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REVIEW

Applications of Raman Spectroscopy to the Study of Polymers and Polymerization Processes

H. G. M. Edwards,* A. F. Johnson and I. R. Lewis
Interdisciplinary Research Centre in Polymer Science and Technology, University of Bradford, Bradford, West Yorkshire BD7 1DP, UK

The application of Raman spectroscopy to polymers and polymerization processes is surveyed and the advent of recent advances in instrumental techniques to polymer analysis is highlighted. Some of the problems of the more widely-used infrared spectroscopic methods, for example in microstructural analysis of polydienes and copolymers, are discussed and the advantages of the Raman spectroscopic technique are explained. The use of near-infrared excitation and Fourier-transform Raman instrumentation for process monitoring and polymer composite studies is discussed. Raman microscopic and waveguide spectroscopic studies of small samples and polymer coatings on substrates are considered. Other applications are mentioned in the areas of polymer orientation, surface-enhanced Raman scattering, conducting polymers, biopolymers and time-resolved studies.

INTRODUCTION

The use of Raman spectroscopy for the analysis of polymers has historically been limited by instrumentation availability; the C—C and C=C bonds found in many polymer backbones should make Raman spectroscopy the preferred choice of infrared spectroscopy for polymer analysis. The emergence of the diode-array detector, tunable lasers and Fourier transform (FT) Raman instrumentation has caused a resurgence of interest in the polymer field for both research and quality control applications.

If the keywords 'Raman' and 'polymer' are selected for a computer literature search using the *Chemical Abstracts* database, over 1000 references are found, of which 150 have been published since the start of 1991. Thus the problem for the reviewers was to select papers which give some indication of how the application of Raman spectroscopy to polymers has been developing in recent times. An exhaustive study of the numerous applications is not possible here; instead, a number of important areas will be highlighted and a comprehensive survey of several others, including polymer structure, orientated polymers, polymerization, surface-enhanced Raman spectroscopy (SERS) studies of polymers, conducting polymers, coatings, studies of small samples such as occluded impurities, thin films and single fibres, processed polymers and composites, made within the broad framework of this paper.

A number of reviews[1,2] and books[3–5] covering Raman spectroscopic and vibrational spectroscopic studies of polymers have appeared over the years, whilst most texts on analytical Raman spectroscopy devote a section to studies of polymers.[6–8] The first of these was by Koenig,[1] who reported Raman spectroscopic studies of more than 15 polymers and documented spectral variations between different isomeric structures of poly(1,3-diene)-type polymers. Gerrard and Maddams[2] produced a more comprehensive review in 1986 that explored further applications of Raman spectroscopy to polymer analysis. The interested reader is referred to three excellent texts[3–5] concerning both theoretical and practical vibrational spectroscopic studies of polymers. The study of macromolecules has been recognized at the International Conference on Raman Spectroscopy (ICORS) meetings where sections of the *Proceedings* have been devoted to polymers and macromolecules.[9]

With the recent advances in instrumentation, Raman spectroscopy is becoming more routinely used for polymer analysis. The main advantage is that the level of sample preparation can be minimized. Infrared spectroscopy suffers from the need for preparing discs, casting films, microtoming and heat pressing and these procedures may well alter the properties of the materials being studied.

POLYMER STRUCTURE

The intensity in the Raman spectrum of the ν(C=C) stretching vibration gives this technique a particular advantage for the study of polymers such as polydienes and other polymers containing unsaturation. It is also possible to study the conformational structure of polymers quantitatively more easily by Raman spectroscopy than infrared spectroscopy.

Koenig and co-workers showed that Raman spectroscopy would be a valuable tool for studying a number of diene and vinyl polymers, polystyrene,[10] polybutadiene,[11] polyisoprene[12] and polychloroprene.[13] They showed that for polybutadiene each structural unit, namely *cis*-1,4-, *trans*-1,4- and vinyl-1,2 possessed a distinct ν(C=C) stretching vibration at 1650, 1664 and 1639 cm^{-1}, respectively. Also, by measuring the peak heights of the ν(C=C) stretching vibrations of the

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* Author to whom correspondence should be addressed.

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various structural units quantitative analysis of the types of unsaturation (microstructure) was possible. More recently, other workers[7,14] have shown that improvements in analytical procedures are possible, especially when the concentration of one type of unsaturation is low. Frankland *et al.*[14] found that Raman spectroscopy provides an accurate method of analysis of microstructure which is in agreement with NMR techniques but at variance with results from infrared spectroscopy. The sensitivity of Raman spectroscopy to microstructure change for polybutadienes is demonstrated in Fig. 1.

