Spectra–Structure Correlations: Polymer Spectra

John M. Chalmers[1], **Robert W. Hannah**[2] **and Dana W. Mayo**[3]

[1] *University of Nottingham, Nottingham, UK*
[2] *Naples, FL, USA*
[3] *Bowdoin College, Brunswick, ME, USA*

1 INTRODUCTION

The aim of this article is to provide the reader with an introduction to a basic approach for the interpretation of the vibrational spectra of polymers. The article is not a review, nor is it a treatise on the fundamental assignment of bands in polymer spectra. A bibliography is appended to some key publications (with references therein) that cover more detailed explanations and other more specific studies. Furthermore, neither inorganic polymers nor biopolymers will be considered in this article.

Features within an infrared (IR) or Raman spectrum of an organic polymer may yield information on chemical structure and composition, isomerism and stereoregularity, conformational order, molecular orientation and state of order. Polymers are complex macromolecules, yet their vibrational spectra may be relatively simple. At the simplest level, one may view an amorphous polymer as being constructed of substructural units (repeat units, often incorporating functional groups) linked by chemical bonds. Bands in the spectrum of a polymer may then be assigned largely on the basis of the characteristic stretching and deformation vibrations of the specific groups that comprise the polymer, as outlined in the first article (**Spectra–Structure Correlations in the Mid- and Far-infrared**) of this section of the Handbook. By using functional group correlation tables it is a relatively simple task, for example, to ascertain whether the spectrum is that of an aliphatic or aromatic hydrocarbon polymer, a polyester, a polyamide, etc. Full identification is usually achieved by pattern-matching a spectrum to that of a standard reference spectrum, such as one contained in a commercial (see, for example, those listed in the Further Reading section) or proprietary collection, or by complementary or confirmatory analysis by another technique(s), such as nuclear magnetic resonance (NMR).

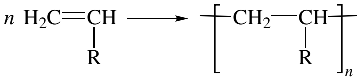
We will also see that more subtle information can be obtained from polymer spectra. For example, the bands in the spectrum of an amorphous polymer are usually broader than those observed for the polymer in a crystalline or semicrystalline state, since, for a specific vibration many more differently phased vibrations occur for the amorphous material than with the more regular structures.

We will consider first the IR spectra of some homopolymers, i.e. polymers in which there is a regular sequence of a single (monomer) repeat unit.

2 HOMOPOLYMER VIBRATIONAL SPECTRA

2.1 Spectra of addition reaction homopolymers

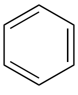
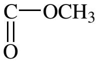
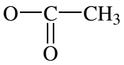
Scheme 1 shows an (head-to-tail) addition reaction. The double bond of the monomer opens and successive additions of a new monomer unit produce the polymer chain. Many important commercial homopolymers are synthesized in this manner. Some examples of polymers in which the side-branch R differs are given in Table 1.



$$n\ H_2C{=}\underset{R}{\underset{|}{CH}} \longrightarrow \left[CH_2{-}\underset{R}{\underset{|}{CH}} \right]_n$$

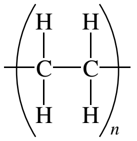
Scheme 1

Table 1. Some addition reaction homopolymers.

R	Homopolymer
H	Polyethylene
CH_3	Polypropylene
Cl	Poly(vinyl chloride)
OH	Poly(vinyl alcohol)
	Polystyrene
 $-C(=O)-OCH_3$	Poly(methyl acrylate)
 $-O-C(=O)-CH_3$	Poly(vinyl acetate)
$CH{=}CH_2$	1,2-Polybutadiene

The process involved in the interpretation of polymer spectra is illustrated by the IR spectrum of a polymer with a simple chemical structure shown in Figure 1. It can be seen that there is no evidence of any absorption band(s) between 3600 and 3200 cm^{-1}, indicating that the polymer has no –NH or –OH functionality. Similarly, the lack of spectral structure between 3100 and 3000 cm^{-1} indicates the absence of aromatic or olefinic (sp^2 hybridized) C–H groups. The C–H stretching vibrations (νCH) between 3000 and 2800 cm^{-1} indicate that the polymer is aliphatic. Absence of a strong band in the region 1800–1650 cm^{-1} precludes the existence of a C=O. The lack of sharp bands near 1600 cm^{-1}, 1500 cm^{-1} and 1450 cm^{-1}, coupled with the absence of a pattern of weak bands between 2000 and 1700 cm^{-1} characteristic of an aromatic substitution, confirms that the polymer is not aromatic. The medium intensity CH deformation band (δCH), scissoring vibration, is in the normal position for an aliphatic hydrocarbon, ~1460 cm^{-1}. (The sharp, medium intensity absorption band near 1378 cm^{-1} is attributed to the symmetric $-CH_3$ deformation ("umbrella mode"). The relative intensity of this band varies; see Section 3. It is associated with chain or side-branch end groups.) The absence of strong absorption features in the region from 1300 to 800 cm^{-1} indicates the absence of polar groups and heteroatoms. The sharp doublet at 730/720 cm^{-1} is a characteristic of the $-CH_2$-rocking-mode vibration of a partially crystalline or highly ordered long-chain aliphatic hydrocarbon.

Since the only strong features in the IR spectrum shown in Figure 1 are those of the CH_2 group, this spectrum may readily be deduced to be that of a polyethylene (PE) **(1)**.



(1)

This interpretation may be confirmed by comparison with standard spectra. Note, we have said "a polyethylene", since the fine detail of the spectrum (such as the intensity of bands due to methyl groups) will depend on both the method of production and also the morphology (thermal history) of the PE. This will be discussed later, in Section 3, when we consider further both the splitting of the rocking mode vibration and also the medium intensity features observed between 1400 and 1300 cm^{-1}, and the weaker absorption bands at 2016 cm^{-1} and 1894 cm^{-1} and between 1200 and 850 cm^{-1}. In PE the trans molecular conformation predominates in the

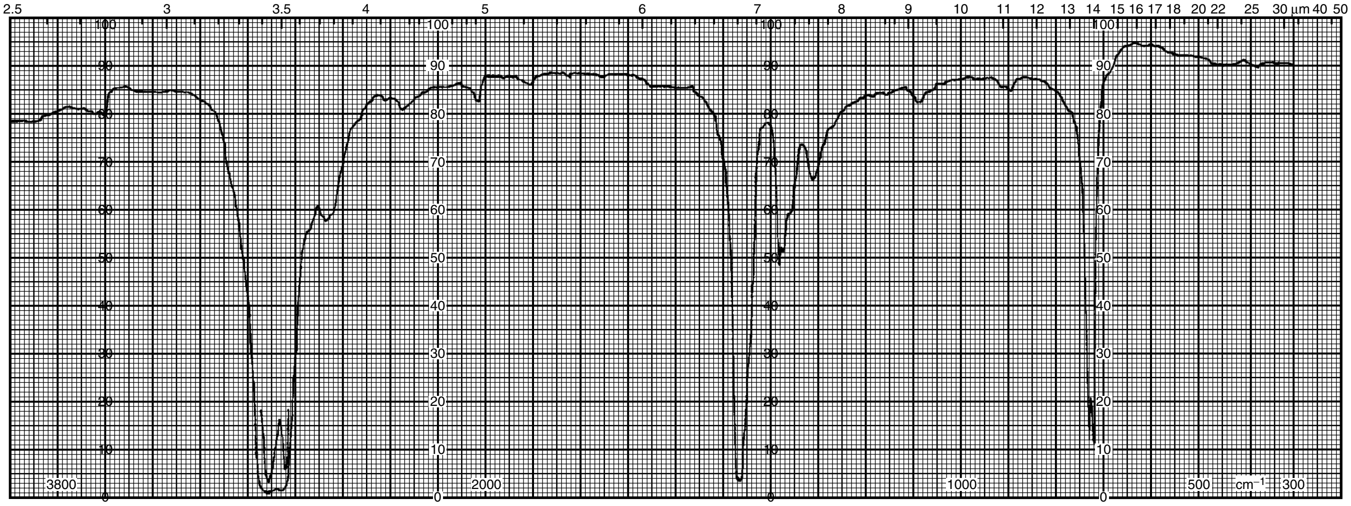


Figure 1. IR transmission spectrum of a low-density polyethylene (LDPE). [Reproduced from spectrum number 1916 in 'Atlas of Polymer and Plastics Analysis', 2nd edition, Vol. 2, Part a/I, D.O. Hummel, Verlag Chemie, Weinheim (1984).]

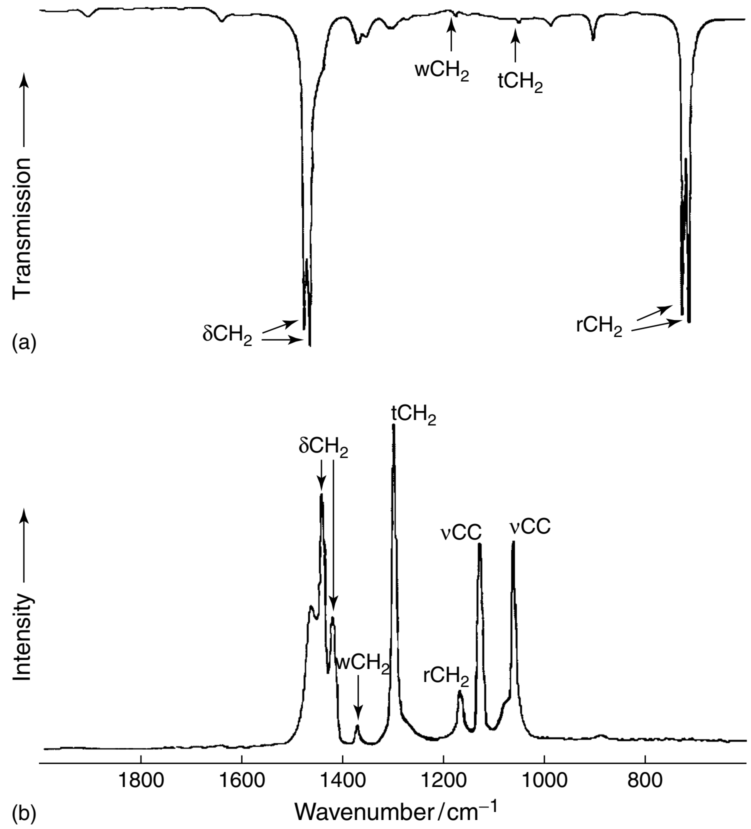
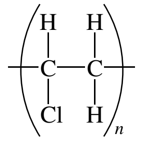


Figure 2. (a) IR transmission and (b) Raman spectra from 2000 to 600 cm^{-1} of PE (w, wag; *ν*, stretch; *δ*, deformation; r, rock; t, twist). [Reproduced, with permission, from H.A. Willis, 'Combination of Spectroscopic Methods in Polymer Structure Analysis', in "Proceedings of 5th European Symposium on Polymer Spectroscopy", ed. D.O. Hummel, Verlag Chemie, Weinheim (1979).]

crystalline phase and the repeat unit is centro-symmetric. Thus there are no vibrational frequencies that occur in both the IR and Raman spectra of highly crystalline PE. (The stretching frequencies are often accidentally degenerate in this region.) This mutual exclusion is illustrated in Figure 2, where it is observed that the strong bands in the IR spectrum have no counterparts in the Raman spectrum, and vice versa. For cases other than PE, such complete distinction of bands is not usually achieved, but generally polymers follow the normal trends that strong bands in the Raman are weak in the IR, while intense bands in the IR spectrum are weak in the Raman.

Figure 3 shows the IR spectra of two more homopolymers. Some key observations for the spectrum shown in Figure 3(a) are: the absence of any significant absorption above 3000 cm^{-1}; medium to strong intensity bands between 3000 and 2800 cm^{-1} that suggest the presence of only CH_2, CH and possibly CH_3 groups; absence of a strong band in the 1800 to 1650 cm^{-1} region, indicating that no carbonyl is present; the CH_2 (CH_3) group deformation band is nearer to 1430 than 1460 cm^{-1}, indicating that the polymer is not simply a hydrocarbon and that polar groups are also possibly present; the strong bands in the 700–600 cm^{-1} region are characteristic of *ν*C–Cl. Comparison against standard spectra shows the spectrum of Figure 3(a) to be that of poly(vinyl chloride) (PVC) **(2)**. The multiplicity of bands attributed to *ν*C–Cl reflects the sensitivity of this mode to its environment (rotational isomeric states). Individual components may be assigned to structures determined by the spatial configuration (arrangement) of the C–Cl groups with respect to each other along the polymer backbone, i.e. to the tactic sequences of the polymer (see later and see **Measurements of the Chemical Characteristics of Polymers and Rubbers by Vibrational Spectroscopy** in Volume 4 of this Handbook). (The configurational structure of PVC depends inter alia on the polymerization temperature.)



$$\left(-\overset{\displaystyle H}{\underset{\displaystyle Cl}{C}}-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}- \right)_n$$

(2)

The IR spectrum of Figure 3(b) shows no significant evidence of *ν*CH, and no evidence whatsoever of *ν*NH, *ν*OH, *ν*C≡C, *ν*C=C or *ν*C=O. The key features are

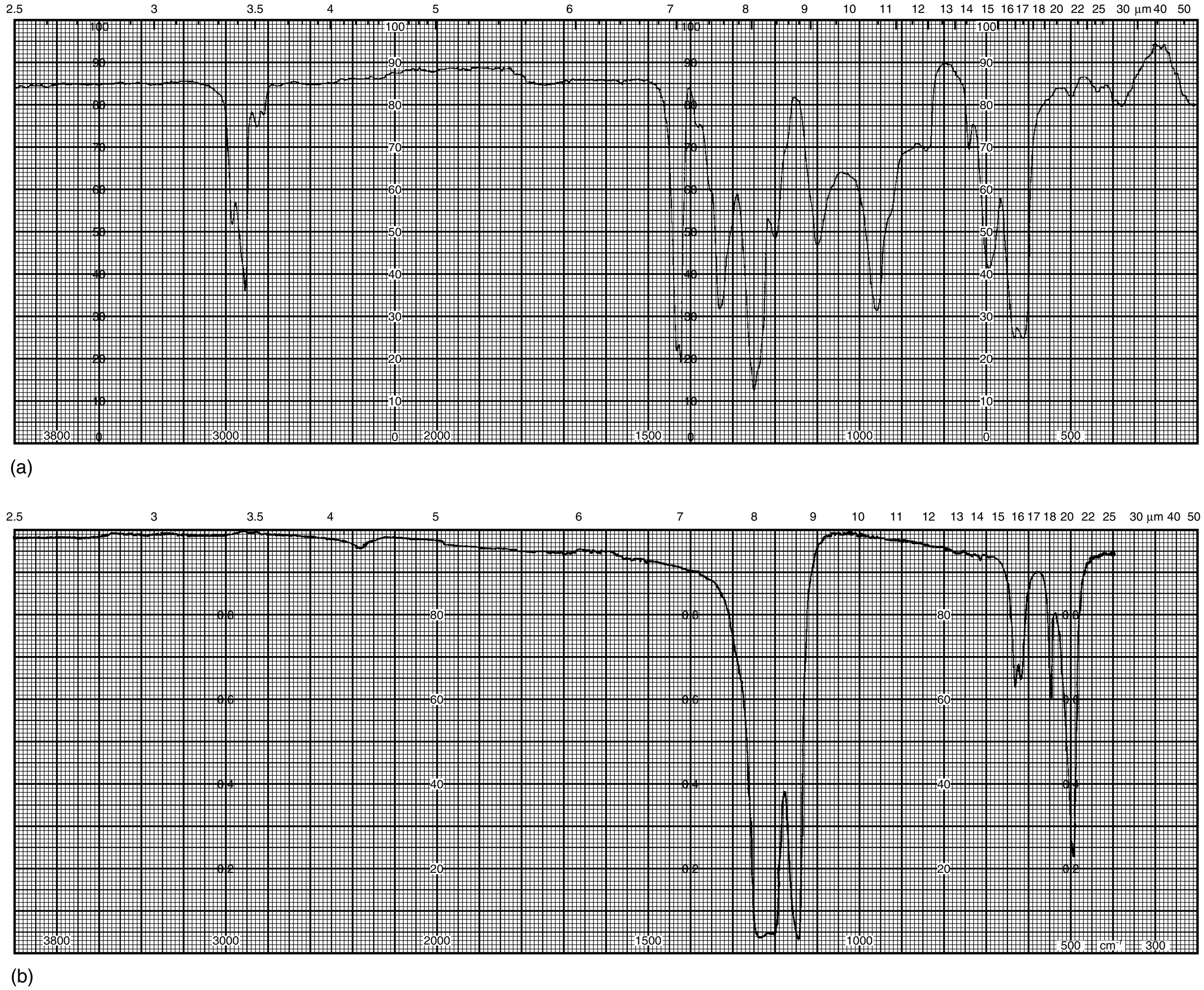
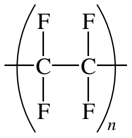


Figure 3. IR transmission spectra of (a) PVC and (b) PTFE. [Reproduced from spectra numbers 2009 and 1992, respectively, in 'Atlas of Polymer and Plastics Analysis', 2nd edition, Vol. 2, Part a/I, D.O. Hummel, Verlag Chemie GmbH, Weinheim (1984).]

strong bands at ~1220 cm^{-1} and 1150 cm^{-1}. These are the antisymmetric and symmetric stretching νCF vibrations, respectively. The medium intensity bands between 700 and 500 cm^{-1} are due to rocking and bending vibrations of the CF_2 group. This spectrum is readily identified as that of poly(tetrafluoroethylene) (PTFE) **(3)**.



