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The use of near-infra-red spectroscopy coupled to the polarization modulation technique to investigate molecular orientation in uniaxially stretched polymers

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The purpose of this brief communication is to demonstrate how near-infra-red (n.i.r.) spectroscopy can be used to characterize molecular orientation in stretched polymers. Combined with the polarization modulation technique, n.i.r. provides a useful way of measuring small anisotropy with high precision in thick polymer films.

(Keywords: near-infra-red spectroscopy; molecular orientation; stretched polymers)

Introduction

Mechanical properties of polymers are strongly influenced by molecular orientation occurring during stretching or during various forming processes. Measurement of this orientation is of particular importance in correlating the processing conditions with the properties of the fabricated sample.

The directions of chain segments are isotropically distributed in an undistorted network. When the network is macroscopically distorted, the segment orientation becomes anisotropic and the state of anisotropy under strain may be accurately characterized by various spectroscopic techniques such as polarized fluorescence[1–3], deuterium n.m.r.[4–7] and vibrational spectroscopy including polarized Raman spectroscopy and infra-red dichroism[8,9]. These techniques directly probe the orientational behaviour of network chains at a molecular level, in contrast to the macroscopic information provided by most other characterization techniques.

The specificity of infra-red absorption bands to particular chemical functional groups makes infra-red dichroism especially attractive for a detailed study of submolecular-level orientations of materials such as polymers.

Fourier transform infra-red (*FT*i.r.) dichroism spectroscopy has been applied to characterize molecular orientation in model poly(dimethylsiloxane) (PDMS) networks[10–12]. The strain dependence of segmental orientation has been analysed through networks of known degrees of crosslinking. It was pointed out that precise experimental measurements are required to test the limits of the validity of the various theoretical models used to estimate molecular orientation under deformation. It was also shown that the measurement of molecular orientation could be highly improved by polarization modulation of the incident electromagnetic field[13]. This technique is able to detect a dichroic effect for very small sample draw ratios.

One practical problem in the case of infra-red dichroism measurements arises from the requirement of band absorbance, which should be roughly lower than 0.7 in order to permit use of the Beer–Lambert law, although absorbances appreciably higher can be used with great care. This implies the use of sufficiently thin films. Depending on the extinction coefficient of the considered band, the required thickness can range from 1 to 200 μm. From this point of view, polymers with strong absorption bands are difficult to study. This difficulty can now be overcome by using near-infra-red (n.i.r.) spectroscopy which examines overtones and combination bands much weaker than the fundamental modes.

The purpose of this paper is to demonstrate, from the example of PDMS, the usefulness of n.i.r. spectroscopy for the measurement of molecular orientation in thick specimens. It should be shown that, in combination with the polarization modulation technique, n.i.r. offers a very elegant approach to the characterization of anisotropy in polymeric materials.

Experimental

Synthesis of model networks of PDMS. Model networks of PDMS were obtained by end-linking stoichiometric mixtures of α,ω-di(hydrogeno)-poly(dimethylsiloxane), with a molecular weight of 12000, with 1,3,5,7-tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane, used as a tetrafunctional crosslinking agent. It should be pointed out that end-linking processes using bifunctional precursor polymers of known molecular weight, reacting with adequate

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multifunctional reagent, allow control of the network structure. Characterized by constant junction functionality and known molecular weight distribution, M_c, between crosslinks[14,15], the resulting elastomeric networks present structures close to ideality with a small number of defects such as dangling chains, loops or double connections.

Infra-red dichroism measurements. The absorption of infra-red radiation arises due to the interaction of the electric field vector of the incident light with the electric dipole-transition moment associated with a particular molecular vibration. The orientation of structural units of a uniaxially stretched polymer can be described by an orientation distribution $f(\theta)$, where θ is the angle between the macroscopic reference axis (usually taken as the direction of strain) and the local chain axis of the polymer (*Figure 1*).

The orientation distribution function is expressed as[8]:

$$f(\theta) = \sum_{n=0}^{\infty}(n + 1/2)\langle P_n(\cos\theta)\rangle P_n(\cos\theta)$$

where $P_n(\cos\theta)$ are the Legendre polynomials, for example:

$$P_2(\cos\theta) = (3\cos^2\theta - 1)/2$$

$$P_4(\cos\theta) = (35\cos^4\theta - 30\cos^2\theta + 3)/8$$

For any absorption band, the dichroic ratio, $R = A_\parallel/A_\perp$ ($A_\parallel$ and $A_\perp$ being the measured absorbance for electric vector parallel and perpendicular, respectively, to the stretching direction), is the parameter commonly used to characterize the degree of optical anisotropy in stretched polymers.