The problems with the infrared spectroscopic method for microstructure analysis have been identified as (a) accuracy of the value for the extinction coefficients, (b) imprecision at high absorbance values, (c) path length (selecting and reproducing an appropriate one) and (d) accidental degeneracies. Points (a)–(c) are not associated with Raman spectroscopy and this makes the *Raman* technique attractive. Despite this, infrared spectroscopy is still used as the main analytical technique industrially for such systems as polybutadienes.

Studies of natural polymers such as natural rubber, *cis*-1,4-polyisoprene, have been severely hampered by fluorescence.[15] Therefore, other workers have used FT Raman techniques to record successfully spectra from 'out-of-the-tree' rubber,[16] the cold soaking processing of rubber[17] and vulcanized polymers,[18] The use of Raman spectroscopy for the study of different crystalline forms of polyisoprene has been reported.[19] The two forms α- and β-*trans*-1,4-polyisoprene have different Raman spectra (Fig. 2). The most obvious differences arise as a shift of the $\nu(C{=}C)$ stretching vibration by 4 cm^{-1}, the intensity of the 2881 cm^{-1} band relative to the 2910 cm^{-1} vibration and the splitting of the 1325 cm^{-1} band into 1329 and 1319 cm^{-1} components.

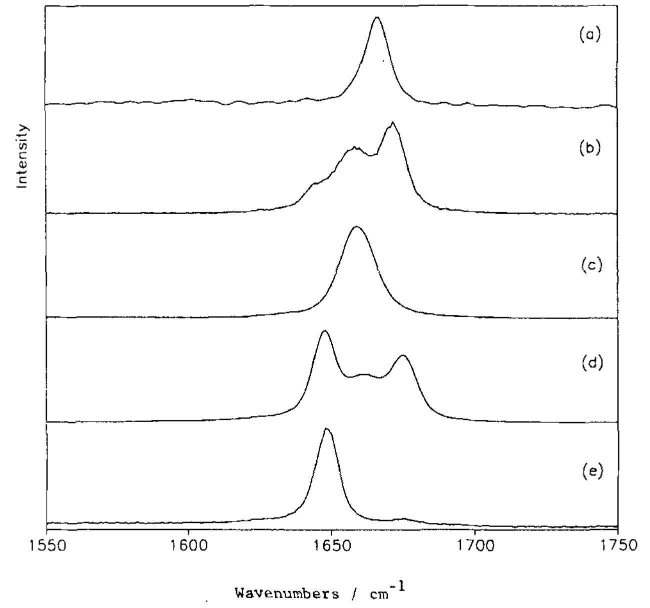

Figure 1. Raman spectra of polybutadiene in the wavenumber range $\Delta\nu = 1550$–1750 cm^{-1}, showing the sensitivity of the technique to microstructural change: (a) high-*trans*-1,4-; (b) mid-*trans*-1,4-; (c) high-*cis*-1,4-; (d) mid-vinyl-1,2-; (e) high-vinyl-1,2-sample.

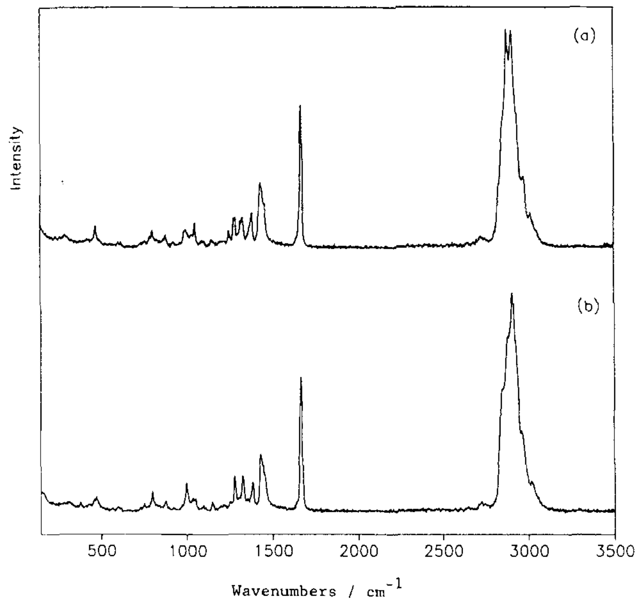

Figure 2. Raman spectra of α- and β-*trans*-1,4-polyisoprene: (a) α-*trans*-1,4- and (b) β-*trans*-1,4- in the range $\Delta\nu = 150$–3500 cm^{-1}.