(3)

The polymer chains of PE, PVC and PTFE all have simple –C–C–backbones. The positional (wavenumber) and intensity differences between the strong absorption features of the IR spectra of Figures 1, 3(a) and 3(b) reflect the influences of the different substituents atoms (side groups).

Let us consider the spectra of two other polyolefins. Figure 4 shows the IR spectra of two more hydrocarbon homopolymers, which have recognizable spectra, and are distinct from that of PE.

Figure 4(a) is the IR spectrum of polyisobutene (PIB) **(4)**. Between 3000 and 2800 cm^{-1}, the spectrum shows only those bands associated with the CH_2 and CH_3 stretching modes, while the corresponding bending fundamentals are near 1470 cm^{-1}. The rest of the absorption spectrum is largely associated with CH_2 rocking and twisting modes and skeletal modes of the molecule. These comprise the

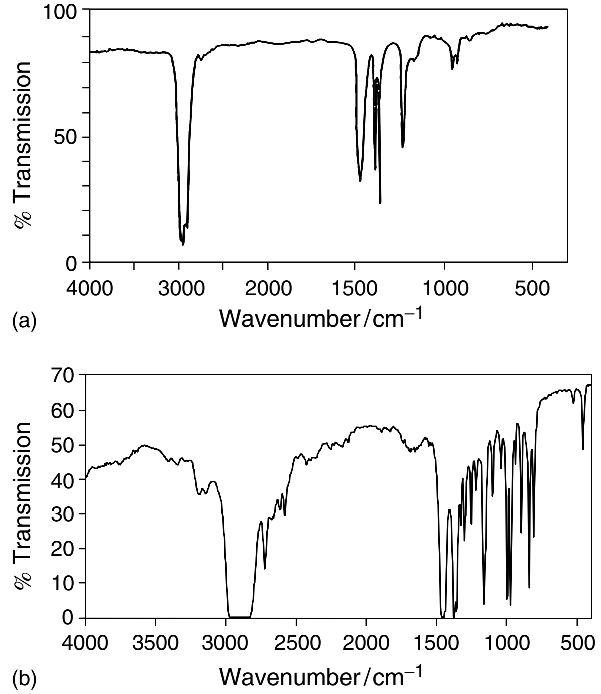
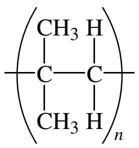


Figure 4. IR transmission spectra of (a) PIB and (b) isotactic polypropylene (i-PP).

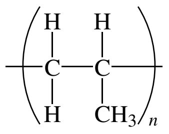
fingerprint bands of the polymer. The most distinctive absorption feature of this spectrum is the doublet near 1380 cm^{-1}, which is characteristic of the isopropyl (*gem*-dimethyl) group.



$$-\left(\begin{array}{ccc} \mathrm{CH_3} & & \mathrm{H} \\ | & & | \\ \mathrm{C} & - & \mathrm{C} \\ | & & | \\ \mathrm{CH_3} & & \mathrm{H} \end{array}\right)_n-$$

(4)

Figure 4(b) has the characteristics of a saturated aliphatic hydrocarbon, but also has a number of sharp bands in the C–C stretching and C–H deformation region, suggesting a well-defined carbon–carbon backbone. The IR spectrum is that of (isotactic) polypropylene (PP) **(5)**. (We will return to a discussion of the effects of tacticity on spectra later in Section 3.)



$$-\left(\begin{array}{ccc} \mathrm{H} & & \mathrm{H} \\ | & & | \\ \mathrm{C} & - & \mathrm{C} \\ | & & | \\ \mathrm{H} & & \mathrm{CH_3} \end{array}\right)_n-$$

(5)

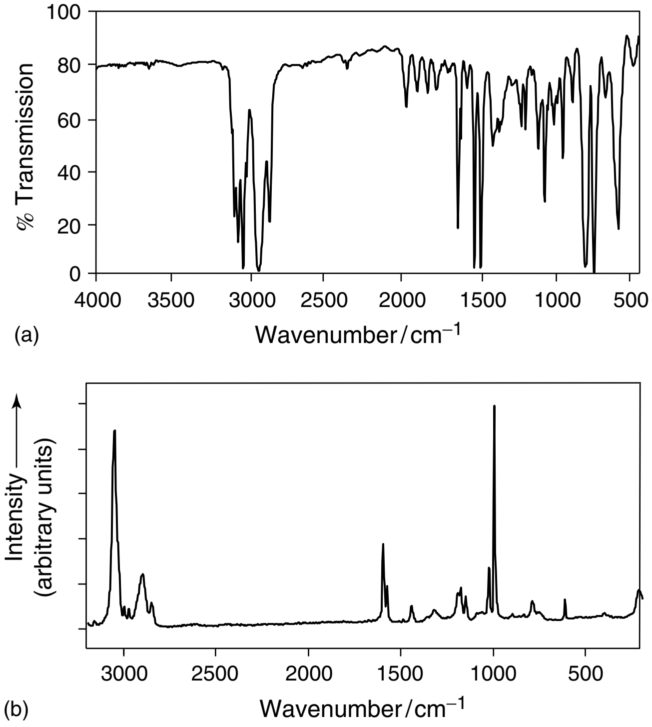
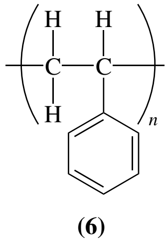


Figure 5. (a) IR transmission and (b) Raman spectra of polystyrene.



(6)

The IR spectrum shown in Figure 5(a) has all the characteristics of a monosubstituted aromatic hydrocarbon, and is, of course, that of the ubiquitous IR wavenumber calibration standard, (atactic) polystyrene **(6)**. Many of the bands are easily assigned by following the normal rules for functional group correlation. The aromatic νC–H bands are located above 3000 cm^{-1}, while the aliphatic νC–H bands are between 3000 and 2800 cm^{-1}. In the IR spectrum, the out-of-plane C–H bending and ring puckering vibrations associated with monosubstituted aromatic systems are clearly seen in the 750–690 cm^{-1} region. The weak pattern of combination bands in the region 2000 to 1650 cm^{-1} also correlates well with monosubstitution. The sharp bands near 1600, 1500 and 1450 cm^{-1} are all associated with aromatic in-plane ring stretching. The intense Raman aromatic ring-breathing mode band at about 1001 cm^{-1} is very characteristic of a 1-, 1,3- or 1,3,5-substituted aromatic; see Figure 5(b). The medium–strong intensity in-plane ring deformation mode band found near 620 cm^{-1} is characteristic of a monosubstituted carbocyclic aromatic ring.

2.2 Spectra of condensation reaction homopolymers

Before we move on to discuss the more subtle and fine detail of polymer vibrational spectra in Section 3, we will continue this initial simple discussion of the interpretation of polymer spectra with a comparison of the spectra of a few more homopolymers. This time, however, we will choose polymers that may be generated by condensation or condensation-like processes. Here two bifunctional monomers react to form the polymer, often by the elimination (evolution) of water. The examples given are a polyamide, two polyesters [poly(ethylene terephthalate) (PET) and an alkyd resin], a polysulfone, a polyketone and a polycarbonate.

2.2.1 Nylons

The prominent band at 3300 cm^{-1} in the IR spectrum shown in Figure 6 occurs at too high a wavenumber and is too broad to be assigned as νCH, and in fact originates from νNH; this band is sometimes called the Amide A band. The νCH modes are found in bands that all occur below 3000 cm^{-1}. These modes are characteristic of alkane moieties. Strong bands at ~1650 cm^{-1} and ~1560 cm^{-1} (Amide I and Amide II, respectively) are indicative of a secondary amide. Another band that is characteristic of amides, known as Amide III, is seen near 1280 cm^{-1}. (The Amide III band is, however, not a good group frequency correlation, since its position is subject to the specific monomers used and the structure around the amide group.) The ~3160 cm^{-1} weak to medium band is a Fermi resonance enhanced overtone of Amide II. The broad, underlying absorption feature near 700 cm^{-1} is associated with the –NH out-of-plane deformation. The spectrum is strongly characteristic of an aliphatic secondary amide polymer, and is in fact that of nylon 6,6 (**7**). Like most nylons, nylon 6,6 is prepared from the polycondensation of two bifunctional monomers, a diamine and a diacid. For nylon 6,6 these are hexamethylene diamine and adipic acid, respectively. (Nylon 6 is atypical in that it is prepared from a ring-opening reaction of ε-caprolactam).

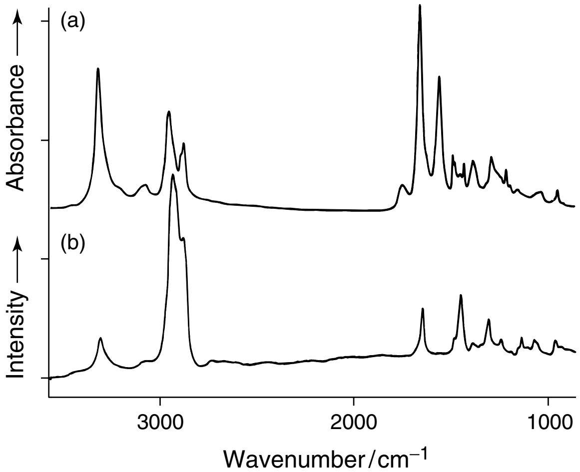
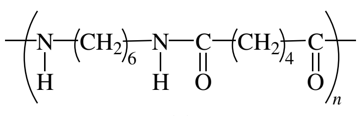


Figure 6. (a) IR absorbance and (b) Raman spectra of Nylon 6, 6. [Reproduced from J.M. Chalmers and N.J. Everall, Chapter 4, ‘Vibrational Spectroscopy’, pp. 69–114, in “Polymer Characterisation”, eds B.J. Hunt and M.I. James, Blackie Academic & Professional, Glasgow (1993).]



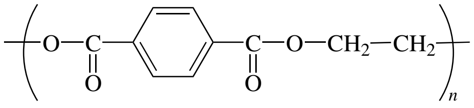
$$\left(-\underset{\mathrm{H}}{\underset{|}{\mathrm{N}}}-(\mathrm{CH_2})_6-\underset{\mathrm{H}}{\underset{|}{\mathrm{N}}}-\underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}-(\mathrm{CH_2})_4-\underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}- \right)_n$$

(7)

One should be wary about assigning the identity of a nylon (e.g. 6; 6,6; 11; 12) solely from its IR (or Raman) spectrum. The weak fingerprint bands are essentially indicative of the morphology of that particular sample and many nylons may exist in several polymorphic (crystalline) forms. The method of sample preparation may have a considerable effect on the spectrum of polyamides. The spectra of the amorphous or crystalline forms of two different nylons may possess a closer resemblance than the spectra of the crystalline and amorphous forms of a given nylon. Moreover, many commercial materials may be nylon copolymers (e.g. a 6/6,6 copolymer). It can be readily observed in Figure 6 that the bands associated with vibrations of the alkyl groups of nylon 6,6 are relatively more intense in the Raman spectrum compared with the IR spectrum of this material. On the other hand, absorption bands arising from vibrations of the amide group dominate the IR spectrum of the nylon.

2.2.2 Polyesters

Figure 7 shows the IR and Raman spectra of PET (**8**), which may be prepared commercially from the condensation of ethylene glycol with either terephthalic acid or the diester, dimethyl terephthalate.



(8)

In accord with its structure, the IR and Raman spectra each show a νC=O band at ~1725 cm^{-1}, and the IR spectrum shows very strong νC–O bands at ~1250 cm^{-1} and ~1100 cm^{-1} that are characteristic of an aromatic ester. Aromaticity is confirmed in the IR spectrum by the sharp ring stretching bands near 1600, 1500 and 1450 cm^{-1}, and

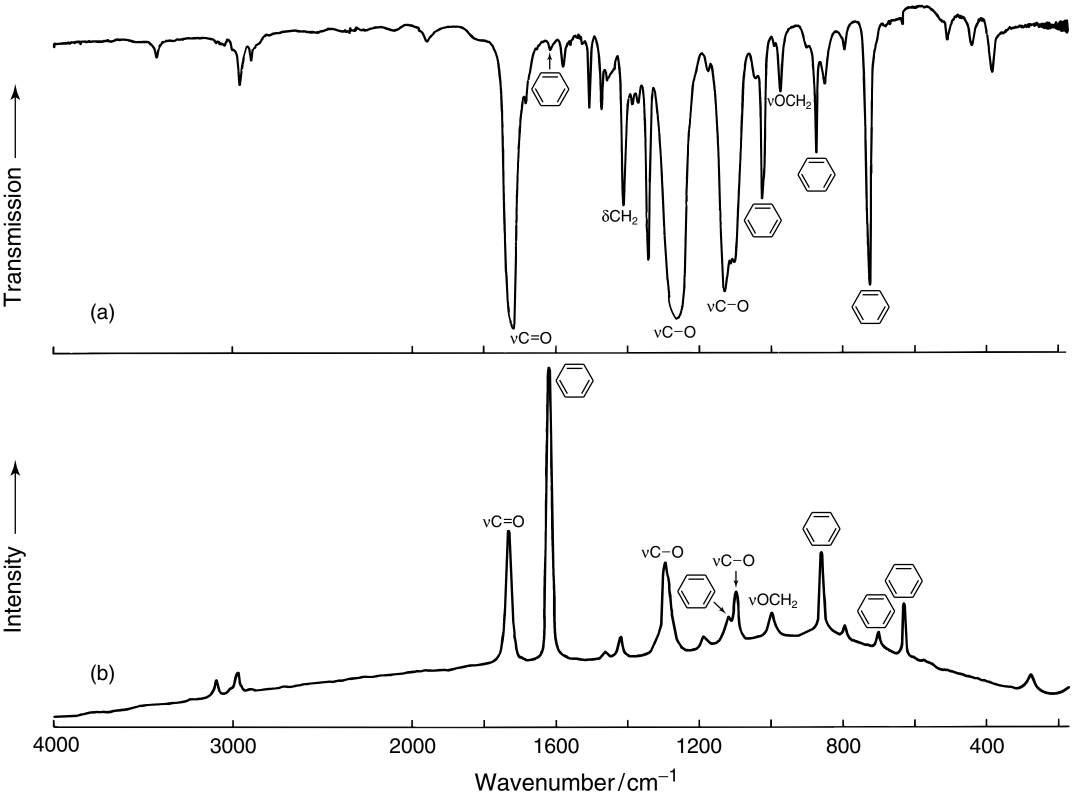


Figure 7. (a) IR transmission and (b) Raman spectra of PET. [Reproduced, with permission, from H.A. Willis,'Combination of Spectroscopic Methods in Polymer Structure Analysis', in "Proceedings of 5th European Symposium on Polymer Spectroscopy", ed. D.O. Hummel, Verlag Chemie, Weinheim (1979).]

in the Raman spectrum by the intense band near $1600\,\mathrm{cm}^{-1}$ and the medium–weak band close to $650\,\mathrm{cm}^{-1}$. The in-all-phase, out-of-plane C–H deformation of the four aryl ring hydrogen atoms occurs at $\sim 726\,\mathrm{cm}^{-1}$ in the IR spectrum, and is shifted down from $\sim 830\,\mathrm{cm}^{-1}$ due to conjugation with the C=Os. Whereas the absorption bands associated with the ester functionality are the most intense in the IR spectrum, aryl ring vibrations are more dominant in the Raman spectrum. The ethylene glycol unit in the polymer chain may take up either a trans or gauche conformation, which can cause dramatic effects on the relative intensities of some of the other bands in the PET spectra. Molecular orientation and crystallinity produced by mechanical and thermal treatments can also change the relative intensities of these and other bands very significantly. We will return to this later.

