

# Polymer Applications of IR and Raman Spectroscopy

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VIBRATIONAL, ROTATIONAL &  
RAMAN SPECTROSCOPY

Applications

The two techniques of Raman and infrared (IR) spectroscopy have some similarities, yet are quite different in a number of ways. They provide complementary vibrational information. The reader is referred to the articles on the fundamentals of these techniques for details. Raman and IR will here be collectively referred to as VS (Vibrational Spectroscopy), except where details of a particular technique warrant discussion. It should also be noted that most of the techniques mentioned can also be used with near-IR radiation, but specific examples will not be cited.

Among the large number of applications of VS, applications to polymeric systems are especially interesting because of the wide variety of chemical structures and physical ordering that is present in polymer systems. The article is arranged as follows. First, the application of VS to the determination of chemical properties of polymeric systems will be illustrated. In particular, the use of VS as an identification tool for complex polymeric systems and the application of VS to the various chemical reaction processes will be detailed. Then the application of VS to the determination of polymer structure on a wide range of length scales will be explained, with particular emphasis on the determination of stereoregularity, chain conformation and crystallinity. The remainder of the article will focus on the study of dynamic properties of polymers such as diffusion and rheological properties and current topics such as millisecond time-resolved and microimaging applications.

## Spectroscopic considerations unique to polymers

In contrast to small-molecule compounds, in polymer molecules the atoms are all linked together to form long chains. The presence of such long chains causes additional vibrational modes to be present that do not exist in small-molecule analogues. These arise owing to the vibrations of the chain as a whole. This topic is best treated using classical physics and normal coordinate analysis, which is beyond the scope of this article. A more indepth discussion of

these topics can be found in the books by Koenig listed in Further reading. In addition, the long chains can possess ordering along the chain as well as between neighbouring chains. This quality is also unique to polymers and is responsible for many of the physical properties that make polymers the material of choice for a wide variety of applications.

Several properties of polymers complicate their analysis via VS. First, a problem unique to transmission IR spectroscopy is that polymers are very strong absorbers of IR radiation. Therefore, in order to be within the linear region of Beer's law, an extremely thin polymer film must be used in transmission. A good rule of thumb is to keep the thickness below 5  $\mu\text{m}$ . While the production of such thin films is possible in the laboratory, it must be remembered that most commonly encountered polymer systems are much thicker than this. As a result, the most commonly used industrial IR techniques are reflectance techniques such as attenuated total reflectance (ATR) or reflection-absorption spectroscopy (RAS), which have much smaller effective optical path lengths, typically on the order 1  $\mu\text{m}$  or below.

A problem unique to Raman spectroscopy is the fact that most polymers fluoresce strongly when exposed to laser radiation. This problem can be reduced by using Fourier transform and resonance Raman techniques. Because of this and other difficulties associated with Raman spectroscopy, the quality of Raman spectra of polymers is typically less than that of IR spectra. Therefore, it is not surprising that a quick search of the literature reveals many more quantitative studies of polymers using IR than using Raman.

Using a combination of IR and Raman spectroscopies can yield valuable information. IR spectroscopy is sensitive to any chemical groups that possess a significant dipole moment, such as C-H, and C=O, which are commonly found in polymer side groups. Raman spectroscopy is more sensitive to highly polarizable groups such as C-C and C=C, which are commonly found in the polymer chain backbone. Thus, when used together, IR and Raman spectroscopy can be used to gain more information than is available from either of the individual techniques.

## Complete structure determination

Vibrational spectroscopy can be used in the complete chemical and physical structure determination of polymers. Four size scales of structure and orientation found in polymers are covered. The most basic is the chemical identity of the chains, including chemical groups present, monomer sequences and stereoregularity. This is followed by studies of the local conformation of individual chains and interactions between chains, and finally orientation induced by the application of macroscopic forces.

### Chemical identity of polymer chains

The techniques used for identification of the basic chemical structure of polymer chains are similar to those used for small molecules. The difference is that there is not a single chemical structure present; rather there is a distribution of chemical structures. The semirandom statistics involved in the polymerization reaction produce a distribution of molecular masses. Therefore, an average molecular mass is reported. Although chromatography and light scattering are most commonly used for molecular mass determination, IR can provide complementary chemical structure information. A number-average relative molecular mass  $M_n$  can be obtained by determining the number of end groups present for a given amount of polymer by

$$M_n = \frac{2}{E_{\text{end}}}$$

where  $E_{\text{end}}$  is the number of mass equivalent weights of end groups per gram of polymer, as determined from a simple Beer's law treatment. This method works if the structure of the end groups and the nature of the polymerization process are known.