Polyethylene and polypropylene have been widely studied by Raman spectroscopy.[20–22] Studies have included crystallinity,[23] low-wavenumber LAM vibrations[24] and effects of strain[25] and orientation[26] on the spectra. An extension to the studies of LAM bands to the measurement of the 'chain length' and lamellae thickness in polyethylene has been made. However, from theoretical studies by Hsu and co-workers,[23,24,26,27] it was deduced that these vibrations are not purely related to 'chain length' and can only be used as a rough guide in this respect.

Raman spectroscopy has also been used to study copolymers of dienes and other monomers both qualitatively and quantitatively.[28–32] The intensity ratios of the characteristic bands of the two homopolymers, which have structural units in the chain similar to those expected in the copolymer, have been used to determine the composition of each monomer in the copolymer. Studies of three-component copolymers such as acrylonitrile–butadiene–styrene and styrene–butadiene–methyl methacrylate would seem, theoretically, to be possible using the 2240–1665–1632 or 1632–1665–1730 cm^{-1} bands, respectively.

POLYMERIZATION

Raman spectroscopy can be used to follow the polymerization process and provide information on the extent of polymerization and structural information on the end-product. Raman spectroscopy is ideally suited for the study of polymerization reactions of unsaturated diene monomers as the intensity of the $\nu(C{=}C)$ stretching vibration is strong. In these cases the intensity of the $\nu(C{=}C)$ stretching vibration of the monomer decreases as the polymerization proceeds. Thus, a simple monitoring of peak intensities and their magnitude relative to the initial peak intensities can yield information about conversion as a function of time at any given temperature.

The instrumentation limitations (speed of data capture) restricted the earlier studies of polymerization processes to those reactions that were slow. Faster reactions were followed by taking samples, killing the reaction, and the off-line analysis of the sampled material.[33] These studies were reasonably successful but time consuming and have been applied to both homo- and copolymerization reactions. An example of the kinetic data obtained in this way, chosen here (Fig. 3), is the anionic homopolymerization of buta-1,3-diene; an alternative example (not shown here) is the free-radical homopolymerization of methyl methacrylate.[34] Here, the loss in intensity of the ν(C=C) stretching vibration of the monomer during the polymerization is monitored and gives the rate of polymerization with conversion of monomer.

Diode-array detectors and FT Raman instruments have made it possible to explore the kinetic behaviour of faster polymerizations. Clarkson *et al.*,[35] using an FT Raman spectrometer and a specially designed low-volume cell, have been able to follow the radically initiated homopolymerization of styrene to high monomer conversion (80%) and were able to derive kinetic data by following the loss of peak intensity of the ν(C=C) stretching vibration of the monomer. A study of the homopolymerization of methyl methacrylate was also undertaken.[36] Here the polymerization could be followed up to and after the onset of the Tromsdorff effect. At that point the growing polymer chains are unable to diffuse within the solution but monomer may still diffuse to the growing chain. Therefore, polymerization proceeds at an accelerated rate. Both these studies have been carried out in real time and offer the potential for industrial large-scale application. Bulk homopolymerization studies of radical systems have been reported for commercial acrylate systems.[35]

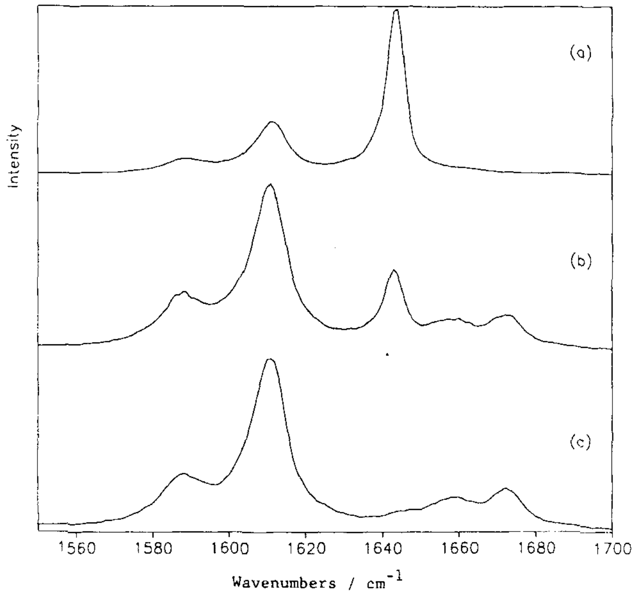

Figure 3. Raman spectra of polymerizing buta-1,3-diene in ethyl benzene in the range $\Delta\nu = 1550$–1700 cm^{-1}: (a) start of the polymerization [band at 1642 cm^{-1} is the ν(C=C) stretching vibration of the buta-1,3-diene monomer]; (b) middle; (c) end [bands at 1639 cm^{-1} (vinyl-1,2-), 1650 cm^{-1} (*cis*-1,4-) and 1665 cm^{-1} (*trans*-1,4-)].