One example of a vast range of polymers synthesized from condensation between two multifunctional monomers is the alkyds or alkyd-like polyesters. These complex polyester resins result from the reaction of a polyfunctional (usually aromatic) acid with a polyfunctional alcohol. They may be modified, for example, with vegetable oils or fatty acids. They often exhibit an IR νC=O band centered near $1735\,\mathrm{cm}^{-1}$, which possesses a profile of overlapping ester carbonyls from, for example, a conjugated aromatic ester ($\sim 1725\,\mathrm{cm}^{-1}$) and a fatty acid ester carbonyl ($\sim 1745\,\mathrm{cm}^{-1}$). While it may be possible to categorize the polyester as an alkyd, it is unlikely that the component monomers can be unequivocally identified directly by vibrational spectroscopy. The physical state of the material should also be taken into account, since this will affect the spectral detail. Figure 8(a) and (b) show the IR spectra of a polyester and an alkyd, an oil-modified polyester. The most distinguishing feature between these two spectra is the difference in relative intensity of the νCH bands in the $3000–2800\,\mathrm{cm}^{-1}$ region. The IR spectra of many alkyds bear a close similarity to those of di-iso-alkyl phthalate plasticizers.

2.2.3 Other condensation polymers

The IR spectrum shown in Figure 9(a) is that of a poly(aryl ether sulfone) (PES) **(9)**. The narrow bands in the IR spectrum of PES suggest the presence of aromatic rings, while the strong bands at $\sim 1300\,\mathrm{cm}^{-1}$ and $1150\,\mathrm{cm}^{-1}$ are indicative of the antisymmetric and symmetric νS=O of an SO_2 group, respectively. The absorption at $\sim 1250\,\mathrm{cm}^{-1}$ is caused by the $\nu_{\text{ring}-\text{O}}$ stretch, while the δ_{oop} at $\sim 850\,\mathrm{cm}^{-1}$

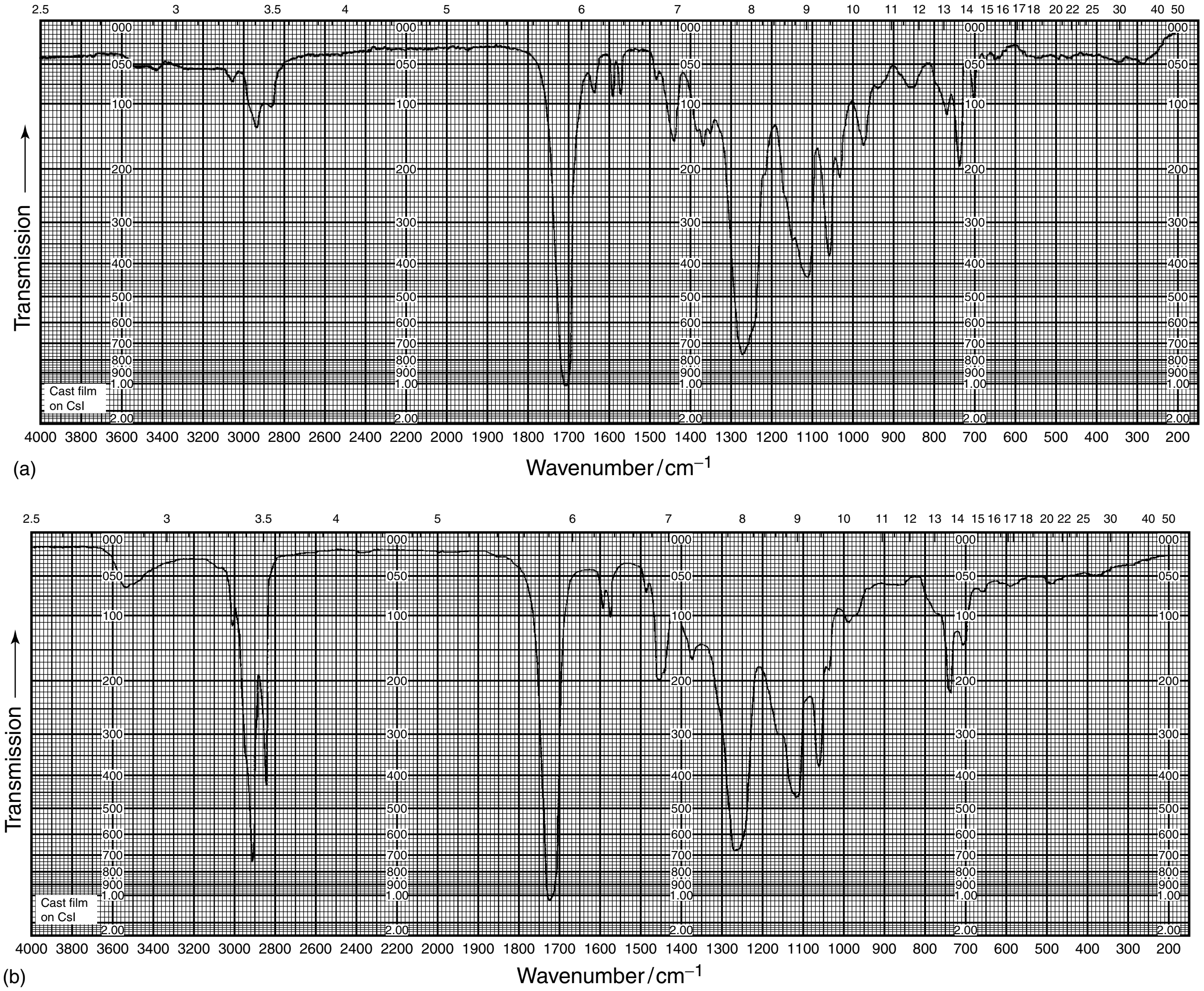
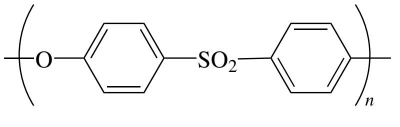


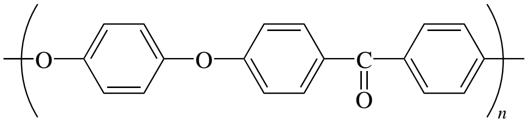
Figure 8. IR transmission spectra of (a) a polyester polymer based on σ-phthalic anhydride (40.8%), maleic anhydride (21.1%), propylene glycol (17.9%) and diethylene glycol (20.2%), and (b) a long oil alkyd based on σ-phthalic anhydride (24%), soybean oil (61%) and glycerine (15%). [Reproduced from spectra numbers 300 and 96, respectively, in 'An Infrared Spectroscopy Atlas for the Coatings Industry', Federation of Societies for Coatings Technology, Pennsylvania (1980).]

is characteristic of the δ_{oop} of a para-substituted aryl ring (raised from 800 cm^{-1} by direct substitution of the ring by oxygen and sulfur and unaffected by poor conjugation with the S=O groups). By comparison with a standard reference spectrum, the spectrum may be confirmed as that of PES.



(9)

The wavenumber at which νC=O is observed is very important for a number of condensation polymers. For example, in the spectrum of PET (see Figure 7), the aryl-conjugated ester νC=O occurred at ~1725 cm^{-1}. In poly(aryl ether ether ketone) (PEEK) **(10)** the ketone νC=O conjugated to two aryl rings occurs at ~1653 cm^{-1} (but in this case the additional drop in the C=O frequency results primarily from the steric expansion of the C–CO–C bond angle); see Figure 9(b).



(10)

The material that gives rise to the IR spectrum shown in Figure 9(c) is known as bisphenol-A polycarbonate **(11)**.

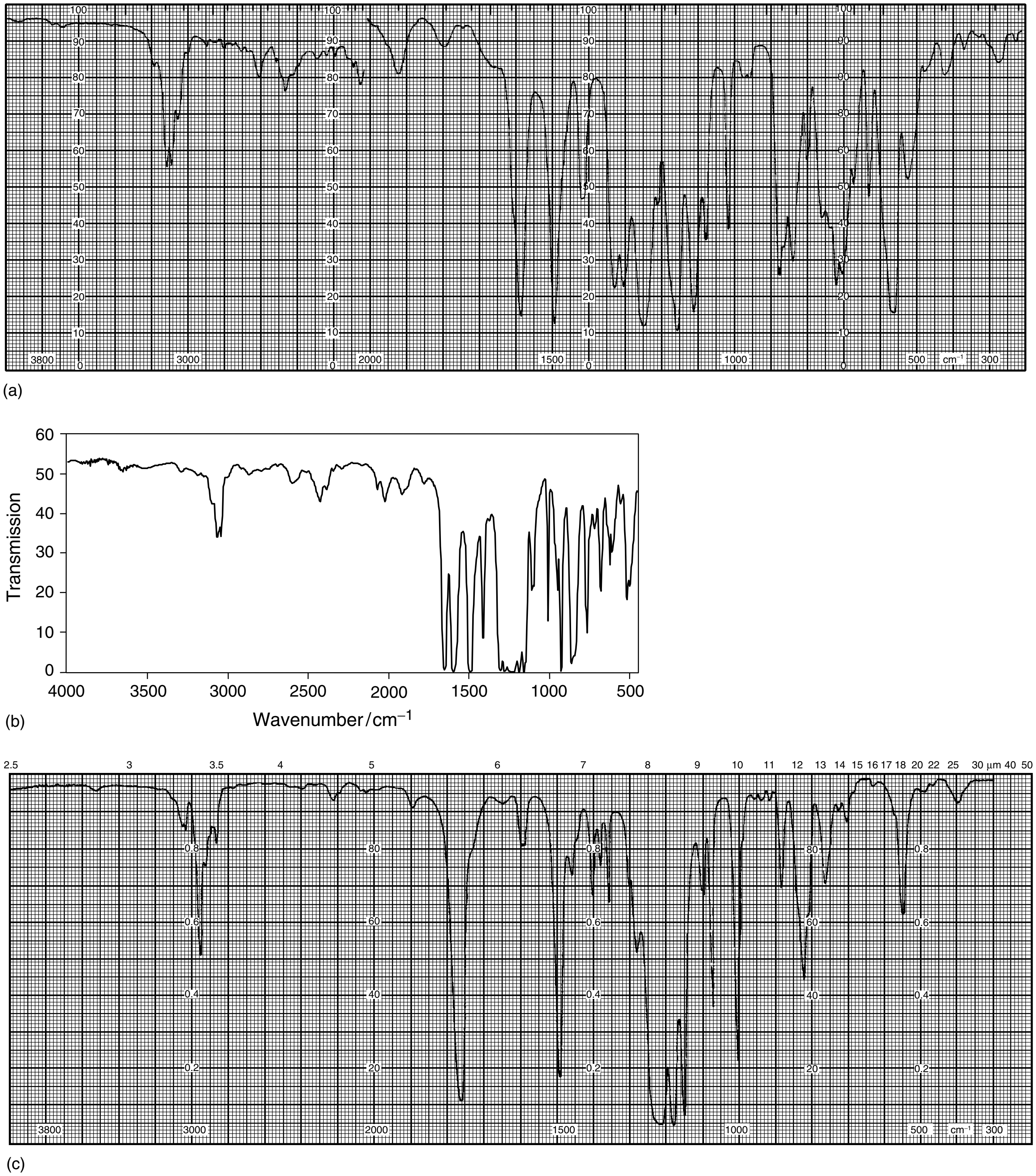
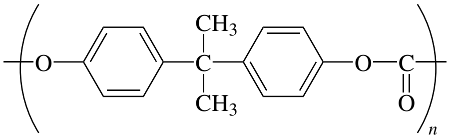


Figure 9. IR transmission spectra of (a) PES, (b) PEEK and (c) Bisphenol-A polycarbonate. [Spectra (a) and (c) reproduced from spectrum number 1574 in Vol. 1, and spectrum number 2109 in Vol. 2, Part a/I, respectively, in 'Atlas of Polymer and Plastics Analysis', 2nd edition, D.O. Hummel, Verlag Chemie GmbH, Weinheim (1984).]

The carbonate νC=O absorbs at ~1780 cm^{-1}. The polymer has the structure shown in **(11)**.



(11)

Although not as prominent as in the spectrum of PIB (Figure 4a), the doublet of δCH bands near 1380 cm^{-1} characteristic of the *gem*-dimethyl group is clearly evident in the spectrum of Figure 9(c).

2.3 Thermoset, cured and crosslinked polymers

Many resin systems are designed to form two- and three-dimensional networks through crosslinking reactions. Well-known examples are the epoxy and phenol-formaldehyde resins. While vibrational spectroscopy may be used to identify the major functional groups of the cured material, a major attribute of the IR and Raman techniques is their ability to follow and characterize the cure and crosslink mechanisms. For example, homopolymerization and crosslinking reactions in epoxy resins may be observed through a decrease of absorption intensity of IR bands associated with the glycidyl group, found most commonly near 910 cm^{-1}, and attributed to the epoxy ring. Additionally, many other changes of intensities of characteristic functional group bands such as those of hydroxyl, amine, ether, anhydride and ester may be observed readily and related to the mechanistic pathways of cure and crosslinking.

3 HOMOPOLYMER VIBRATIONAL SPECTRA – MORE DETAILED ANALYSIS

Much of the discussion so far has been concerned with assigning prominent bands in spectra, so that a homopolymer may be classed generically, prior to pattern-matching its spectrum to that of a reference spectrum in a standard or proprietary collection. However, as we have intimated, the fine detail of homopolymer spectra can often be put to invaluable use in supplying higher-level information. As an example, we will first consider different types of PE.