Another unique property of polymerization and copolymerization reactions is the presence of a distribution of chemical connectivities in the final polymer, which come about from the orientation of monomer addition. This is commonly referred to as regiochemistry or regioisomerism. In a typical monosubstituted vinyl polymerization, the monomer has two options of addition to the growing chain, commonly referred to as head or tail addition, depending on whether the propagating chain attacks the monomeric carbon with the pendant group or the unsubstituted carbon, respectively. The ratio of head-to-head, head-to-tail, etc. groups present in the final polymer can be determined by comparing the ratios of spectral bands associated with these linkages. In a

similar manner, copolymer systems can be analysed to determine the statistics of the polymerization process. NMR is the most commonly used technique for this type of analysis, but not all polymers can be analysed using this method. VS can be used in these cases and also to verify the NMR results.

Perhaps the most common application of VS in the determination of chemical makeup in polymeric systems is the identification of components in complex polymer mixtures. Polymeric products are rarely composed of a single component. There are always additives present that aid in processing, appearance, adhesion, chemical stability or other properties important to the function of the final product. In an industrial setting, it is important to be able to determine both the identity and quantity of polymers and additives in a specific formulation for quality control purposes. This can be a fairly routine operation if tools such as spectral libraries are utilized. In this method, a computer search algorithm compares a spectrum with a catalogue of standard spectra to determine the identity of the compound or compounds present. Advanced statistical techniques, such as partial least squares (PLS) and principal-component analysis (PCA), are also often used to identify known and unknown components in polymeric systems. The details of these methods are described elsewhere in the Encyclopedia.

In certain polymerization processes, the final polymer may contain side branches. The most notable example of this is polyethylene, which commonly contains short branches that result from chain transfer reactions during the polymerization process. For each type of branch, up to six carbons in length, the methyl rocking band around the  $900\text{ cm}^{-1}$  has a unique frequency. By comparing the intensities of these branch peaks to peaks associated with the main chain, the relative amount of each type of branch can be determined.

Owing to the length of typical polymer chains, the arrangements of side groups along the chain becomes important in the determination of the chemical properties of the polymer. The polymerization process permanently locks in this arrangement of side groups. The persistence of a specific pattern along the entire chain is known as stereoregularity. Stereoregular effects appear in vibrational spectra as spectral peak splitting or other changes in band shape. An example is shown in Figure 1, which shows the IR spectra from the three pure stereoisomers of polystyrene. As can be seen, the bands around  $1070$ ,  $550$  and  $900\text{ cm}^{-1}$  are quite different for each stereoisomer, revealing that the local molecular environments are different in each case.