Recently, it has been shown[37] that Raman spectroscopy has great potential for the study of the kinetics of the copolymerization of vinyl monomers; Bowley *et al.*[38] have studied styrene and methyl methacrylate and the possibility of studying ter- and multi-component systems would appear feasible. In that work rate constant data were found for free radical copolymerization. In addition to the intensity of the ν(C=C) stretching vibration the substituents attached to the double bond affect the observed wavenumber of the ν(C=C) bond. Therefore, shifted ν(C=C) vibrations are observed for a homologous series of monomers; an example of this is the acrylate series,[37] where an increase in chain length by one CH_2 unit causes a shift of 1 cm^{-1} in the observed position of the ν(C=C) vibration. These shifts would allow Raman spectroscopic studies of copolymerization and the calculation of the reactivity ratios for a number of binary or multi-component copolymerizations.

Near-infrared spectroscopic process monitoring has recently been used to study reacting polymerization systems.[39] Large-scale process monitoring seems to be possible using FT Raman spectroscopy as this technique can be made non-invasive. To overcome the problem of sample alignment a number of workers[40–43] have built systems which utilize fibre-optics to carry out remote sensing. It can be stated that the favoured system which involves a probe that both delivers the laser radiation and collects the scattered radiation has been successfully used to study polymers.[41] The remote FT Raman area is still novel in application and from the initial results there appears to be a possibility of using Raman spectroscopy for reaction control of systems other than polymers.

PROCESSED POLYMERS AND POLYMER MATRIX COMPOSITES

Many commercial applications of composites require the moduli of the pure polymers to be enhanced. This has been achieved by adding fibres, matrices or fillers to the polymers in question. These modifiers have complicated the analysis of the polymer, e.g. glass-fibre reinforced polyurethanes.[44] Also, Raman excitation using an argon ion laser have yielded spectra of polyurethanes masked by fluorescence. Archibald and co-workers[45,46] have studied the effect of excitation wavelength on spectral quality for reaction–injection moulded polyurethanes and found the best method of obtaining Raman spectra was the use of *1064 nm excitation* coupled with FT instrumentation. An example for polyurethane recorded on a Bruker FT Raman system is presented in Fig. 4. A comparison of FT Raman and DRIFT spectroscopy by Miller *et al.*[47] suggests that FT Raman could be used routinely to study phase separation to provide information about the mixing and chemistry occurring in the mould, by quantitative measurements of the degree of hydrogen bonding in RIM-produced polyurethanes. The extent of hydrogen bonding was found to change for different mouldings

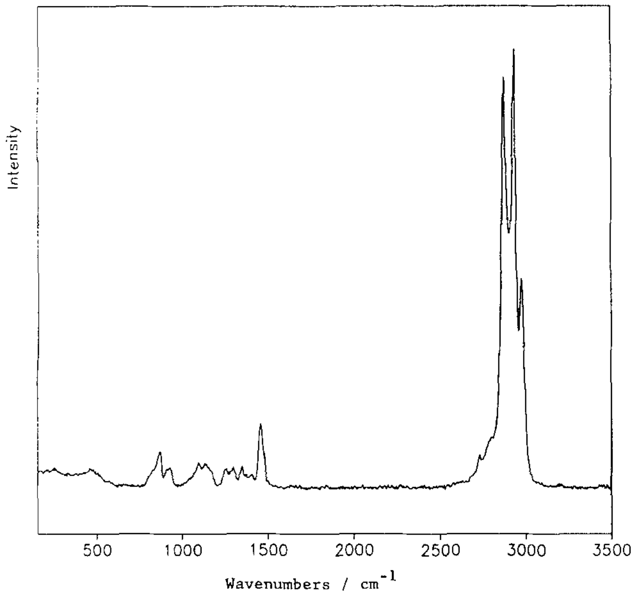

Figure 4. Raman spectrum of a polyurethane produced by reaction injection moulding; $\Delta\nu = 150$–$3500\ \mathrm{cm}^{-1}$.