The IR spectra of aliphatic hydrocarbon polymers in which the absorption band maxima (transmission minima) of the major bands are scaled to full intensity are often of minimal use. It is often advantageous to record a spectrum from a thicker specimen (typically 0.1 mm thickness or greater) in order to increase the contrast between the weaker bands and the strong νCH near 2900 cm^{-1} and δCH near 1460 cm^{-1}. Figure 10 contrasts the IR spectra of three different classes of commercial "polyethylenes".

The spectrum of a high-density polyethylene (HDPE) is characterized by a much lower –CH$_3$ content, since these arise almost entirely as main chain end groups. The spectrum recorded from an LDPE is characterized by a relatively high –CH$_3$ content observed by the relative intensity at 1378 cm^{-1} of the δ_{sym} C–CH$_3$. The methyl groups occur mostly as a consequence of side-chain branches that are a characteristic of LDPE. Chain branching reduces the possibility for regular order in the chains, and thus reduces the crystalline content. The intensity of a band near 1303 cm^{-1} appears to be associated with the amorphous character of a sample, whereas the sharp features near 1175 and 1050 cm^{-1} have been shown to increase in intensity with growing polymer crystallinity. The band at 1894 cm^{-1} (see Figure 1) has been assigned to an all-trans configuration in the crystalline phase of a PE, while both the amorphous and crystalline phases contribute to the intensity of the band at 2016 cm^{-1}. With respect to the chain axis, the vibrations giving rise to these two bands have opposite transition moments, being essentially perpendicular and parallel, respectively. (They are useful for quantifying the degree of orientation in drawn samples of PEs; see later.)

The pattern of bands between 1000 and 800 cm^{-1} associated with the out-of-plane deformation modes of the hydrogen atoms of olefinic unsaturated groups may offer further differentiation of PE types. These groups occur at either the polymer chain ends or as in-chain defect structures. HDPEs are also generally distinguishable by their much higher level of vinyl unsaturation (–CH=CH$_2$), which shows up as absorption bands at 910 and 990 cm^{-1}, the former being more intense than the latter. In many LDPEs, the dominant feature in the 1000–850 cm^{-1} region is the vinylidene (pendant methylene) group (>C=CH$_2$), which absorbs at 888 cm^{-1}. A band at 965 cm^{-1} is assigned to the chain trans unsaturation group (–CH=CH–). Differentiation between PEs becomes much more complex when one also considers LLDPEs (Figure 10). These are ethylene/α-olefin copolymers, in which a low concentration of another alkene has been incorporated into a linear PE type. The "alkene modifiers" are typically propylene, butene, hexene or octene, and sometimes 4-methyl pent-1-ene. The spectra of many examples still exhibit a relatively high level of vinyl unsaturation, but also now exhibit a medium to strong δ_{sym} C–CH$_3$ absorption at 1378 cm^{-1} from the short chain branches. Commercial products may be an individual PE or contain blends of PEs. Vibrational spectroscopy cannot generally be used to distinguish readily such blends from homopolymers. Complementary information must be obtained from

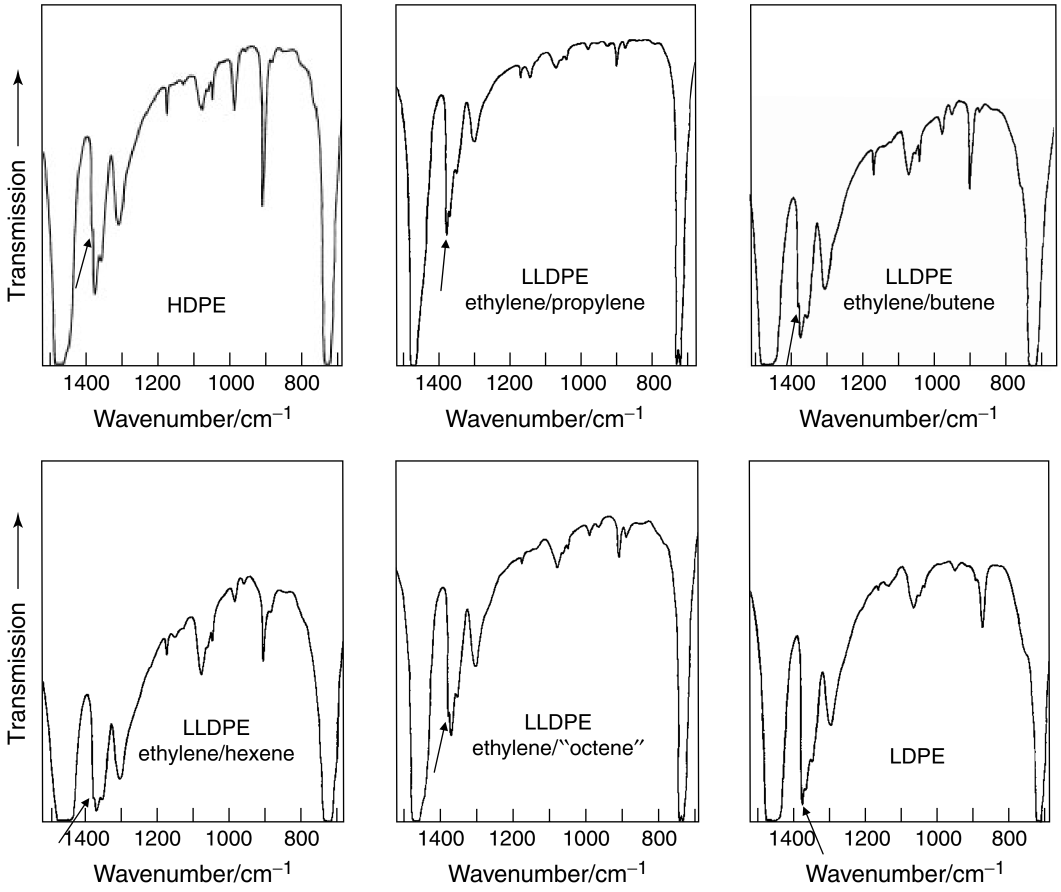


Figure 10. IR transmission spectra over the range 1500 to 700 cm^{-1} recorded from films of six different commercial PEs: HDPE; LDPE; and LLDPE, linear low-density polyethylene. The α-olefin copolymer determined by NMR is labeled for each LLDPE. For the figure labeled "octene" this signifies ($\geq$)octene, as the chain length determined from the NMR measurement. The arrows indicate the position of the δ_{sym} C–CH$_3$.

another technique(s) such as NMR or differential scanning calorimetry (DSC) if a material is to be characterized unequivocally.

As mentioned already the methyl groups are usually present as end groups in HDPE, as opposed to mainly side-chain branches in a LDPE. In many polymers, particularly polycondensation-type polymers, the functionality of an end group or the end group balance in the final product can be a key property in determining the processing performance and thermal stability of the polymer. Excess of one particular monomer may be used in the polymerization to try to secure a particular end group or balance in the final material, or in some circumstances a chain transfer or chain termination agent may be employed to control molecular weight. While the concentration of these groups may be very low, and perhaps only identifiable through a combination of NMR and matrix-assisted laser desorption ionization–mass spectrometry, characterizing and quantifying the concentration of some end groups in certain polymers is an important analytical use of vibrational spectroscopy.

The location of bands characteristic of end groups may sometimes be established through the use of difference spectroscopy and/or examining materials of differing molecular weights. Band intensities may then be correlated with independent measures of concentration, such as NMR or chemical titration. Figure 11 shows the principle underlying the classic IR measurements used for determining the concentration of alcohol and carboxylic end groups in PET, which nowadays may be calibrated against NMR and chemical titration measurements, respectively. Ward and co-workers pioneered this work in the mid-1950s (see references 121–123 of **Qualitative and Quantitative Analysis of Polymers and Rubbers by Vibrational Spectroscopy** in Volume 4 of this Handbook). The band positions of the –OH (3542 cm^{-1}) and –COOH (3256 cm^{-1}) were established by isotopic exchange with D$_2$O to produce –OD and –COOD end groups. The heavier atom reduces the vibrational frequency of the absorptions (lowering the wavenumber positions of the bands by roughly a factor of 1.35–1.38). The key to successful analyses of this kind is that the

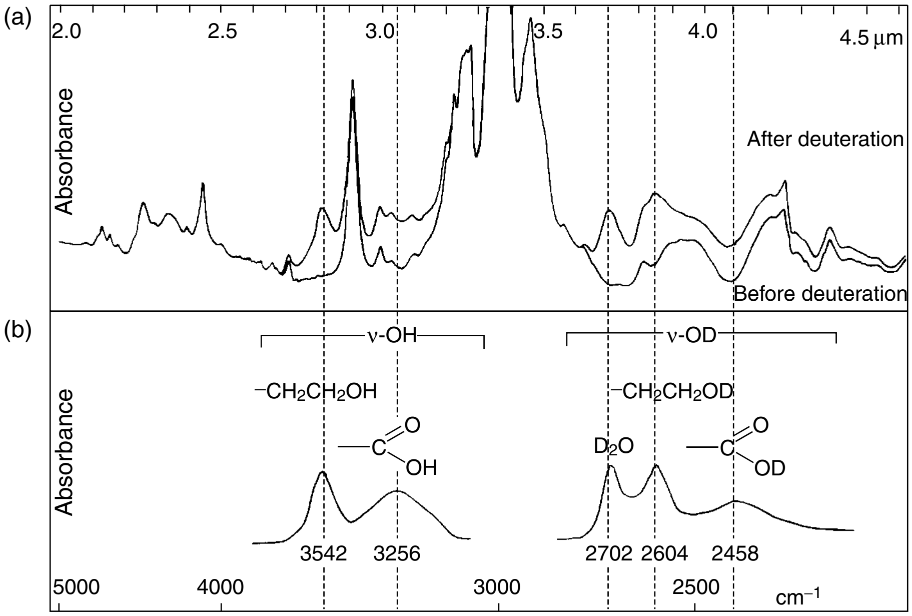
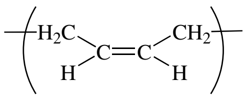
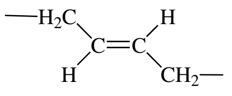
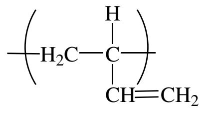


Figure 11. (a) IR absorbance spectra of a dried PET film before and after exposure to D_2O. (b) Difference IR absorbance spectra between PET film spectra before and after deuteration. [Reproduced from J.M. Chalmers, 'Infrared Spectroscopy in Analysis of Polymers and Rubbers', in "Encyclopedia of Analytical Chemistry", ed. R.A. Meyers, 7702–7759, Vol. 9 (2000). © John Wiley & Sons, Ltd. Reproduced with permission.]

interrogated polymer is dry. Polymers such as PET may exist in equilibrium with significant amounts of adsorbed water, as much as 2% in some cases. This adsorbed water has absorption bands that will interfere with any quantitative measurements of –OH end group concentrations, and must therefore be removed by drying before any quantitative analysis is undertaken. In PET it is most evident as a band at about 3650 cm^{-1} that severely overlaps the –OH end group absorption band. In many polymers, individual water molecules may be entrapped in a way that they do not appear to be hydrogen-bonded with the polymer. For example, in PES and PEEK one observes two bands at 3650 and 3550 cm^{-1}, that are removed by drying (or leaving the sample in the spectrometer beam), which may be assigned tentatively to the antisymmetric and symmetric ν-OH modes of water, respectively (Figure 12).

Table 2. Polybutadiene chain units for addition of the monomer.

Addition	Characterstic IR bands[a]
1,4 *cis-* 	740 cm^{-1}
1,4 *trans-* 	966 cm^{-1}
1,2- 	910 cm^{-1} and 990 cm^{-1}

[a] Positions are for the approximate maximum of the δ_{oop} of hydrogen atoms associated with the C=C groups. The νC=C bands are observed more readily in the Raman spectra at 1639 (vinyl, 1,2-), 1650 (*cis*-1,4-) and 1644 cm^{-1} (*trans*-1,4-).[1]

As we have already seen, a variety of isomeric possibilities can have a considerable effect on the vibrational spectrum of a polymer. The three aliphatic hydrocarbon homopolymers of PE, PP and PIB are all structural isomers that exhibit rotational isomerism, which affects the relative intensities of various bands in their spectra. Rotational isomerism introduces significant shifts in the position of the νC–Cl band in the spectrum of PVC. Distinct spectral differences are also observed in the case of geometric isomerism about double bonds, especially for the out-of-plane deformation modes of hydrogen atoms attached to the carbon atoms of double bonds. This is well illustrated in the IR spectra of the various forms of polybutadiene, where the appropriate characteristic bands (Table 2) are evident for the trans and cis 1,4 forms and the 1,2 form. The three spectra shown in Figure 13 each shows differing amounts

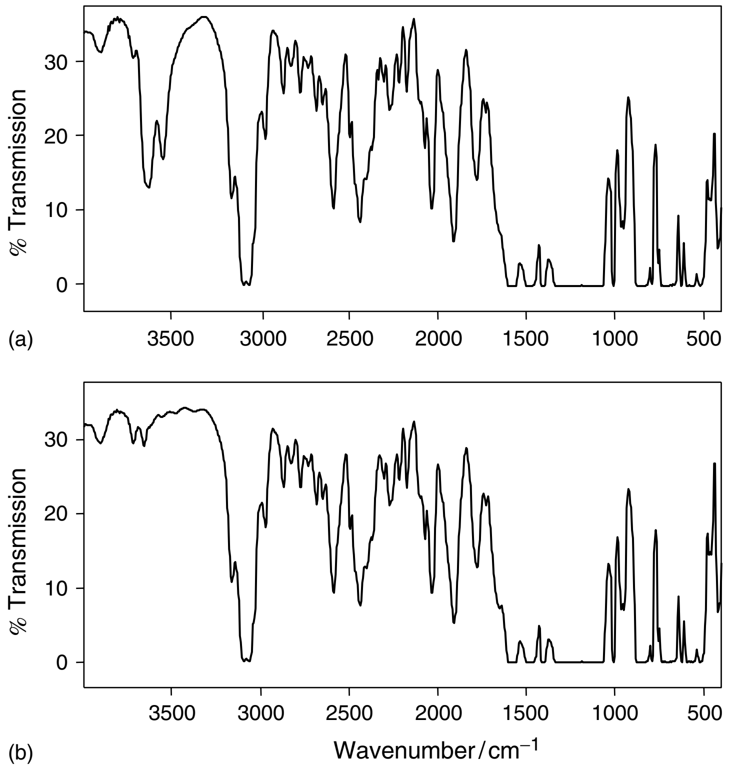


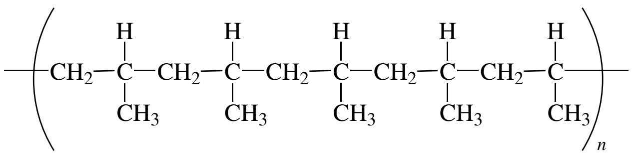
Figure 12. IR transmission spectra recorded from a PES film (a) before and (b) after drying.

of the three forms. (1,2-Polybutadiene can exist in different stereoisomeric (configurational isomers) forms that yield different spectra. The structural groups present are the same in both isomers; the spectral differences arise from the change from an isotactic to a syndiotactic arrangement.)

If we draw a PP molecule as a straight chain with all the methyl groups on one side of the main chain, then the repeat units have the same sequence and this is the isotactic species (and that most commonly found in commercial materials). In the syndiotactic species the pendent groups alternate from one side to the other of the main chain. There is another less regular species, the atactic form, which has the pendent groups randomly oriented with respect to each other along the polymer carbon chain. The tactic sequences for PP are shown as structures **(12)**–**(14)**.