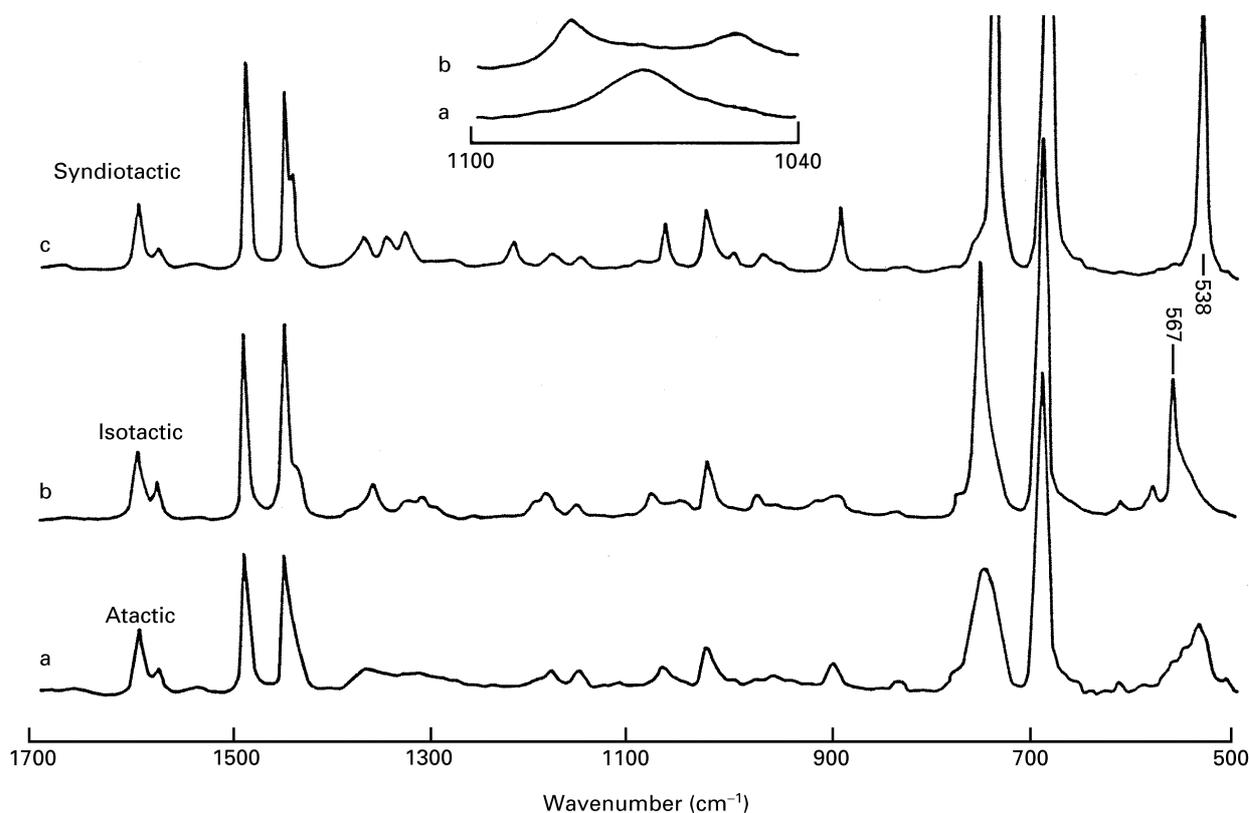


Figure 1 Infrared spectra of the pure stereoisomers of polystyrene.

### Orientation of a single polymer chain

The next highest level of order in polymer chains is the presence of rotational isomers, which result from stable configurations of the polymer chain. The presence of *cis* and *trans* configurations and the relative ratios of each can be determined using VS because each of these structures possess a unique spectral band. Owing to the complementary nature of IR and Raman spectroscopy, a wealth of information about the chain conformation can be determined. Raman is particularly useful in this application owing to its enhanced sensitivity to the local environments around carbon-carbon bonds in the chain backbone. Using a simple thermodynamic treatment, this technique can be extended to determine quantitatively the activation energy barrier between the two conformers. The kinetic rate constant,  $k$ , can be determined from spectral information using the expression:

$$k = \frac{A_1/a_1}{A_2/a_2}$$

where  $A_1$  and  $A_2$  are the absorbances of the bands associated with each conformer, and  $a_1$  and  $a_2$  are

the corresponding extinction coefficients of the bands. By acquiring spectra at a range of different temperatures, the activation energy,  $\Delta G$ , can be determined from the well-known relation

$$\Delta G = RT \ln k$$

where  $R$  is the gas constant and  $T$  is the temperature.

Stable crystalline forms arise from the propagation of a particular sequence of conformations along the entire length of the chain, resulting in a helical arrangement. The most commonly used method for analysing crystalline materials is X-ray diffraction, which can detect long-range crystalline order, like that found in semicrystalline polymers such as poly(vinylidene fluoride) and polyethylene. VS probes the local molecular environment, and therefore has the advantage over X-ray methods that it can detect the short-range order present in the amorphous phase. The presence of helical order shows up in a predictable manner in both IR and Raman spectra.

VS has been applied to polystyrene, which can possess several localized crystalline forms. In this particular case, order results from a planar zigzag

arrangement of the chains that pack together to form structures that possess either trigonal or orthorhombic symmetries. As subtle as this ordering may seem, it can be detected effectively using VS. This can be seen in Figure 2, which shows that the pure crystalline forms of syndiotactic polystyrene have distinct IR spectra. This particular example illustrates the spectral subtraction technique used to determine the spectra of pure crystalline forms of polymers. The spectrum from a completely amorphous sample is subtracted from the spectrum of a partially crystalline sample to yield the 'pure' crystalline spectrum. This is repeated for all crystalline forms. Using these spectra, the crystal forms present in any sample can then be determined. This method of spectral subtraction is commonly used to isolate the spectral contributions of individual components to determine which structures are present.