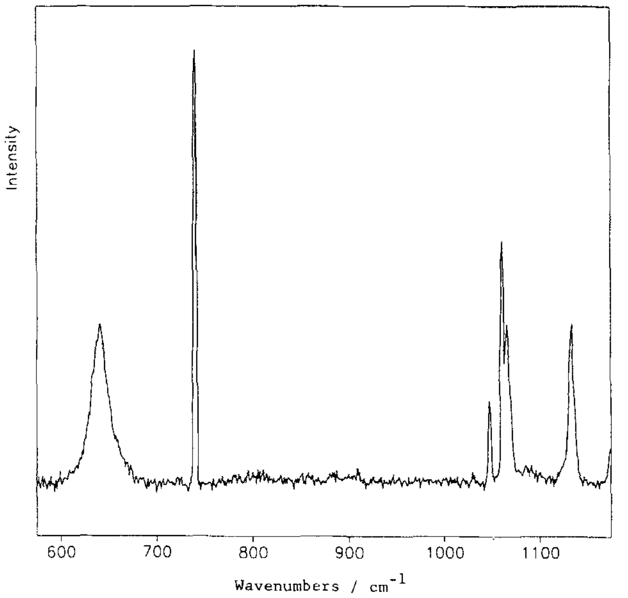

Figure 5. Polyethylene containing titanium dioxide which may be used as a marker for determining residence time distribution; $\Delta\nu = 575$–$1175\ \mathrm{cm}^{-1}$.

and, with each moulding, was dependent on the position of sampling.[47]

Resonance Raman studies of copolymers of urethane with diacetylene have been reported.[48] These included both structural analysis and studies of the copolymer during deformation. The wavenumber position of the carbon–carbon triple bond in the polymerized diacetylene was found to shift with applied strain and Hu *et al.*[48] postulated that this could be used as an internal strain gauge.

In addition to studies of RIM-produced polymers, Raman spectroscopy has been used to study extruded polymers and also provide information about the extrusion process. Edwards *et al.*[49] used measurements of the levels of added titanium dioxide in the feeds to determine a residence time distribution (RTD) for different feed rates, which is useful if reactive extrusion of the polymer is to be undertaken (Fig. 5). Hendra *et al.*[50] studied the in-line extrusion of molten PET, with a simple glass die, and from the spectra molecular shape changes were inferred which were found to be dependent on shear rate and melt temperature.

The study of polymer composites has produced much interest recently and here Raman spectroscopy coupled with a microprobe has given information about band shifts and strain-sensitive properties of fibres.[51–56] Examples of fibres studied are polydiacetylenes,[53] aramids[54] and carbon-reinforced PEEK.[55] An excellent review of this field was provided by Galiotis.[56]

STUDIES OF SMALL SAMPLES

Studies of small samples fall into two major categories: microscopic studies of inclusions[57] and fibres,[54,58,59] e.g. aramid[54] and Kevlar;[58,59] and studies using integrated optics for thin films.[60–67]

Raman spectroscopic studies of thin films less than 5 μm thick are extremely difficult owing to the small scattering volume of the sample.[60] Therefore, a number of workers[61] have developed an integrated optical system coupled to a conventional spectrometer using argon ion laser excitation. This technique has subsequently become known as waveguide Raman spectroscopy (WRS).[62,63] In this technique, the polymer sample is cast out and supported on a substrate. The radiation beam is coupled into the film using a prism and, on total internal reflection, an evanescent wave moves through the substrate. The resultant Raman scattering is observed as a 'streak'. This technique has been used to study organic films,[64] laminates[65] and inclusions in thin films[66] and recent work has been extended to depolarization ratio studies[67] and orientation studies of isotactic poly(methyl methacrylate).

More recently, near-infrared FT Raman spectroscopic applications of WRS have been demonstrated.[68] Zimba *et al.*[68] found that the use of a fibre-optic collection system, which converts the line image from the sample to a circular image for the interferometer entrance, was advantageous as this image then best filled the instrument. Spectra were obtained of polystyrene, poly(vinyl alcohol) and cellulose acetate with and without occluded guest molecules. This technique seems to have potential for advancement within the coatings industries and with the potential use of other substrates may well become more widely used.[69]

The Raman microprobe allows the examination of small samples of polymers. Louden[70] has shown that the Raman microprobe can provide quality spectra of small samples of polymers, e.g. a 15 × 10 μm sample of polystyrene. Louden[70] also evaluated a number of microscopic illumination techniques for Raman microprobe studies of polymer films and laminates. These techniques use transmitted polarized light, reflected polarized light, reflected dark-field illumination and reflec-