The differences in tacticity can cause changes in the ordering and packing of the chains in the solid state. Polymers like those listed in Table 1 may have the possibility to form stereoregular structures, in which successive repeat units may follow each other in a regular configurational sequence. For example, *syndiotactic* PP has been made to exist in either a helical or a planar zigzag conformation; these have very different spectra, but in both cases the PP is stereoregular.

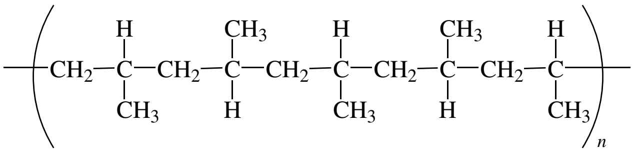
It might be inferred intuitively therefore that vibrational spectroscopy would be a good technique for studying



$$\left(\mathrm{CH_2}-\overset{\mathrm{H}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}-\mathrm{CH_2}-\overset{\mathrm{H}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}-\mathrm{CH_2}-\overset{\mathrm{H}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}-\mathrm{CH_2}-\overset{\mathrm{H}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}-\mathrm{CH_2}-\overset{\mathrm{H}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}\right)_n$$

isotactic (same)

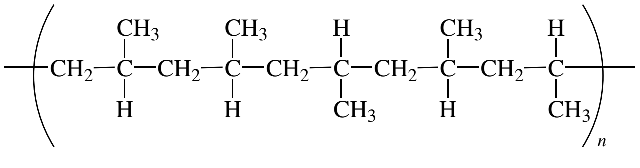
(12)



$$\left(\mathrm{CH_2}-\overset{\mathrm{H}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}-\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\underset{\mathrm{H}}{\mathrm{C}}}-\mathrm{CH_2}-\overset{\mathrm{H}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}-\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\underset{\mathrm{H}}{\mathrm{C}}}-\mathrm{CH_2}-\overset{\mathrm{H}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}\right)_n$$

syndiotactic (alternating)

(13)



$$\left(\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\underset{\mathrm{H}}{\mathrm{C}}}-\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\underset{\mathrm{H}}{\mathrm{C}}}-\mathrm{CH_2}-\overset{\mathrm{H}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}-\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\underset{\mathrm{H}}{\mathrm{C}}}-\mathrm{CH_2}-\overset{\mathrm{H}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}\right)_n$$

atactic (random)

(14)

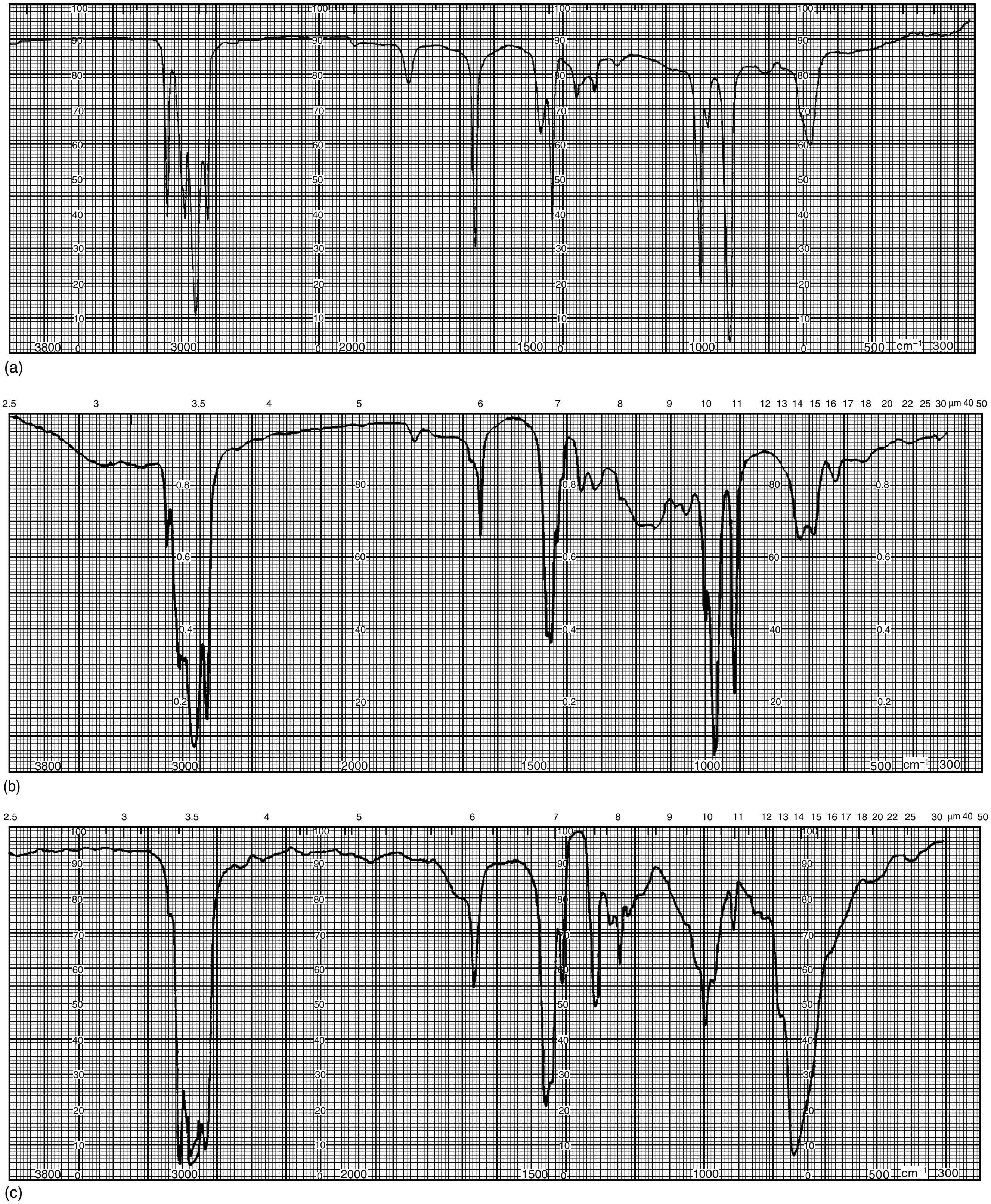


Figure 13. IR transmission spectra recorded from various polybutadienes: (a) polybutadiene with a high proportion of 1,4 trans units; (b) polybutadiene with 1,2 units and 1,4 cis and trans units; and (c) polybutadiene with 96.5% 1,4 cis units. [Spectrum (a) reproduced from spectrum number 116 in Vol. 1, and spectra (b) and (c) reproduced from spectrum numbers 2369 and 2368, respectively, in Vol. 2, Part a/I, in 'Atlas of Polymer and Plastics Analysis', 2nd edition, D.O. Hummel, Verlag Chemie GmbH, Weinheim (1984).]

polymer tacticity, but this is often not the case. While some studies of polymer tacticity have been undertaken using vibrational spectroscopy, the primary method for detailed studies of tacticity is NMR.

Atactic polymers exhibit no overall regularity of configuration of successive repeat units when examined by X-ray diffraction, although short period regularity within polymer chains may still be evident in an NMR spectrum. The vibrational spectra of *atactic* polymers are similar to those of the amorphous polymer. IR and Raman spectra of various tactic forms of PP are shown in Figures 14 and 15, respectively.

Like many stereoregular polymers, *isotactic* PP coils up into a helix. The *isotactic* PP helix is a 3_1 helix. Viewed from one end of the chain, one can observe that the methyl groups are arranged at the corners of an equilateral triangle, because in three monomer units, the structure has completed one turn of the helix. It is a combination of both the tactic arrangement and its preferred helical conformation in space that gives rise largely to the observed IR spectrum. Stereoregular polymer chains that assume preferred regular spatial conformations (conformational isomerism) may also pack regularly to form crystalline arrangements. The greater propensity of sharp bands in the IR and Raman spectra of *isotactic* PP reflects that it is able to pack with higher order than either of the other two forms.

In general increasing crystallinity and order leads to a sharpening and increased intensity of some bands in the mid-infrared and Raman spectra. For example, the IR spectrum of molten *isotactic* PP resembles that of an amorphous PP; bands appearing in the IR spectrum of *isotactic* PP at 1165, 998, 899 and $840\,\mathrm{cm}^{-1}$ disappear on melting; on resolidification, these bands reappear. The crystalline form of this material has a rigid rod-like structure, which does not allow any rotation about single bonds. Decoupling the influences of tacticity, conformational order and crystallinity on a vibrational spectrum is not an easy or indeed always a possible task, since they may be inextricably responsible for the observed data. For *isotactic* PP, a property of its tacticity is that it leads to a three-fold helix conformation of the polymer chain in the solid state. The combination of very regular chain conformation and isotacticity allows for the presence of crystallinity in a sample of isotactic PP.

The regularity of *isotactic* PP means that bond angles are known with high precision and also that the force constants are well known. A calculated spectrum of band frequencies may then be a good fit to the experimental spectrum. The crystal of *isotactic* PP is monoclinic with four chains in the unit cell. Thus, there are 12 monomer units or 108 atoms per unit cell (which translates, $3N$-6, to 318 vibrational modes). The spectrum, however, appears to be much simpler than the number of predicted normal modes. This simplification can be explained on the basis of a single helix rather than on the basis of tacticity alone or the fact that the sample simply might be crystalline. The calculated molecular vibrations break down into two distinct groups: "A" modes, the parallel modes, in which during the vibrations the direction of the dipole moment is approximately parallel to the helix axis; and "E" modes, in which the direction of the transition moment (dipole moment change) is approximately perpendicular to the helix axis.

Polarized radiation may be used on drawn (stretched) polymers to interrogate the directional properties of vibrational modes and to examine the degree of orientation of an oriented sample. For example, if we first measure the IR spectrum of a one-way drawn sample of PP with the electric vector of radiation along (parallel to) the direction of draw, we will get the "parallel" spectrum, in which the parallel bands (A modes) feature most strongly. The perpendicular modes (E modes) are very weak or nonexistent. If the electric vector of the polarized radiation is now rotated through 90°, the perpendicular modes become dominant, while the parallel modes are now comparatively much weaker or disappear.

An example of the interrogation of vibrational spectra using linearly polarized radiation is shown in Figure 16, which shows an isolated PET chain. We can deduce that the vibration leading to the $1018\,\mathrm{cm}^{-1}$ IR absorption band is almost parallel to the chain axis, while the $875\,\mathrm{cm}^{-1}$ band is almost perpendicular. For the Raman case, the $1615\,\mathrm{cm}^{-1}$ has parallel character, while, as might be expected, the νC=O has greater intensity in the perpendicular view.

Care must be taken not to confuse vibrational spectral changes associated with conformational isomerism with polymer crystallinity. As mentioned in Section 2.2, the PET alkyl sub-unit may exist in either a gauche or trans conformation. While the former only exists in amorphous regions, the trans entity can exist in both amorphous and crystalline phases. Bands attributed to the trans conformer will appear strong in the spectra of both a highly oriented amorphous sample as well as a crystalline sample. Figure 17 compares the IR spectra recorded from a largely amorphous PET film, a fairly well oriented amorphous PET film and a bi-axially oriented crystalline PET film. The spectra show many differences associated with conformational changes, molecular ordering and packing.

The presence of regular chain structures (*regularity*) in polymers is conducive to crystalline phase formation, whereas the presence of side chains hinders development of large crystalline domains. Regular structure per se does not however imply an ability to crystallize. PES is essentially amorphous, while PEEK may attain levels of 40% or greater crystallinity as measured by X-ray diffraction. The side chains in LDPE inhibit good lateral packing and so

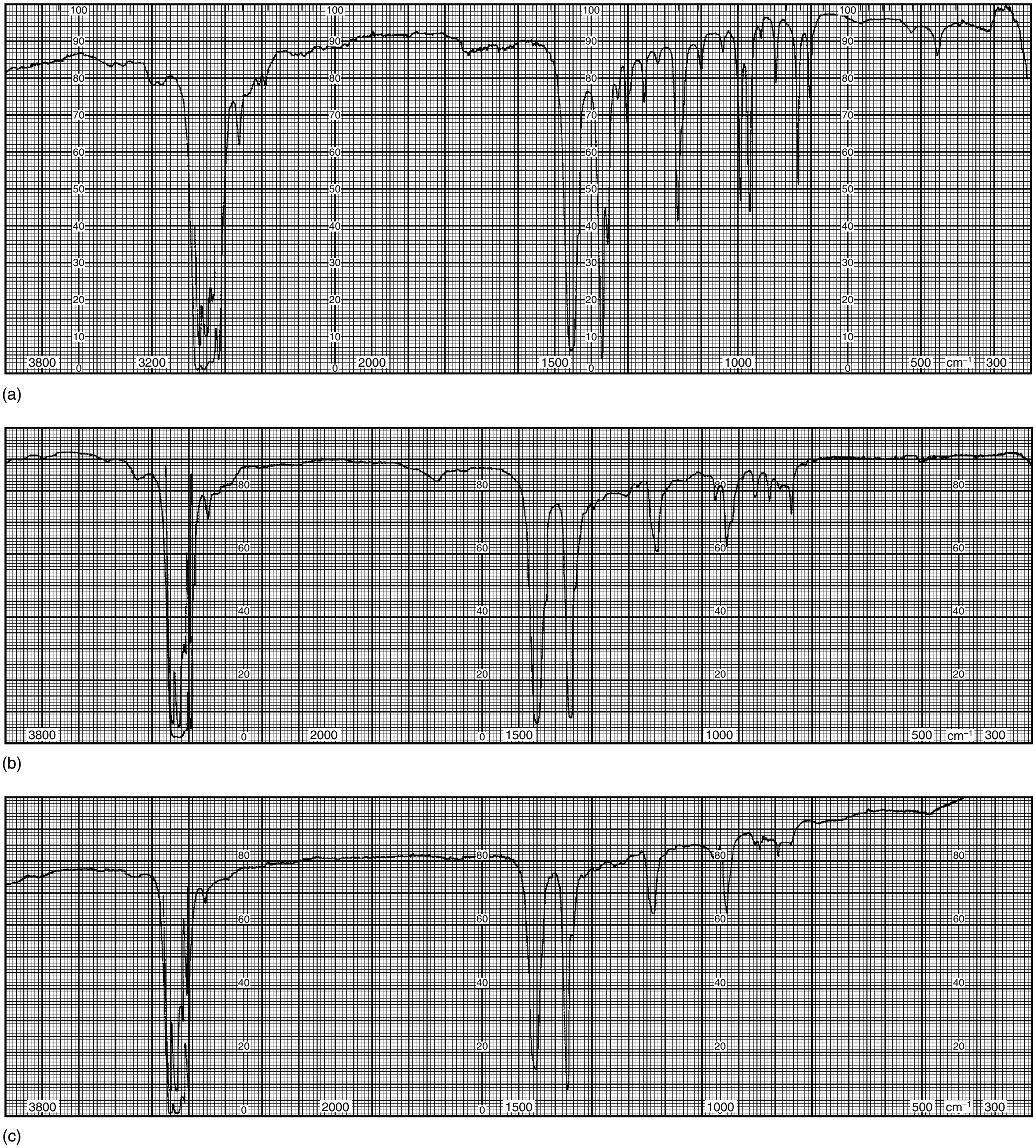


Figure 14. IR transmission spectra of configurational isomers of PP: (a) *isotactic* PP; (b) *syndiotactic* PP; and (c) *atactic* PP. [Spectra (a), (b) and (c) reproduced from spectra numbers 16, 18 and 19, respectively, in 'Atlas of Polymer and Plastics Analysis', Vol. 1, 2nd edition, D.O. Hummel, Verlag Chemie GmbH, Weinheim (1984).]