### Interactions between chains

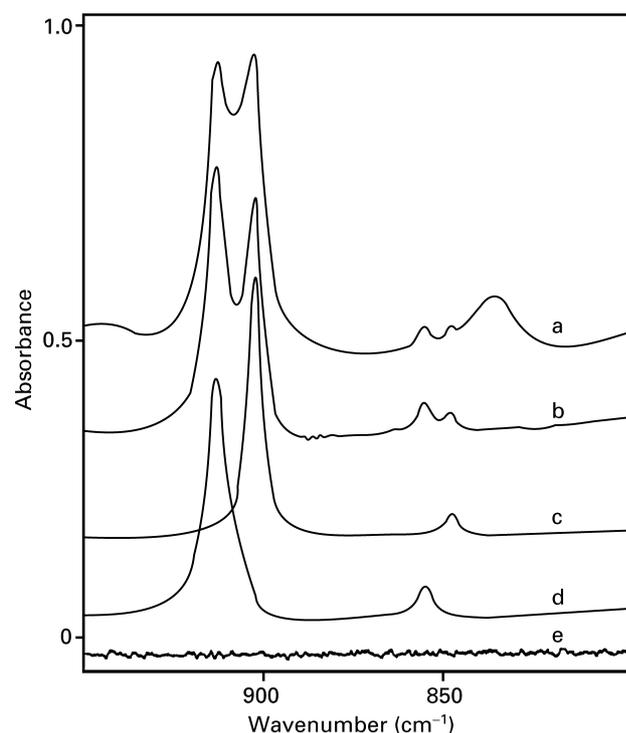
To achieve desirable properties, polymers are often blended to form stable mixtures. The formation of

successful polymer blends depends on the presence of favourable interactions, such as hydrogen bonding, between chains. These strong interactions show up in the vibrational spectra as the appearance or disappearance of peaks or as peak shifts. The most commonly studied blend systems involve polymers with carbonyl groups, which show different carbonyl bands for hydrogen-bonded and nonbonded groups. In these studies, the degree of compatibility can be determined by monitoring the spectral shifts and relative peak intensities of the bonded and nonbonded forms for a range of concentrations and temperatures. With the proper mathematical treatment, thermodynamic and kinetic parameters for these processes can be determined. The details are described in depth in the book by Coleman *et al.* (see Further reading). This technique has also been used to probe the interactions between polymers that do not contain such obvious interacting groups, such as the classic totally miscible pair polystyrene and poly(phenylene oxide).

### Orientation induced by processing

The production of polymer products typically involves processes in which the polymer is raised above its glass transition temperature ( $T_g$ ) and forced into some desired shape. The most common of these methods include injection moulding and blow moulding and depend on the desired geometry of the final product. During this process, the highly flexible polymer chains in different parts of the mould orient according to the local shear and elongational stresses. These stresses cause orientation of both the crystalline and amorphous regions of the polymer and can produce ordered regions with undesirable anisotropic mechanical properties in the final products. This orientation can be measured using a variety of methods involving transmission, ATR or RAS depending on the sample geometry and transparency. These reflectance methods are especially useful for determining the orientation at or near the surface of the finished product. The three-dimensional orientation of the chains near the surface can be quantified in this manner.

The most commonly used method for quantifying the extent of orientation in polymeric systems is the determination of the dichroic ratio. Two spectra are collected: one with radiation polarized parallel to a reference direction and one perpendicular to this direction. The reference direction is most commonly chosen along the direction of orientation. The ratio of these two spectra, often called the dichroic ratio spectrum, can then be used to characterize the orientation in the system. Dichroic ratios greater



**Figure 2** Infrared spectra of polystyrene with (curve a) a mixture of crystalline and amorphous forms, (curve b) a mixture of crystalline forms only, (curve c) one 'pure' crystalline form obtained by spectral subtraction, (curve d) another 'pure' crystalline form obtained by spectral subtraction and (curve e) subtraction result of curves b - c - d. Reproduced with permission of John Wiley & Sons Limited from Musto P, Tavone S, Guerra G and De-Rosa C (1997) Evaluation by Fourier transform infrared spectroscopy of the different forms of syndiotactic polystyrene samples. *Journal of Polymer Science B* 35: 1055-1066.

than unity indicate orientation along the reference direction, while those less than unity indicate orientation in the orthogonal direction. A value of 1 is indicative of a lack of orientation.