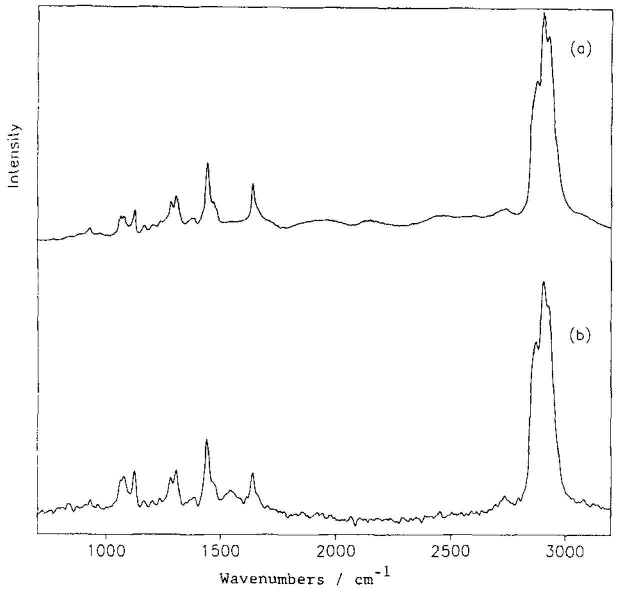

Figure 6. Raman spectra of nylon 6 using (a) FT Raman macrosampling of a fibre bundle and (b) FT Raman microprobe sampling of a 20 μm single fibre in the range Δν = 700–3200 cm^{-1}.

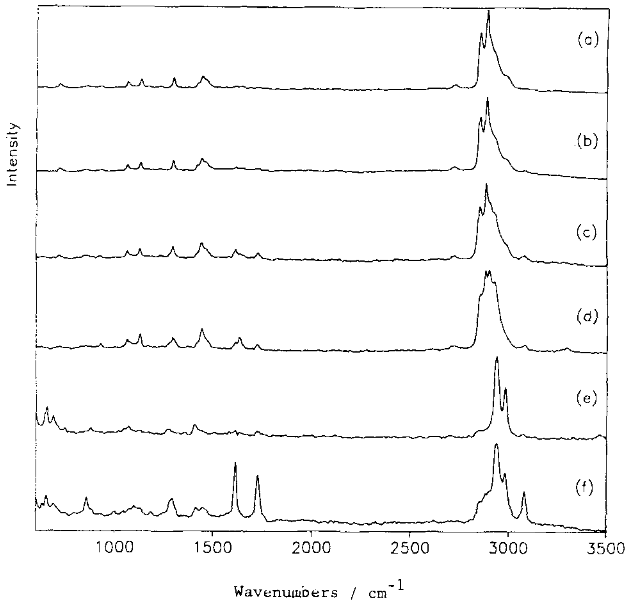

Figure 8. Polymer laminate spectra mapping using the FT Raman microprobe utilizing a 10 μm step between spectra; Δν = 600–3500 cm^{-1}.

ted differential interference contrast illumination (DIC) techniques. DIC techniques have been successfully used to study ethylene–propylene copolymers.[71] Prentice[71] was able to isolate small areas of high ethylene content that appeared as spherulites and probed them using the Raman microprobe. Figure 6 contrasts the spectral quality of a nylon 6 sample when examined by both macro- and micro-sampling arrangements.

Raman microscopy has also been applied to the identification of a 30 μm inclusion of quartz in polyethylene[70] and a 40 μm inclusion of polystyrene in a high-impact polystyrene copolymer.[72] The studies of inclusions have not been solely limited to Raman microscopy and Williams and Mason[73] showed that an 80 μg impurity particle of poly(ethylene–vinyl acetate) could be resolved from the host polymer film using FT Raman spectroscopy. The ability to study small samples will allow the analysis of impurities which are contaminating a product such as a polymer sheet or moulding to be identified. This could allow Raman microscopy to be used industrially as a tool for quality assurance.