prevent these materials from attaining the same levels of crystallinity as HDPEs. As synthesized, solid PTFE may be very highly crystalline as measured by wide-angle X-ray scattering and determined by other methods.[2] As we stated earlier, the most likely consequence in the mid-infrared region of an increase of crystallinity will be a reduction in the half-band width of the bands of the conformer in the crystalline phase. Indeed, the half-band width of the νC=O

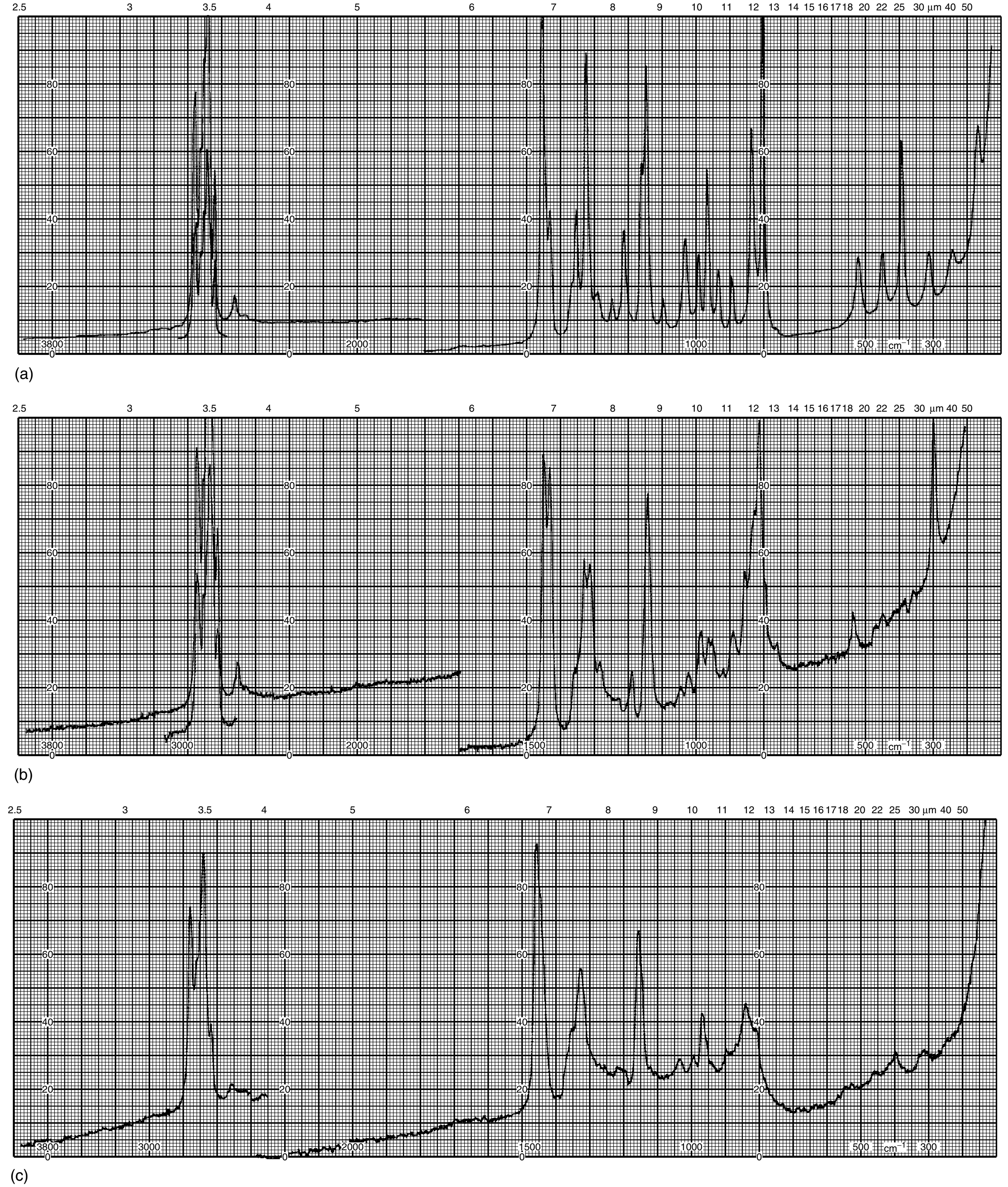


Figure 15. Raman spectra of PP: (a) *isotactic* PP; (b) *syndiotactic* PP; and (c) *atactic* PP. [Spectra (a), (b) and (c) reproduced from spectra numbers 4469, 4470 and 4471, respectively, in 'Atlas of Polymer and Plastics Analysis', Vol. 2, Part a/II, 2nd edition, D.O. Hummel, Verlag Chemie GmbH, Weinheim (1984).]

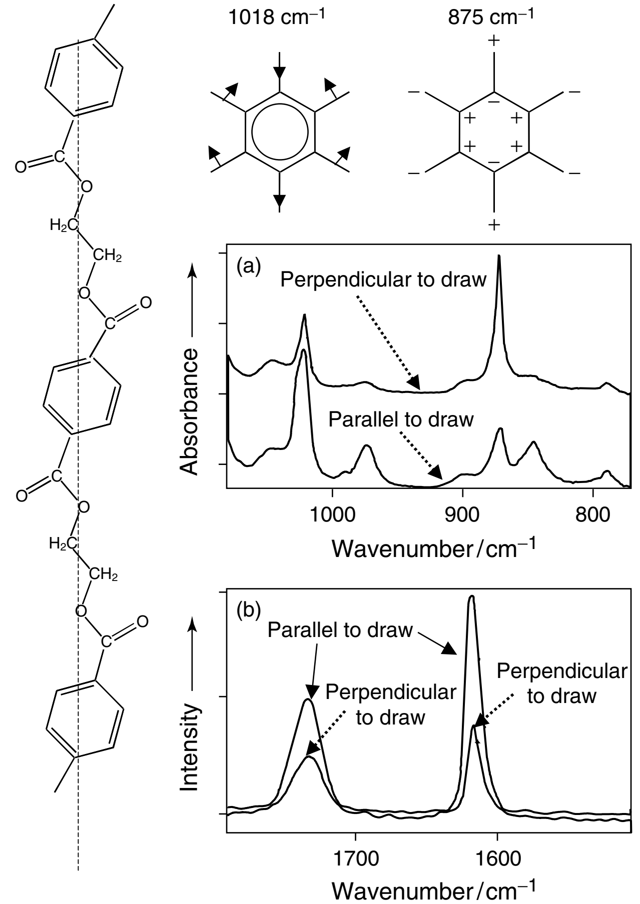


Figure 16. PET orientation: schematic of an oriented PET chain, and IR active modes at $1018\,\mathrm{cm}^{-1}$ and $875\,\mathrm{cm}^{-1}$, and polarized (a) IR absorbance and (b) Raman spectra recorded from a uniaxially oriented PET. Parallel and perpendicular refer to the alignment of the electric vector of the radiation with respect to the draw (chain) axis of the polymer.

band in the Raman spectrum for both PET and PEEK has been correlated with polymer density, and by implication polymer crystallinity.

In some circumstances, there are peaks in a spectrum of a polymer that are quite definitely associated with crystalline regions, because they originate from the interaction of two or more chains in the crystallographic unit cell. PE is perhaps the most quoted (and only really good) example. Because the $-CH_2-CH_2-$ unit cell of crystalline PE has a center of symmetry, the rule of mutual exclusion applies; the bands that are IR active are absent in the Raman spectrum and vice versa. The fundamental bands in both the IR and Raman spectra of linear PE may be very sharp, since it can form into a highly crystalline material and the molecules are well-ordered. As mostly encountered, PE crystallizes into an orthorhombic arrangement, with two chains per unit cell. The various vibrations of these two chains can occur symmetrically or antisymmetrically, and there is a slight energy difference between these, so there is splitting of the bands into pairs. This is particularly easy to observe in the case of the CH_2 rocking mode, for which two bands occur at ~720 and $\sim 730\,\mathrm{cm}^{-1}$ (Figures 1 and 2).

The polymer chains in the crystalline regions of polymers adopt a more or less fixed conformational arrangement, usually an all-trans arrangement for alkyl units, as part of a planar zigzag or regular helical structure. In contrast, chains in amorphous regions are conformationally irregular and unordered, with many gauche bands in the case of alkyl chains. A variety of conformational structures may occur over a distance of a few repeat units. The vibrational frequencies of each of these differ slightly and the overall effect is to broaden the band. Thus, the bands of a polymer in the amorphous state are generally broader than bands due to the crystalline phase. Additional bands may occur in the crystalline phase because of chain–chain interactions.

Polymorphism, the existence of more than one crystalline form, is not uncommon for polymers that are potentially highly crystalline. Caution has already been stressed in the case of the absolute identification of some nylons on the basis of their vibrational spectra alone. The polymorphs may have different spectra for two reasons. Polymorphs may differ in the number of chains passing through the unit cell. If there is only one chain per unit cell, there is no chain–chain interaction, and no band-splitting. While the IR spectrum of orthorhombic PE shows a pair of bands with maxima at 720 and $730\,\mathrm{cm}^{-1}$, monoclinic PE, which has one chain per unit cell, has a single rocking mode absorption band at $715\,\mathrm{cm}^{-1}$. Polymorphs have different spatial structures, and symmetry properties. For example, polyoxymethylene normally occurs as a hexagonal system and individual chains have nine units in five turns, i.e. a 9_5 helix. This can be shown to have 33 spectroscopically active modes. A second form can be obtained with some types of polymerization, in which the chains are planar zigzag, and which adopt an orthorhombic unit cell. This arrangement gives 20 spectroscopically active modes. Polybutene (polybut-1-ene) is another example in which large differences are observable in the spectra of the different crystalline forms. This polymer has two common morphological forms, one having a 3-fold (3_1) helix like PP, and the other a four-fold (4_1) helix, that is four repeat units for one complete turn. A polybutene film prepared from the melt will likely exist in the Type II crystalline modification, but with time this will revert to the higher density Type I form (Figure 18). This change is from the tetragonal 4_1 helix crystalline phase to one with 3_1 helix rhombohedral crystalline domains. The major alterations observed in the mid-infrared spectrum are a consequence of changes of spatial molecular conformation.

As pointed out in the far-infrared article (**Far-infrared Spectroscopy**) in Volume 1 of this Handbook,

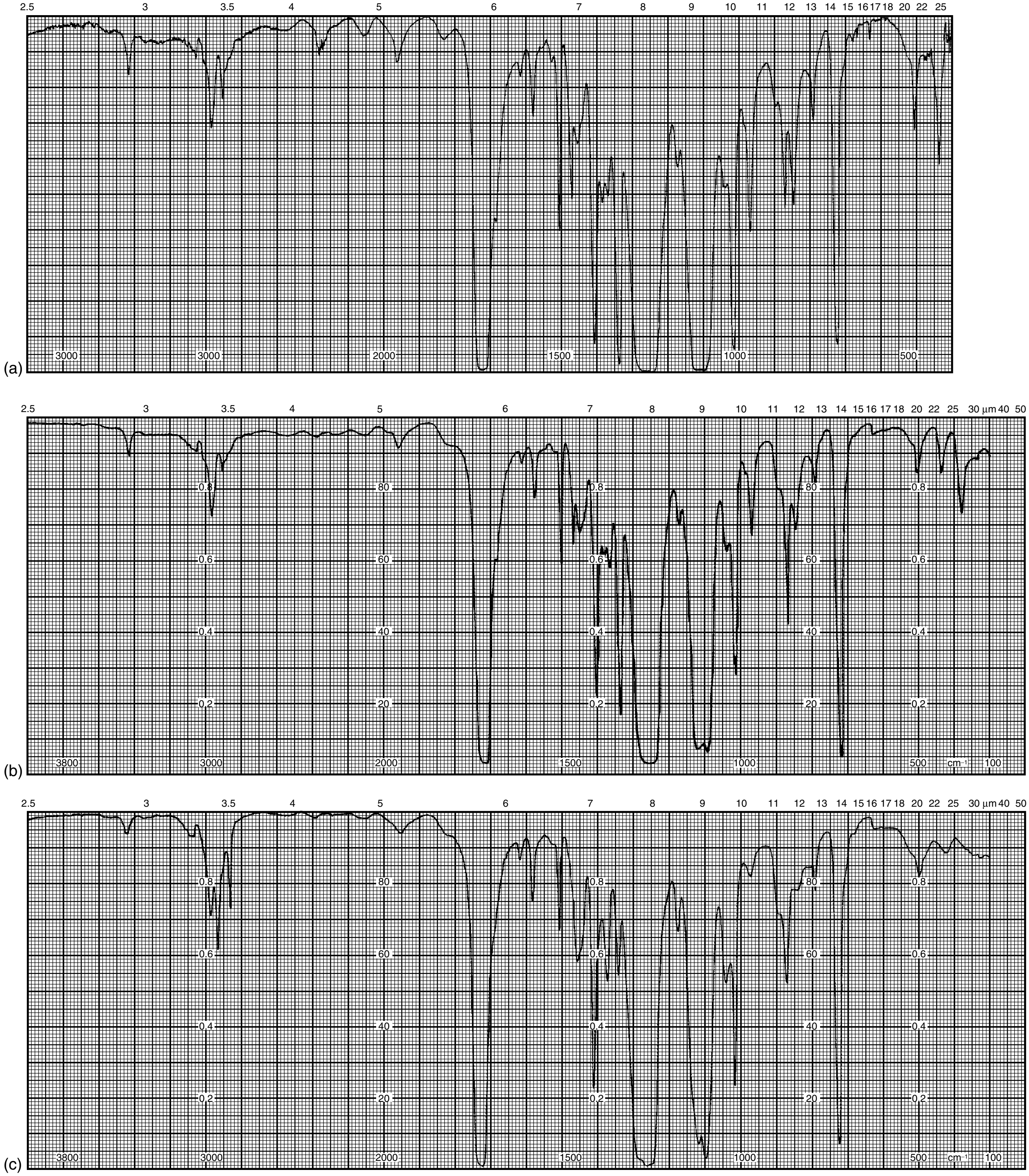


Figure 17. IR transmission spectra recorded from various PET film samples. The spectra approximate to: (a) a film that is essentially bi-axially oriented and crystalline; (b) an amorphous film that is fairly well oriented; and (c) a film that is largely amorphous. (These categorizations are far from exact, but are given merely to highlight the kind of spectral changes one may observe in the IR spectra of PET film samples of differing thermal and rheological histories.) [Spectra (a), (b) and (c) reproduced from spectra numbers 2085, 2086 and 2087, respectively, in 'Atlas of Polymer and Plastics Analysis', Vol. 2, Part a/I, 2nd edition, D.O. Hummel, Verlag Chemie GmbH, Weinheim (1984).]

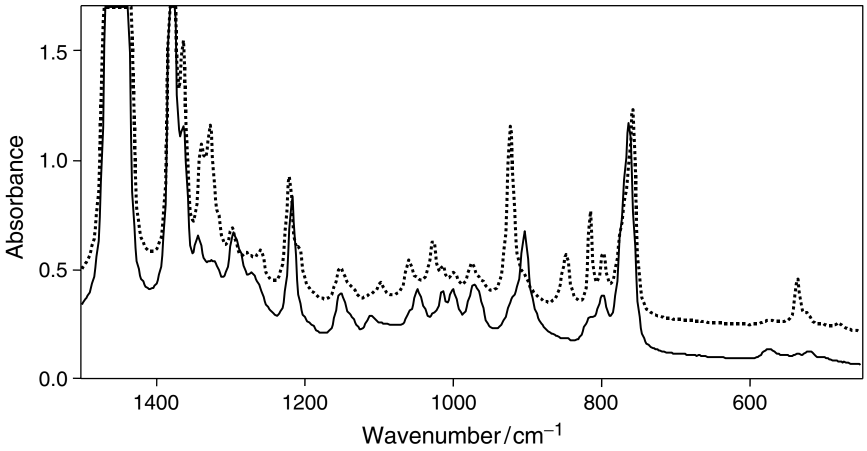


Figure 18. IR absorbance spectra recorded from type I (dashed line) and type II (solid line) polybutene. See text for details.

