at 700-660 cm⁻¹ (14.29-15.15 μm) and 525-460 (19.05-21.74 μm), a medium-to-strong intensity band at 360-320 cm⁻¹ (27.78-31.25 μm) and weak bands at 185-170 cm⁻¹ (54.05-58.82 μm) and 100-80 cm⁻¹ (100.00-125.00 μm). The region below 200 cm⁻¹ (above 50 μm), which is easily accessible in Raman, can be used to distinguish between rutile and anatase.

**Silica**

Table 21.6 Silica

<table>
<thead>
<tr>
<th>Functional Groups</th>
<th>Region cm⁻¹</th>
<th>Intensity μm</th>
<th>IR</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica</td>
<td>1225-1200</td>
<td>8.16-8.33</td>
<td>m-w</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1175-1150</td>
<td>8.51-8.70</td>
<td>m-w</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1100-1075</td>
<td>9.09-9.30</td>
<td>vs</td>
<td></td>
</tr>
<tr>
<td></td>
<td>805-785</td>
<td>12.42-12.74</td>
<td>m</td>
<td></td>
</tr>
</tbody>
</table>

**Antimony Trioxide**

Antimony trioxide has strong absorption bands at 770-740 cm⁻¹ (12.99-13.51 μm) and 385-355 cm⁻¹ (25.97-28.17 μm), a medium-to-weak intensity band at 415-395 cm⁻¹ (24.10-25.32 μm) and a weak band at 200-180 cm⁻¹ (50.00-54.05 μm).

**Infrared Flowcharts**

The flowcharts given below have been based on strong bands, bands which occur in relatively interference free regions, or bands that are easy to identify. However, in using the flowcharts, it should be borne in mind that the spectra of polymers may differ from those on which the flowcharts have been based. This is especially true where copolymers are concerned.
copolymers, the spectra observed are dependent on the percentages of the individual components present. For example, some styrene-butadiene copolymers contain certain small amounts of acrylonitrile, this resulting in a band near 2220 cm⁻¹ (4.50 μm). The presence of the band near 2220 cm⁻¹ (4.50 μm) could be misleading. It should also be borne in mind that polymers prepared by different methods, or using different catalysts, may have slightly different spectra.

If polymers are examined spectroscopically without removing additives such as fillers, plasticisers, stabilisers, lubricants, etc., then their infrared spectra may be affected drastically by the presence of these substances. Also, if care has not been taken during the preparation of a sample, bands due to contaminants such as water, silicate, phthalates, polypropylene (from laboratory ware), etc., may appear in the spectra and so result in some confusion. Hence, the flowcharts given below should be used with some degree of caution. In order to confirm an assignment made by use of the flow chart, it is important finally to make use of known infrared reference spectra. However, it should be borne in mind that stereoregular polymers may have spectra which differ from their atactic form and that sample preparative techniques may also affect the spectrum obtained for a particular polymeric sample.

**Table 21.8** List of polymers used in flowcharts

<table>
<thead>
<tr>
<th>Name</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acrylonitrile–butadiene–styrene</td>
<td>ABS</td>
</tr>
<tr>
<td>Alkyd resin - aliphatic</td>
<td>ALK-A</td>
</tr>
<tr>
<td>Alkyd resin - aromatic</td>
<td>ALK-AR</td>
</tr>
<tr>
<td>Aramide</td>
<td>AR</td>
</tr>
<tr>
<td>Butadiene acrylonitrile (Nitrile rubber)</td>
<td>NBR</td>
</tr>
<tr>
<td>Butyl rubber</td>
<td>BUTYL</td>
</tr>
<tr>
<td>Cellulose film</td>
<td>CF</td>
</tr>
<tr>
<td>Cellulose acetate</td>
<td>CA</td>
</tr>
<tr>
<td>Cellulose ether modified Ar</td>
<td>CE-M</td>
</tr>
<tr>
<td>Cellulose ether</td>
<td>CE</td>
</tr>
<tr>
<td>Cellulose nitrate</td>
<td>CN</td>
</tr>
<tr>
<td>Epoxy</td>
<td>EP</td>
</tr>
<tr>
<td>Epoxy – Aliphatic</td>
<td>EP-A</td>
</tr>
<tr>
<td>Epoxy – Aromatic</td>
<td>EP-AR</td>
</tr>
<tr>
<td>Epoxy – Aromatic (Modified)</td>
<td>EP-M</td>
</tr>
<tr>
<td>Ethyl cellulose</td>
<td>EC</td>
</tr>
<tr>
<td>Ethylacrylate acrylonitrile</td>
<td>EAAAN</td>
</tr>
<tr>
<td>Ethylene vinylacetate</td>
<td>EVA</td>
</tr>
<tr>
<td>Ethylene polysulphone</td>
<td>EPS</td>
</tr>
<tr>
<td>Ionomer</td>
<td>ION</td>
</tr>
<tr>
<td>Melamine–formaldehyde</td>
<td>MF</td>
</tr>
<tr>
<td>Methyl cellulose</td>
<td>MC</td>
</tr>
</tbody>
</table>