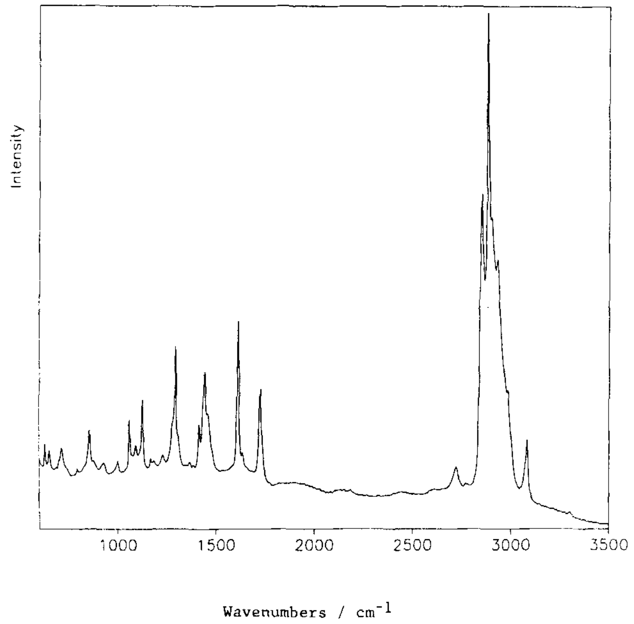

Figure 7. Polymer laminate spectrum recorded using macrosampling of a food packaging material; Δν = 600–3500 cm^{-1}. Laminate contains nylon 6, PET and PE.

Figures 7 and 8 show the use of Raman microscopy for studying and identifying the individual layers of a polymer laminate used as a food packaging material. This again illustrates the use of Raman microscopy for the identification of individual polymer components in a complex finished polymer product.

RAMAN SPECTROSCOPIC STUDIES OF COATINGS

Until recently, vibrational spectroscopic structural information from coatings has been limited to infrared measurements due to fluorescence masking the Raman signal. These infrared measurements have including horizontal attenuated total reflectance (H-ATR), specular reflectance and photoacoustic techniques. In order to eradicate fluorescence found when studying these systems by argon-excited Raman spectroscopy, FT Raman techniques have been applied to problems in the coating areas. An excellent review comparing Raman and infrared spectroscopic studies for the analysis of coatings has recently appeared.[74]

Raman spectroscopic studies of coating systems have not been limited to the characterization of the finished coating but have also been applied to the polymerization process and the curing reaction.[75–77] The paint systems studied by Ellis *et al.*[75] are based on acrylates and the loss in intensity of the ν(C=C) stretching vibration was used quantitatively to follow the polymerization process. The curing reaction was also studied with time and it was found that curing was a longer process than originally believed. The use of a whitening pigment of titanium dioxide in these paint systems was found to reduce the time needed for complete curing. In order to understand the curing process more fully, model systems have been designed and successfully studied.[78]

Another important area of interest is the degradation of coatings to determine lifetime, ageing and the chemistry of degradation. The use of artificially weathered paint surfaces to model weathering in coatings has been reported.[79] From studies of the weathering process for alkyd resins, it was found that titanium dioxide stabilized the system by absorbing the UV radiation. Jenden[79] also found that Raman spectroscopy could be used successfully to obtain kinetic information related to photodegradation, by studying the rate of production of aliphatic volatile residues by yielding information that may be used to infer information on the mechanism of breakdown.

Other degradation studies have involved the important coating/covering PVC films[80] and the use of Raman spectroscopy to study the coatings on polymeric packaging materials for foods[81] and the effect of heating on deformations of coatings.[82]

ORIENTATED POLYMERS

The ability to obtain polarization data from oriented polymers has aided the identification and assignment of the bands[83–85] by identifying the symmetric vibrations.

Initial applications were limited as highly oriented samples could not be prepared. Processing technology has improved and it has become a simpler procedure to produce oriented samples. Initial methods of preparation involved the stretching of films[86] but more recently uniaxially oriented samples have been prepared by drawing the sample.[87] The literature up to 1975[88] and 1979[89] on polarization data on polymers has been reviewed.

At present, polarization investigations have been limited to only a select number of polymers, such as PET,[90–92] PEEK,[93] PE,[94–96] PP[96–98] and polyacetylene.[99,100] Merino *et al.*[101] have developed a specialized cell for studying the *in situ* drawing of polymers at elevated temperatures. Studies were made of polyethylene at different temperatures and draw ratios. Polarization studies of extruded materials have also been made by polymers both off-line[95] and in-line.[50]

Inorganic polymers of NaSICON have also yielded useful information from polarization experiments.[102]

SERS STUDIES OF POLYMERS

The observation of the SERS effect was first made by Fleischmann *et al.*[103] In these experiments the Raman spectrum of a sample adsorbed on a metal surface, normally silver, gold or copper, is greatly enhanced. The mechanism of enhancement has been the subject of much work and the literature up to 1991 has been reviewed by Otto.[104]