It should also be noted that the presence of orientation in samples can give rise to errors in quantitative studies. The presence of orientation changes the measured absorbance values, which affects the results of quantitative analysis. One way around this is to calculate the equivalent absorbance value with no orientation, the so-called structure factor  $A$ :

$$A = \frac{A_x + A_y + A_z}{3}$$

where  $A_x$ ,  $A_y$ , and  $A_z$  represent the absorbances obtained with  $x$ ,  $y$ , and  $z$  polarization, respectively. The structure factor is then used in place of absorbance in quantitative studies.

The behaviour of polymers can also be followed using a time-resolved technique known as rheo-optical spectroscopy or dynamic IR linear dichroism (DIRLD). In this technique, a strain is applied to a polymer sample, and the spectral changes are monitored over time. This strain is usually either a sinusoid or a step function, these being the easiest to reproduce experimentally. With the inclusion of stress and strain gauges, the spectral changes can be directly related to the mechanical properties. This technique has been used to directly study strain-induced conformational changes. A more advanced application is the study of the mechanical behaviour of polymer blends. When a miscible blend is examined, it can be seen that the spectral bands corresponding to different chains respond in phase, implying that they are molecularly mixed and act as one unit. The spectral responses have different phases for an immiscible blend, which shows that each polymer functions alone.

## Chemical property determination

### Polymerization reactions

Perhaps the most obvious chemical application is the monitoring of polymerization reactions involved in the production of polymers. Like most chemical reactions, the polymerization process shows up very well in vibrational spectra as the simultaneous disappearance and appearance of spectral bands. For example, in the polymerization of a typical vinyl monomer, carbon-carbon double bonds are broken and carbon-carbon single bonds are formed. This

can be seen clearly in the spectra as the disappearance of the vinyl stretch band around  $1500\text{ cm}^{-1}$  and the simultaneous appearance of carbon-carbon single-bond stretching bands and aliphatic carbon-hydrogen stretching bands. This technique can be used to determine both the kinetic order of the polymerization reaction and the kinetic rate constants.

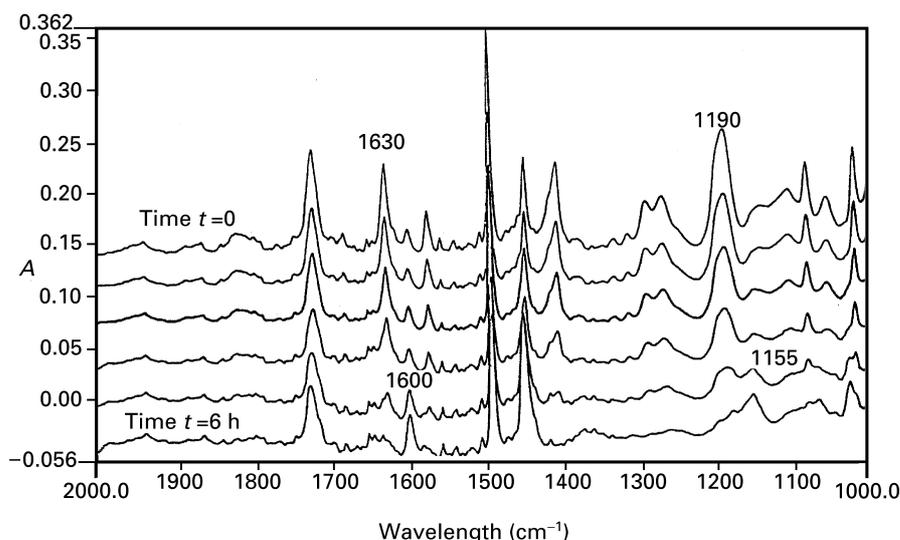
On-line monitoring has also received much recent interest in this area. This application allows spectra to be collected during the polymerization reaction without the necessity of stopping the reaction or performing the experiment under restrictive laboratory conditions. With the advent of low-loss fibreoptics, it is possible to monitor a polymerization reaction in a variety of harsh conditions far away from the spectrometer. This is particularly useful for large production settings commonly found in the polymer industry. An example of the quality of spectra that can be obtained using this method is shown in **Figure 3**, which shows several spectra from different times during a copolymerization reaction between styrene and 2-ethylhexyl acrylate. As can be seen, the quality of the spectra is quite good despite the drastic experimental conditions.