*Chart 21.1* Infrared – polymer flowchart I

Yes → Strong band 1810–1700 cm⁻¹?  
No → Absorption at ~3010 & bands at ~1600, ~1590 and 1495 cm⁻¹?  
Yes → Strong broad band ~830 cm⁻¹?  
No → Medium intensity, sharp band ~430 cm⁻¹?  
Yes → PVC-PVA Sharp band ~2220 cm⁻¹?  
No → PC-A, EAAAN, PMCA  
Yes → Band ~1800 cm⁻¹?  
No → UP-A  
Yes → UP-A, Strong band ~1800 cm⁻¹?  
No → PC-A, PAMMA, PEA, PVA

*Table 21.8 (continued)*

<table>
<thead>
<tr>
<th>Name</th>
<th>Abbreviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neoprene</td>
<td>NP</td>
</tr>
<tr>
<td>Nitrated polystyrene</td>
<td>NPS</td>
</tr>
<tr>
<td>Nylon-11</td>
<td>N11</td>
</tr>
<tr>
<td>Nylon-6, 10</td>
<td>N610</td>
</tr>
<tr>
<td>O.O-Novolac</td>
<td>OONOV</td>
</tr>
<tr>
<td>Phenol–formaldehyde</td>
<td>PF</td>
</tr>
<tr>
<td>Phenolic resin</td>
<td>PHR</td>
</tr>
<tr>
<td>Plasticised polystyrenechloride/vinylidenechloride</td>
<td>PVC-PVDC</td>
</tr>
<tr>
<td>Plasticised polystyrenechloride</td>
<td>PPVC</td>
</tr>
<tr>
<td>Poly(4-methyl penten-1)</td>
<td>TPX</td>
</tr>
</tbody>
</table>

(continued overleaf)
Chart 21.2 Infrared – polymer flowchart II

No strong band 1810–1700 cm⁻¹

Absorption at 3010 cm⁻¹ and bands at 1600, 1590 and 1495 cm⁻¹?

Yes → Band 3490–3330 cm⁻¹?

No → Band 3490–3330 cm⁻¹?

Strong bands at 1665 cm⁻¹?

No → Strong band 1430 cm⁻¹?

Yes → Strong band 1540 cm⁻¹?

No → Strong band at 1360–1300 & 1170–1120 cm⁻¹?

Yes → Strong band at 1055 cm⁻¹?

No → Sharp band -1660 cm⁻¹?

Yes → Sharp band -1055 cm⁻¹?

No → Strong bands at 1250–1000 cm⁻¹?

Yes → Strong band -1055 cm⁻¹?

No → Strong bands at 1155 cm⁻¹?

Yes → Strong band at 1155 cm⁻¹?

No → Strong bands at 1115–1000 cm⁻¹?

Yes → Strong band at 1115–1000 cm⁻¹?

No → Strong bands at 765 cm⁻¹?

Yes → Strong bands at 765 cm⁻¹?

No → Strong bands at 710–590 cm⁻¹?

Yes → Strong bands at 710–590 cm⁻¹?

No → Strong bands at 705 cm⁻¹?

Yes → Strong bands at 705 cm⁻¹?

No → Strong bands at 690–670 cm⁻¹?

Yes → Strong bands at 690–670 cm⁻¹?

No → Strong bands at 675 cm⁻¹?

Yes → Strong bands at 675 cm⁻¹?

No → Strong bands at 660 cm⁻¹?

Yes → Strong bands at 660 cm⁻¹?

No → Strong bands at 650 cm⁻¹?

Yes → Strong bands at 650 cm⁻¹?

No → Strong bands at 635 cm⁻¹?

Yes → Strong bands at 635 cm⁻¹?

No → Strong bands at 620 cm⁻¹?

Yes → Strong bands at 620 cm⁻¹?

No → Strong bands at 615 cm⁻¹?

Yes → Strong bands at 615 cm⁻¹?

No → Strong bands at 610 cm⁻¹?

Yes → Strong bands at 610 cm⁻¹?

No → Strong bands at 605 cm⁻¹?

Yes → Strong bands at 605 cm⁻¹?

No → Strong bands at 600 cm⁻¹?

Yes → Strong bands at 600 cm⁻¹?

No → Strong bands at 590 cm⁻¹?

Yes → Strong bands at 590 cm⁻¹?