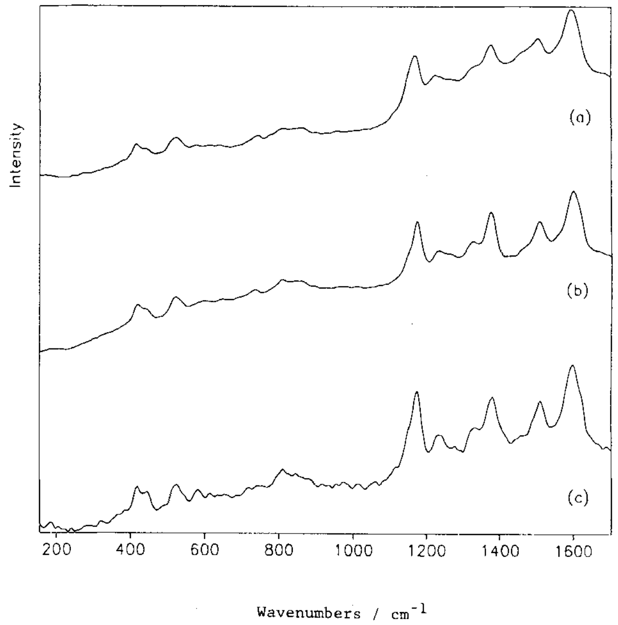

Figure 9. SERS spectrum of polyaniline coated on gold recorded with the FT Raman microprobe in the range $\Delta\nu = 150\text{–}1700\ \mathrm{cm}^{-1}$: (a) bulk area: (b) thin area; (c) thinnest area.

Studies have revealed that all substrates require an atomically rough surface for enhancement to occur. Even though no complete theoretical explanation of the enhancement in SERS occurs,[105] SERS is being used to study polymer–metal interfaces,[106,107] the orientation of adsorbed polymers[108] and the polymerization of selected monomers, such as acrylamide[109] and pyrrole.[110] The specific application of SERS to polymers up to 1984 has been reviewed by Kerker.[111]

A SERS spectrum of polyaniline coated on gold is given in Fig. 9. The coverage of polyaniline was uneven and thus three areas differing in their thickness of coverage are presented.

CONDUCTING POLYMERS

A mechanism of action of certain conducting polymers involves electron transport from conjugated unsaturation or from dopants. These conjugated systems may be studied by Raman spectroscopy or by resonance enhanced Raman spectroscopy. A complete theory of resonance Raman spectroscopy has been described by Clark and Dines.[112]

The initial applications of resonance Raman spectroscopy to conducting polymers involved studies of poly(acetylenes).[113–115] Studies have also included the effects of isotopes, hydro- and deutero-,[113] conformation[113,115] and doping[114,116] on the Raman spectrum of poly(acetylenes). More recently, FT Raman spectroscopy has been used to study poly(acetylenes).[117]

Other conducting polymers which have attracted interest are poly(*p*-phenylene,[118,119] poly(arylenevinylenes),[117,118] polyanilines[120] and polypyrroles.[119,121–123] A comprehensive review up to 1991 concentrating on infrared and Raman vibrational spectroscopic studies of conjugated and conducting polymers has been published.[124]

OTHER APPLICATIONS

There are a number of other applications of Raman spectroscopy in the field of biopolymers, such as peptides[125–127] and skins,[128–130] polymer/drug delivery systems[131,132] and picosecond studies of polymers.[133,134] Picosecond time-resolved CARS and CSRS studies of polydiacetylene, conjugated aromatic heterocyclic polymers and polyphenylacetylenes have been undertaken.[134] Q-switched pulsed lasers have been used to excite the Raman spectrum of poly(ethylene terephthalate).[135] Use of this instrumentation should allow the study of polymers, such as polychloroprene,[136] which are sensitive to heating even when studied by FT Raman instrumentation using a continuous-wave Nd:YAG laser.

A recent paper by Williams and Klenerman[137] has shown that UV-excited resonance Raman studies at 266 nm are possible for polymers containing the necessary chromophores. In the degradation of PVC the conjugated polyene formed from the loss of HCl was observed at levels of approximately 1 ppm. It was also shown that the problem of fluorescence masking the Raman spectrum is reduced at this wavelength. This advance should allow the observation of Raman spectra from polymers in low concentrations in solutions and reaction mixtures. Chadha *et al.*[138] have also shown that UV excited resonant and non-resonant enhanced Raman spectra of polymers can be obtained between 218 and 242 nm.

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