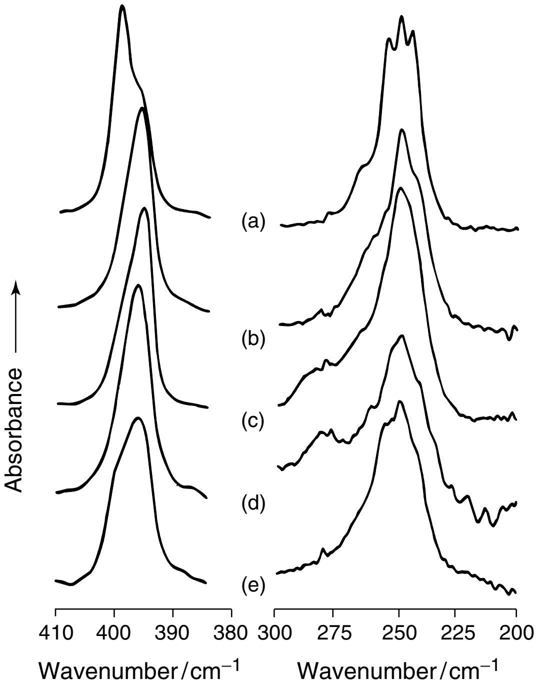


Figure 19. Far-infrared spectra recorded from various polymorphs of i-PP at 100 K: (a) highly crystalline α i-PP; (b) quenched (amorphous) α i-PP; (c) β i-PP; (d) "smectic" i-PP; and (e) γ i-PP. [Reproduced from D.R. Beckett *et al*., *Eur. Polym. J.*, **21**, 849 (1985) by kind permission of Elsevier Science.]

low frequency vibrations in the spectra of polymers can arise from both intra- and intermolecular modes. Among the examples discussed in the far-infrared article was distinguishing α and γ conformation crystalline modifications in nylons. Considered also was the crystalline sensitivity of bands in the far-infrared spectrum of i-PP, in which narrowing and splitting, consequent upon higher intermolecular interactions, occurred with increasing crystallinity. The spectra shown were recorded from a sample consisting of largely the α form of i-PP. Four different crystalline forms of i-PP have been identified by X-ray diffraction. These polymorphs are usually referred to as the α, β, γ and *smectic* forms, with unit cell structures of monoclinic, hexagonal, triclinic and pseudo-hexagonal, respectively. Figure 19 shows part of the far-infrared spectra of various forms of i-PP at 100 K. The splitting of certain A modes, as a consequence of internal interactions, reflect the environment of the isolated i-PP chain within particular cell configurations.

A feature that has received much attention in the low wavenumber region of Raman spectra is that of longitudinal acoustic modes (LAMs). These may be observed in a number of semicrystalline polymers. The position of this symmetrical "accordion-like" skeletal vibration of the extended chain relates to the crystalline stem length within lamellae thickness, for example, see Figure 20.

4 COPOLYMER VIBRATIONAL SPECTRA

The discussions so far have only considered homopolymers. Yet, many commercial materials are co- or terpolymers. Near- and mid-infrared and Raman spectroscopy are used extensively in industry for the quantitative quality assurance of the composition of copolymers. Examples of this may be found in many other articles in this Handbook. Some peculiarities and properties of copolymer vibrational spectra will be discussed here.

Figure 21(a) and (c) shows the IR spectra of two homopolymers that are amorphous, or of very low crystallinity, and the prominent bands in both spectra relate to the polymer molecular subgroups. The spectrum of a copolymer may therefore appear to be virtually indistinguishable from that of an appropriate sum of the spectra of the two homopolymers (Figure 21b). Consequently, it may be extremely difficult to distinguish

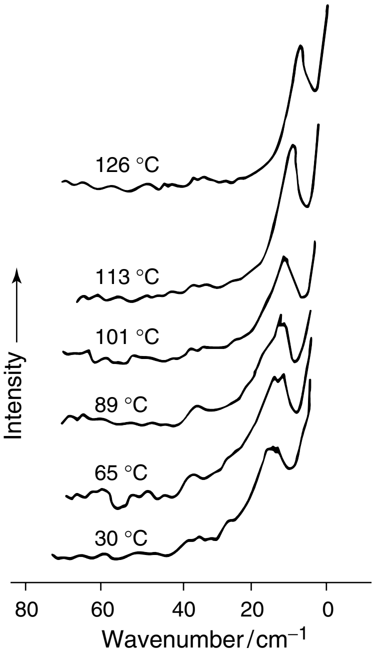


Figure 20. LAM Raman spectra of a PE sample. The PE was originally quenched in ice water and subsequently annealed for 1 h at a series of temperatures. [Reproduced from J.L. Koenig and D.L. Tabb, *J. Macromol. Sci.–Phys.*, **B9**, 141 (1974) by courtesy of Marcel Dekker, Inc.]

between a blend and a copolymer. For the case of poly(vinyl acetate) (PVA) and PE shown in Figure 21, the two polymers are completely incompatible. A blend of these two polymers does not have any useful mechanical properties. On the other hand, blends of different types of PE, or blends of PE with ethylene/vinyl acetate (EVA) copolymers, are compatible and may have commercially attractive properties. So, beware over-interpretation; seek complementary evidence.

As can be seen from Figure 22, the Raman technique is also fraught with danger in analyzing these particular materials, because of its comparative insensitivity to the polar functional groups compared with IR.

On close inspection of the IR spectra of EVA copolymers of differing composition, subtle differences between spectra may be observable. For example, when the relative concentration of VA in the copolymer increases, the half-band widths of the VA bands increase. On going from 1% VA to 28% VA, the bandwidths of both the νC=O and νC–O increase significantly. This broadening effect is most likely due to bunching of the VA groups that are adjacent to one another. (For a 28% VA EVA copolymer diluted with PE, these half-band widths have been noted to stay the same, so the effect is real and not an intermolecular effect.)

Copolymers may be synthetically formed from two monomers such that they are linked essentially in either a "random" fashion or in a "block" manner, in which long sequences of similar repeat units are linked together. These situations are shown in Scheme 2 for two repeat units A and B.

The vibrational spectra of random and block copolymers prepared from the same two monomers are likely to be significantly different. Consider the case of a methyl methacrylate/styrene copolymer. The IR spectra of long chain methacrylate polymers possess two pairs of highly characteristic absorption bands in the 1200 cm^{-1} region. These pairs occur as partially resolved doublets, with one pair near 1270 and 1240 cm^{-1}, and the other pair near 1190 and 1150 cm^{-1}. This set of absorption bands has been assigned to the C–O–C stretching vibrations of the pendant groups. If the polymer is composed of short sequences of poly(methyl methacrylate) (PMMA), as might exist in a random copolymer, these bands will change substantially in appearance compared to those of the block copolymer. They become two single and rather broad bands near 1210 and 1130 cm^{-1}. Figure 23 shows the IR spectra of the two homopolymers. Figure 24 compares the IR spectra recorded from a block (a) and a random (b) copolymer.

Local order within a block copolymer can result in local crystallinity effects (conformational regularity) that can lead to a sharpening and narrowing of absorption bands. This should be borne in mind when interpreting the spectra of copolymers. Propylene/ethylene copolymers are very common and are commercially available in a number of different grades. They are manufactured by varying the monomer feed concentration to the polymerization vessels. Materials can be produced in which the copolymerized ethylene units are all present essentially as isolated units within the copolymer chain. Alternatively, these polymers can also be manufactured as grades in which the ethylene units are present mostly as longer sequences (block copolymers) within the copolymer chain. Finally, the PE units are sometimes found in long sequences at the end of a PP chain (end-block). Some grades may even contain distributions of each of these possibilities. In a normal head-to-tail polymerization mechanism an isolated copolymerized ethylene unit between two copolymerized propylene units leads to a contiguous –(CH_2)– sequence of –$(CH_2)_3$–. The rocking mode vibration characteristic of this sequence has an absorption maximum at about 733.5 cm^{-1} (Figure 25b). Adjacent copolymerized ethylene units within a PP chain will lead to a sequence of –$(CH_2)_5$–. This sequence and longer runs of ethylene units is characterized by an absorption band with a maximum near 720 cm^{-1}. Local order may occur within domains containing long ethylene sequences such that crystalline phases exist which can give rise to the characteristic 730/720 cm^{-1} doublet (Figure 25a). The isolated –CH_2– unit arising from head-to-tail PP sequences gives rise to an absorption band near 810 cm^{-1}. (A tail-to-tail PP unit

Figure 21. IR transmission spectra: (a) PVA; (b) EVA copolymer containing ∼4% VA; (c) PE. [Spectra (a), (b) and (c) reproduced from spectra numbers 3091, 1930 and 1916, respectively, in 'Atlas of Polymer and Plastics Analysis', Vol. 2, Part a/I, 2nd edition, D.O. Hummel, Verlag Chemie GmbH, Weinheim (1984).]

Random copolymers:

—A—B—A—A—B—B—A—B—A—A—B—A—B—B—

—A—A—A—A—A—B—A—A—A—B—A—A—A—A—A—A—A—A—B—A—A—

Block copolymers:

—A—A—A—A—B—B—B—B—B—B—B—A—A—A—A—A—A—A—B—B—B—B—B—

—A—A—A—A—A—A—A—A—A—A—A—B—B—B—B—A—A—A—A—A—A—A—A—A—

—A—A—A—A—A—A—A—A—A—A—A—A—A—A—A—A—A—B—B—B—B—B—B—B— (end-block)

Scheme 2

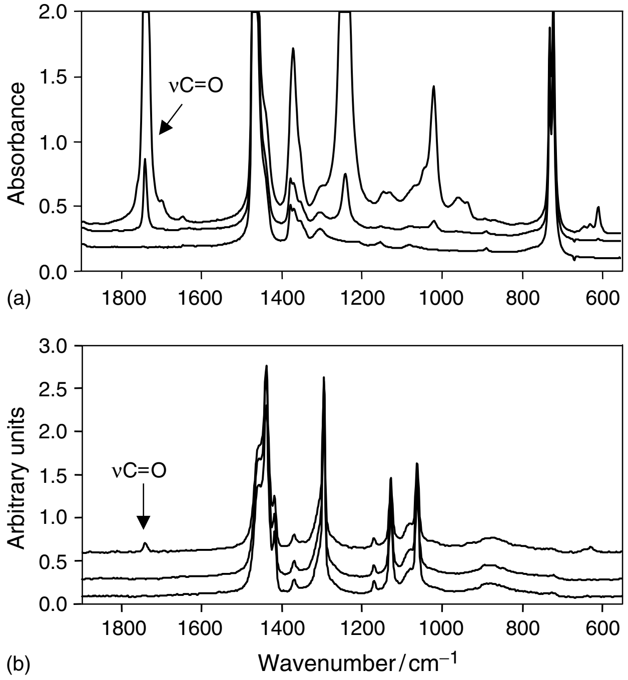


Figure 22. (a) IR absorbance and (b) Raman spectra recorded from two EVA copolymers containing 7.7% and 0.65% VA, and an LDPE. The LDPE spectrum is the lower in each series; the higher VA content copolymer is the uppermost spectrum in each set.

would give rise to two contiguous –CH$_2$– units, identified by an absorption band near 751 cm^{-1}.)

5 VIBRATIONAL SPECTRA OF COMMERCIAL "POLYMERS" AND POLYMER PRODUCTS

Many polymers are supplied or used commercially as formulated products. The other constituents will likely contribute additional characteristic bands to the vibrational spectra recorded from the bulk polymer (or copolymer). These additives may include stabilizers and property enhancers, such as anti-oxidants, UV stabilizers, slip-agents, impact modifiers, processing aids or fire-retardants, or they may be fillers or reinforcing agents.

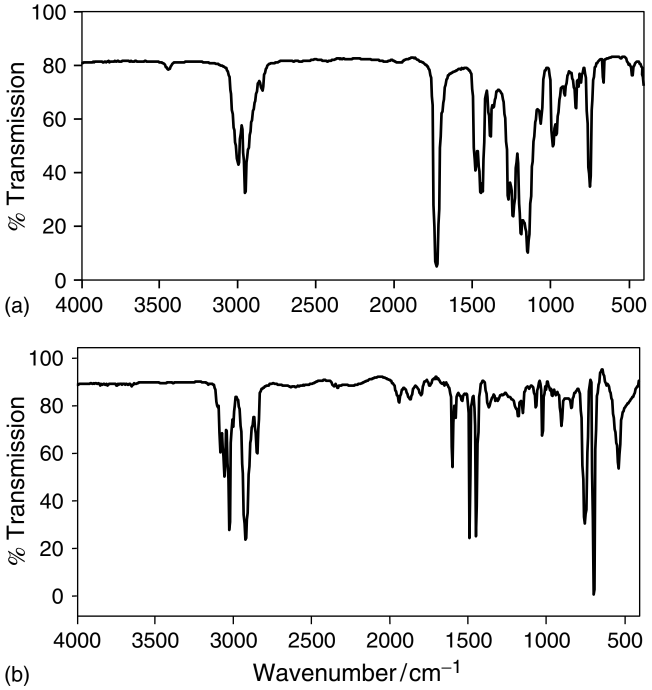


Figure 23. IR transmission spectra of (a) PMMA and (b) polystyrene.

Figure 26 shows the IR spectrum of a phthalate plasticized PVC sample. Among the absorptions characteristic of the *o*-dialkyl phthalate are the νC=O near 1725 cm^{-1} and the weak sharp doublet between 1600 cm^{-1} and 1550 cm^{-1} (see **Mid-infrared Spectroscopy: Anomalies, Artifacts and Common Errors** in this Handbook). Figure 27 shows

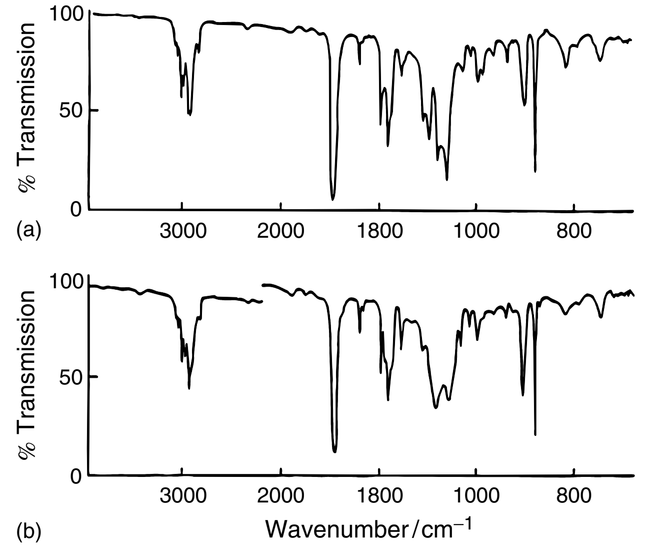


Figure 24. IR transmission spectra of methyl methacrylate/styrene copolymers: (a) a "block" copolymer; (b) a "random" copolymer.

one IR and one Raman spectrum of inorganically filled polymers. These are: Figure 27(a), a talc (magnesium silicate) filled PP (cf. Figure 4b); and Figure 27(b), a TiO_2 filled PET. The specific features, often intense, of the inorganic components are clearly evident. The spectra of Figures 26, 27(a) and 27(b) should be compared with the "pure" polymer spectra shown as Figures 3(a), 4(b) and 7 (Raman), respectively.