No → Strong bands at 585 cm⁻¹?

Yes → Strong bands at 585 cm⁻¹?

No → Strong bands at 580 cm⁻¹?

Yes → Strong bands at 580 cm⁻¹?

No → Strong bands at 575 cm⁻¹?

Yes → Strong bands at 575 cm⁻¹?

No → Strong bands at 570 cm⁻¹?

Yes → Strong bands at 570 cm⁻¹?

No → Strong bands at 565 cm⁻¹?

Yes → Strong bands at 565 cm⁻¹?

No → Strong bands at 560 cm⁻¹?

Yes → Strong bands at 560 cm⁻¹?

No → Strong bands at 555 cm⁻¹?

Yes → Strong bands at 555 cm⁻¹?

No → Strong bands at 550 cm⁻¹?

Yes → Strong bands at 550 cm⁻¹?

No → Strong bands at 545 cm⁻¹?

Yes → Strong bands at 545 cm⁻¹?

No → Strong bands at 540 cm⁻¹?

Yes → Strong bands at 540 cm⁻¹?

No → Strong bands at 535 cm⁻¹?

Yes → Strong bands at 535 cm⁻¹?

No → Strong bands at 530 cm⁻¹?

Yes → Strong bands at 530 cm⁻¹?

No → Strong bands at 525 cm⁻¹?

Yes → Strong bands at 525 cm⁻¹?

No → Strong bands at 520 cm⁻¹?

Yes → Strong bands at 520 cm⁻¹?

No → Strong bands at 515 cm⁻¹?

Yes → Strong bands at 515 cm⁻¹?

No → Strong bands at 510 cm⁻¹?

Yes → Strong bands at 510 cm⁻¹?

No → Strong bands at 505 cm⁻¹?

Yes → Strong bands at 505 cm⁻¹?

No → Strong bands at 500 cm⁻¹?

Yes → Strong bands at 500 cm⁻¹?

No → Strong bands at 495 cm⁻¹?

Yes → Strong bands at 495 cm⁻¹?

No → Strong bands at 490 cm⁻¹?

Yes → Strong bands at 490 cm⁻¹?

No → Strong bands at 485 cm⁻¹?

Yes → Strong bands at 485 cm⁻¹?

No → Strong bands at 480 cm⁻¹?

Yes → Strong bands at 480 cm⁻¹?

No → Strong bands at 475 cm⁻¹?

Yes → Strong bands at 475 cm⁻¹?

No → Strong bands at 470 cm⁻¹?

Yes → Strong bands at 470 cm⁻¹?
### Table 21.8 (continued)

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</thead>
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<td>PIPPS</td>
</tr>
<tr>
<td>Poly-methylstyrene</td>
<td>PPS</td>
</tr>
<tr>
<td>Polyacrylamide</td>
<td>PAM</td>
</tr>
<tr>
<td>Polyacrylonitrile</td>
<td>PAN</td>
</tr>
<tr>
<td>Polyamide – aromatic</td>
<td>PA-AR</td>
</tr>
<tr>
<td>Polyamide – aliphatic</td>
<td>PA-A</td>
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<tr>
<td>Polybutadiene</td>
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<tr>
<td>Polytetramethylene ethylenemide</td>
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<tr>
<td>Polycarbonate – aliphatic</td>
<td>PC-A</td>
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<tr>
<td>Polycarbonate – aromatic</td>
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<td>Polycaprolactam-Nylon-6</td>
<td>N6</td>
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<tr>
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<td>PCR</td>
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<tr>
<td>Polycyanoacrylate</td>
<td>PCA</td>
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<td>PDPS</td>
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<tr>
<td>Polyester – aliphatic amine</td>
<td>UP-NH</td>
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<tr>
<td>Polyester – aliphatic</td>
<td>UP-A</td>
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<td>PE</td>
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<td>IRC</td>
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<td>PMCA</td>
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<td>PMS</td>
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<td>PVDC</td>
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<td>SARAN</td>
</tr>
<tr>
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<tr>
<td>Polyvinylpyrrolidone</td>
<td>PVP</td>
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<td>SBPS</td>
</tr>
<tr>
<td>Styrene – butadiene</td>
<td>SAN</td>
</tr>
<tr>
<td>Styrene – butadiene</td>
<td>SBR</td>
</tr>
<tr>
<td>Trichloroethylene-phosphate</td>
<td>TCEP</td>
</tr>
<tr>
<td>Urea formaldehyde</td>
<td>UF</td>
</tr>
</tbody>
</table>

### References

47. J. Wang et al., Polymer, 1989, 30, 524.
Tables and Charts

Frequencies

Characteristic Group

Infrared and Raman

Third Edition

George Socrates

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