Several types of reactions involving polymers themselves have been studied using VS, including cross-linking, vulcanization, and degradation. The same methods are used for these processes as are used to study polymerization reactions.

### Time-dependent phenomena and spatially resolved studies

Vibrational spectroscopy is perhaps the most frequently used technique for the study of diffusion in polymeric systems because it provides a rapid way to quantitatively describe this phenomenon. The two areas of this type of research include the diffusion of small molecules into polymers and polymer-polymer interdiffusion. The easiest and most commonly used technique for this purpose is ATR. In this experiment, a polymer film is placed in contact with an ATR crystal, and the diffusing species is placed on top of the polymer. As diffusion progresses, the diffusing species moves closer to the ATR crystal and shows up in the spectrum obtained as an increase in the diffusant specific spectral band. This spectral change can be used to determine the diffusion coefficient of the system with the appropriate diffusion equation. This technique is limited to IR because of the optics and sample geometry required.

A more modern approach to this problem is to use microscopic techniques, such as an IR microscope or Raman microprobe, which directly monitor the movement of diffusing species. In this technique, the



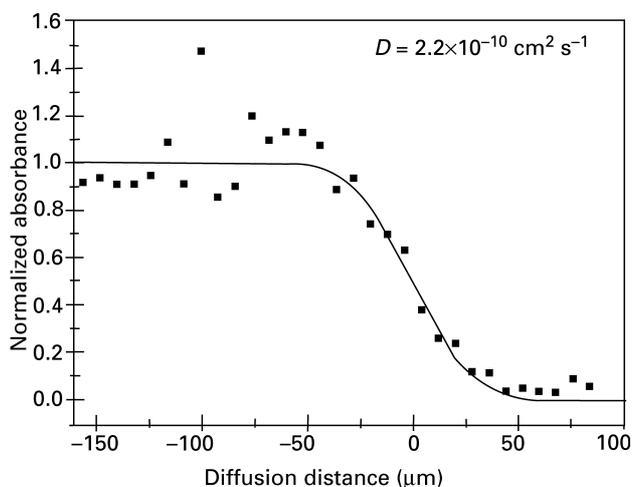
**Figure 3** *In situ* infrared spectra measured during the progress of a copolymerization reaction using a fibreoptic probe. Reproduced with permission of John Wiley & Sons Limited from Chatzi EG, Kammona O and Kipanssides (1997) Use of a midrange infrared optical-fiber probe for the on-line monitoring of 2-ethylhexyl acrylate/styrene emulsion copolymerization. *Journal of Applied Polymer Science* **63**: 799.

contact method is used, in which a thin film of polymer is placed into edge-on contact with the diffusing species. After diffusion has been allowed to progress for a certain period of time, the diffusion process is stopped by quenching, and spectra are collected along the diffusion direction to yield spatially resolved concentration information. As in the ATR method, this data are fitted to the appropriate diffusion equation to yield a diffusion coefficient. This method is more difficult to apply than ATR because of the difficulty in sample preparation, but it has the advantage of utilizing a simplified diffusion equation.