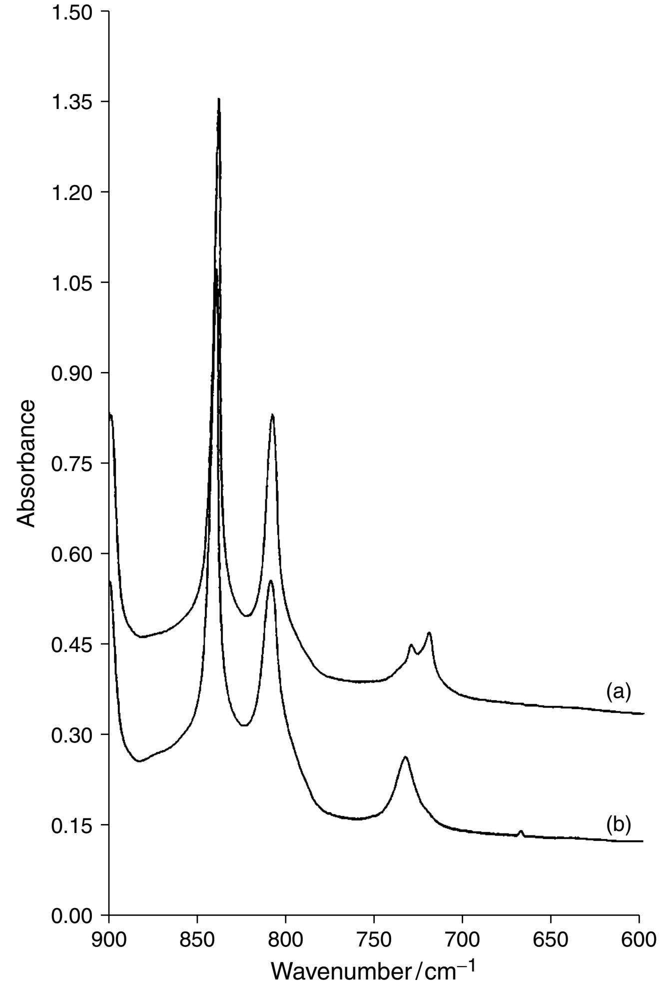


Figure 25. IR absorbance spectra over the range 900 cm^{-1} to 600 cm^{-1} recorded from films prepared from propylene/ethylene copolymers containing ~5% copolymerized ethylene: (a) a "block" copolymer containing long –(CH_2)– sequences; (b) a "random" copolymer containing essentially only isolated ethylene units.

6 SUMMARY

The vibrational spectrum of a polymer can result from a complex superposition of many effects, but a consequence of these effects is that the spectrum of the material may contribute very valuable analytical information. A polymer is not composed of a single compound, but involves a large collection of different molecules, which will determine its spectrum. Polymer chains have a molecular weight distribution, and the chains have terminal groups, which may be different from those comprising the main chain, and whose balance may differ with chain length. Chains may also have side branches, which may be of differing lengths. The materials may be crosslinked. Polymer chains may also contain irregularities through the different insertion of monomer units. For example, unsaturated aliphatic (alkene) monomer units may polymerize via head-to-head or head-to-tail insertion, or through a vinyl group by 1,2- or 1,4-addition. The latter type of insertion gives rise to either a cis or trans geometric configuration. Local order and sequencing effects can also influence significantly the appearance of copolymer spectra. In co- and ter-monomer polymerizations there may be a wide distribution of comonomer compositions, which may or may not vary with molecular weight. Many commercial polymer formulations may also require extensive clean up (separation from additives and fillers) before the polymer may be characterized by vibrational spectroscopy.

However, from the discussions above it is clear that vibrational spectra of homopolymers are not overly complex and the ordinary rules, such as symmetry, normal coordinate calculations, etc., apply, and can be used to calculate and interpret spectra. The influence of the end group, and molecular conformation and orientation, and finally packing must however be borne in mind when evaluating a spectrum.

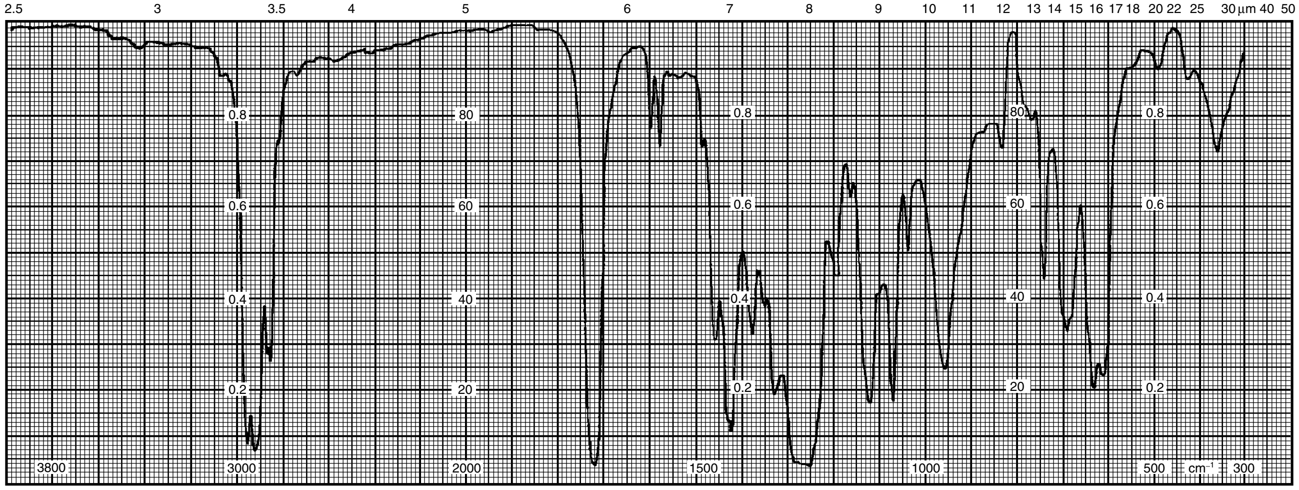


Figure 26. IR transmission spectrum recorded from a "phthalate plasticized" PVC. [Reproduced from spectrum number 2018 in 'Atlas of Polymer and Plastics Analysis', 2nd edition, Vol. 2, Part a/I, D.O. Hummel, Verlag Chemie GmbH, Weinheim (1984).]

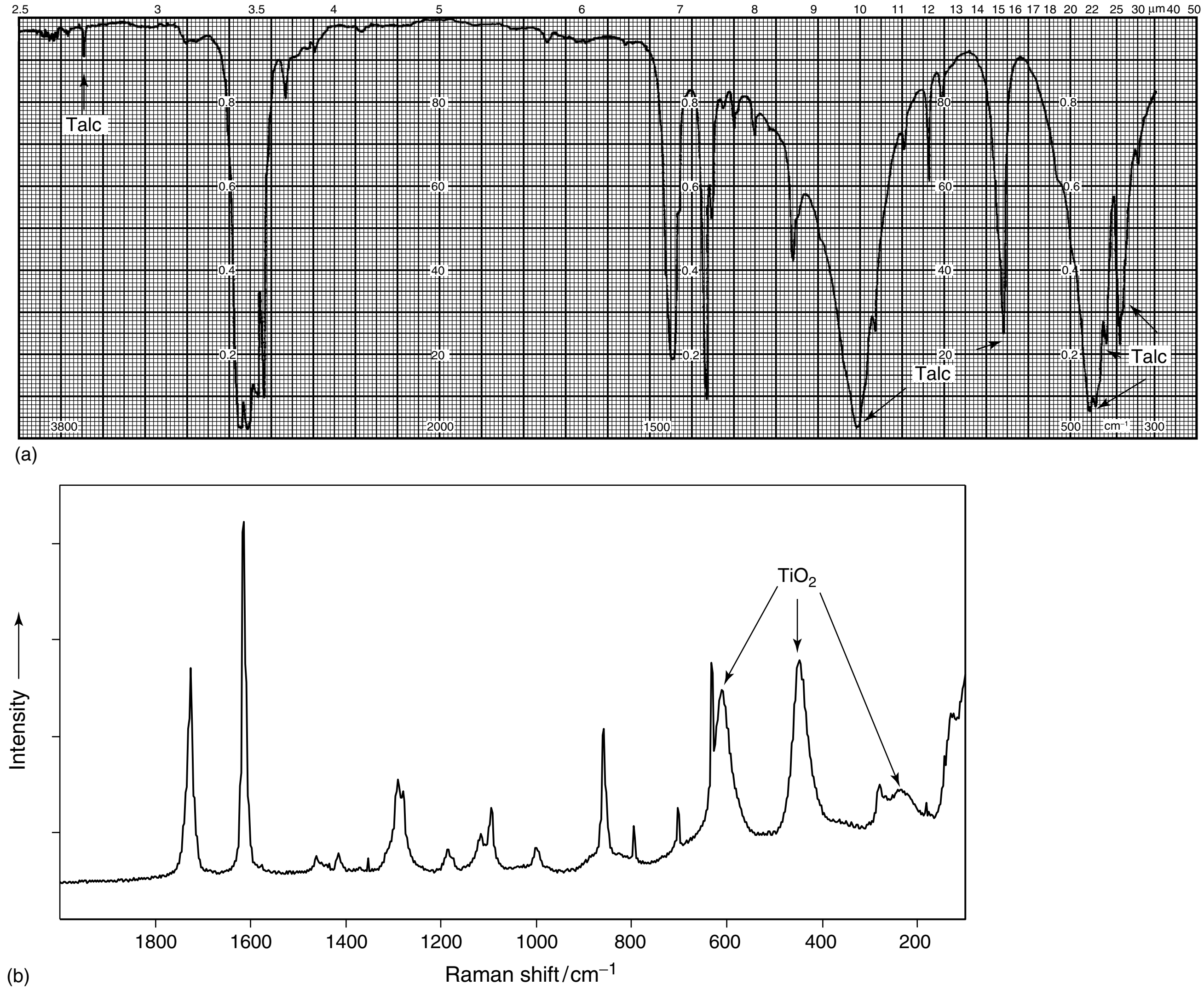


Figure 27. Spectra recorded from inorganically filled polymer samples: (a) IR transmission spectrum from a talc filled PP; (b) Raman spectrum from a rutile TiO$_2$ filled PET. [Spectrum (a) reproduced from spectrum number 1942 in 'Atlas of Polymer and Plastics Analysis', 2nd edition, Vol. 2, Part a/I, D.O. Hummel, Verlag Chemie GmbH, Weinheim (1984).]

ACKNOWLEDGMENTS

In preparing this article, we have illustrated the discussion with the work of too many others to mention each specifically. We would however acknowledge particularly the lecture notes of the late Harry Willis, which formed the base from which much of this article was developed. These notes of Dr Willis formed the basis for one of several lectures that he gave over many years at the Bowdoin College Summer Infrared Courses. This particular area continues to be addressed in these Courses by those of us (RWH and DWM) who have continued in his footsteps.

ABBREVIATIONS AND ACRONYMS

EVA	Ethylene/vinyl acetate
HDPE	High-density Polyethylene
i-PP	Isotactic Polypropylene
LAM	Longitudinal Acoustic Mode
LDPE	Low-density Polyethylene
LLDPE	Linear Low-density Polyethylene
PE	Polyethylene
PEEK	Poly(aryl ether ether ketone)
PES	Poly(aryl ether sulfone)
PET	Poly(ethylene terephthalate)
PIB	Polyisobutene
PMMA	Poly(methyl methacrylate)
PP	Polypropylene
PTFE	Poly(tetrafluoroethylene)
PVA	Poly(vinyl acetate)
PVC	Poly(vinyl chloride)

FURTHER READING

Books and reviews

V.A. Bershtein and V.A. Ryzhov, *Adv. Polym. Sci.*, **114**, 43 (1994).

D.I. Bower and W.F. Maddams, 'The Vibrational Spectroscopy of Polymers', Cambridge University Press, Cambridge (1989).

J.M. Chalmers and N.J. Everall, 'Vibrational Spectroscopy', in "Polymer Characterisation", eds B.J. Hunt and M.I. James, Blackie Academic, Glasgow, 69–114 (1993).

N. Everall, 'Raman Spectroscopy of Synthetic Polymers', in "Analytical Applications of Raman Spectroscopy", ed. M.J. Pelletier, Blackwell Science Ltd, Oxford, 127–192 (1999).

B. Fanconi, *Ann. Rev. Phys. Chem.*, **31**, 265 (1980).

A. Garton, 'Infrared Spectroscopy of Polymer Blends, Composites and Surfaces', Carl Hanser Verlag, Munich (1992).

J. Haslam, H.A. Willis and D.C.M. Squirrell, 'Identification and Analysis of Plastics', 2nd edition, Butterworth, London (1972).

D.O. Hummel, 'Infrared Analysis of Polymers, Resins and Additives: An Atlas. Vol. I, Plastics, Elastomers, Fibers and Resins. Part 1: Text', eds D.O. Hummell and K. Scholl, John Wiley & Sons, Inc., New York (1971).

D.O. Hummel (ed.), 'Polymer Spectroscopy', Verlag Chemie GmbH, Weinheim (1974).

H. Ishida (ed.), 'Fourier Transform Infrared Characterization of Polymers', Plenum Press, New York (1987).

B. Jasse, 'Fourier Transform Infrared Spectroscopy of Synthetic Polymers', in "Developments in Polymer Characterisation-4", ed. J.V. Dawkins, Applied Science, London, 91–129 (1983).

J.L. Koenig, 'Chemical Microstructure of Polymer Chains', John Wiley & Sons, Inc., New York (1980).

J.L. Koenig, *Adv. Polym. Sci.*, **54**, 87 (1983).

J.L. Koenig, 'Spectroscopy of Polymers', 2nd edition, Elsevier Science, New York (1999).

S. Krimm, *Fortschr. Hochpolym.-Forsch.*, **2**, 51 (1960).

P.C. Painter, M.M. Coleman and J.L. Koenig, 'The Theory of Vibrational Spectroscopy and its Application to Polymeric Materials', John Wiley & Sons, New York (1982).

H.W. Siesler and K. Holland-Moritz (eds), 'Infrared and Raman Spectroscopy of Polymers', Marcel Dekker, Inc., New York (1980).

G. Xue, *Prog. Polym. Sci.*, **19**, 317 (1994).

R. Zbinden, 'Infrared Spectroscopy of High Polymers', Academic Press, New York (1964).

Collections of spectra

P.J. Hendra and J.K. Agbenyega (eds), 'The Raman Spectra of Polymers', John Wiley & Sons Ltd, Chichester (1993).

D.O. Hummel (ed.), 'Atlas of Polymer and Plastics Analysis', 3rd edition (4 volumes), VCH Publishers, Weinheim (1991).

A.H. Kupstov and G.N. Zhizhin (eds), 'Handbook of Fourier Transform Raman and Infrared Spectra of Polymers', Elsevier Science, New York (1998).

'An Infrared Spectroscopy Atlas for the Coatings Industry', Federation of Societies for Coatings Technology, Pennsylvania (1980).

'Monomers & Polymers', 'Adhesives & Sealants', 'Plasticizers', 'Additives', and 'Rubber Chemicals', Bio-Rad Laboratories, Sadtler Division, Philadelphia, PA, USA.

REFERENCES

1. H.G.M. Edwards, A.F. Johnson, I.R. Lewis and J.M.G. Cowie, *Polym. Int.*, **31**, 391 (1993).
2. R.J. Lehnert, P.J. Hendra, N. Everall and N.J. Clayden, *Polymer*, **38**, 1521 (1997).