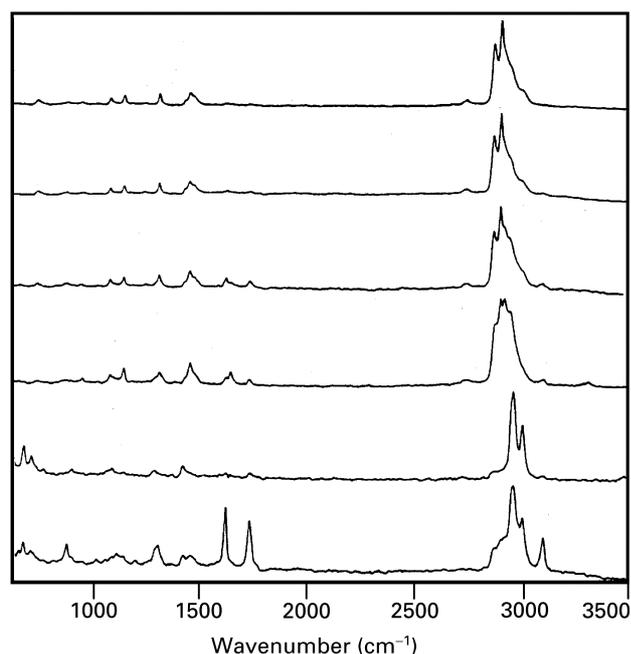
A recent trend is the incorporation of two-dimensional detectors into IR and Raman microscopes. For IR studies, focal plane array detectors are used, while charge-coupled device (CCD) detectors are used for Raman studies. When combined with the appropriate hardware, these systems are capable of collecting images of high spatial and spectral resolution in a matter of a few minutes. This allows systems that vary in time to be monitored *in situ*, and in real time depending on the rapidity of the process under study. This technique has the advantage of producing spatially resolved, chemically specific spectral images, which aids in the visualization of the process, in addition to providing high-fidelity quantitative information. An example of the quality of data that can be obtained is shown in Figure 4, which shows a diffusion profile obtained using an IR microscope equipped with a  $64 \times 64$  element focal plane array detector. The normalized absorbance values of the diffusant peak are plotted against diffusion distance and fitted to a Fickian diffusion profile, which is also shown. This

data was extracted from an image that was acquired in less than 3 minutes.

The determination of the spatial distribution of chemical species in polymeric systems is perhaps the most basic and most commonly encountered use of microspectroscopy. This technique is frequently used for the identification of defects in finished polymer products and for the identification of phase-separated regions of polymer blends. Polymer laminate films, which typically consist of layers between 2 and 10  $\mu\text{m}$  thick, are also frequently studied using this technique. Raman techniques are typically more useful than IR



**Figure 4** Diffusion profile obtained from an infrared image along with the fit to the diffusion equation.  $D$  = diffusion coefficient.



**Figure 5** Raman spectra taken at 10  $\mu\text{m}$  increments from a multilayer polymer laminate film. Reproduced with permission of Elsevier Science Limited from Xue G (1997) Fourier transform Raman spectroscopy and its application for the analysis of polymeric materials. *Progress in Polymer Science* 22: 313–406.

techniques owing to the higher spatial resolution attainable. This is shown in Figure 5, which shows Raman spectra obtained from 10  $\mu\text{m}$  regions of a laminate film. As can be seen, the identity of each layer can be distinguished from the others by the spectral features. Another technique, known as confocal Raman microscopy, allows the acquisition of spectra from thin regions, typically around 1  $\mu\text{m}$ , through the depth of the sample. This method has advantages over other methods because it can be used as a non-destructive quality control test to determine the thickness and chemical identity of the individual layers of a thin film.

An additional technique that can obtain spatially resolved spectral information is step-scan photoacoustic IR spectroscopy. Spectra can be obtained from different depths of a layered sample quickly and with higher spatial resolution (in some cases less than 1  $\mu\text{m}$ ) than the diffraction-limited optics of IR microscopes are capable of obtaining.

### Mechanical property determination using Raman spectroscopy

An interesting application of Raman spectroscopy is in the determination of the modulus of pure crystalline forms of a polymer. Raman is very sensitive to

the longitudinal acoustic vibrational modes of simple polymer chains. Using a combination of normal coordinate analysis and experiment, the modulus of pure crystalline forms of simple straight-chain polymers, such as polyethylene and poly(oxyethylene) have been determined. Similar techniques have been used to study the pressure-dependent band shifts that occur when a polymer sample is placed under stress. This technique is complementary to mechanical analysis because it gives insight into what is occurring at the molecular level during mechanical deformation.

### List of symbols

$a_1, a_2$  = extinction coefficients of bands associated with conformers 1, 2;  $A$  = structure factor;  $A_1, A_2$  = absorbances of bands associated with conformers 1, 2;  $A_{x,y,z}$  = absorbances obtained with  $x, y, z$  polarized radiation;  $k$  = kinetic rate constant;  $M_n$  = number-average relative molecular mass;  $R$  = gas constant;  $T$  = temperature;  $T_g$  = glass transition temperature;  $\Delta G$  = activation energy.

See also: **ATR and Reflectance IR Spectroscopy, Applications; IR Spectral Group Frequencies of Organic Compounds; Nuclear Quadrupole Resonance, Instrumentation; Photoacoustic Spectroscopy, Applications; Rayleigh Scattering and Raman Spectroscopy, Theory.**

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