R is related to the second moment of the orientation function as follows:

$$\begin{aligned}\langle P_2(\cos\theta)\rangle &= [(R-1)/(R+2)][2/(3\cos^2\beta - 1)]\\ &= F(\beta)[(R-1)/(R+2)] \qquad (1)\end{aligned}$$

where $F(\beta)$ only depends on the angle β between the transition moment of the vibrational mode considered and the local chain axis of the polymer or any directional vector characteristic of a given chain segment. This angle β can usually be obtained from theoretical considerations arising from group theory. Alternatively, if the orientation function is known using a well-defined absorption, the orientation of the transition moment vector relative to the chain axis can be determined for any other absorption band.

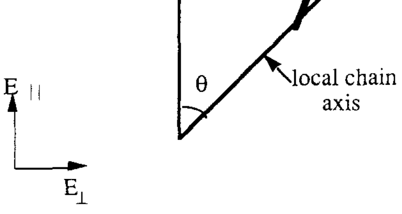

Figure 1 Positions of local chain axis and transition moment with respect to the stretching direction

Equation (1) can be rewritten as:

$$\langle P_2(\cos\theta)\rangle = F(\beta)\frac{A_\parallel - A_\perp}{A_\parallel + 2A_\perp} = F(\beta)\frac{\Delta A}{3A_0}\sqrt{\alpha} \qquad (2)$$

where $(A_\parallel - A_\perp)$ represents the dichroic difference ΔA and $(A_\parallel + 2A_\perp)$ is linked to the structural absorbance A by: $A = (A_\parallel + 2A_\perp)/3$. For a uniaxially oriented film, A decreases owing to a reduction in sample thickness during elongation as $A_0/\sqrt{\alpha}$, where A_0 is the absorbance of the system under isotropic conditions and α is the extension ratio ($\alpha = l/l_0$, l_0 and l being the undeformed and deformed lengths, respectively).

Near infra-red spectroscopy. The n.i.r. region of the spectrum covers the interval from about 12 500 to 4000 cm^{-1} (800–2500 nm). The bands in the n.i.r. are primarily overtones and combinations of the fundamental absorbances found in the classical mid-i.r. region. The absorption bands appearing in the n.i.r. range arise from overtones and combinations of fundamental vibrations of hydrogen-containing groups such as C–H, N–H and O–H. As these bands are much weaker than the corresponding fundamental absorptions, an n.i.r. spectrum is considerably simplified compared to the usual mid-i.r. region. Consequently, the principal advantage of n.i.r. analysis is the ability to examine specimens several millimetres thick. In other words, the n.i.r. region which complements the mid-i.r. region is analytically useful for spectroscopic applications involving analysis of samples containing very strong mid-i.r. absorbers.

Polarization modulation FT*i.r. spectroscopy.* In a conventional measurement of the dichroic ratio, the oriented sample and polarizer are placed in the beam of the spectrometer and the parallel and perpendicular absorptions ($A_\parallel$ and $A_\perp$) are successively measured. However, for slightly oriented samples the dichroic ratio is very close to unity and the classical method lacks sensitivity. The measurement of the dichroic difference $\Delta A(= A_\parallel - A_\perp)$ with the aid of polarization modulation equipment leads to a neat increase in sensitivity[16,17].

A polarization modulation set-up can be coupled to an *FT*i.r. spectrometer operating in either the mid- or near-infra-red range. The polarization modulation method consists basically of a fast modulation of the polarization state of the incident field between directions parallel and perpendicular to the stretching direction of the investigated polymer. By improving considerably the signal-to-noise ratio, this method is particularly recommended for polymer samples exhibiting anisotropies nearly undetectable by the standard method.

The optical set-up used in polarization experiments is shown in *Figure 2*. At the output of the interferometer of a Nicolet 740 FTIR. Spectrometer, the beam is polarized with a polarizer and then passes through a Hinds photoelastic modulator which modulates at a fixed frequency (62 kHz) the state of polarization between directions parallel and perpendicular to the drawing axis. The photoelastic modulator is made from a cubic i.r.-transparent crystal of CaF_2 or ZnSe, depending on the spectral range investigated. After transmission through the sample, the beam is focused by a lens onto the photoactive area of an InSb fast detector cooled at 77 K.

The experimental procedure and signal analysis will not be presented here since they have been fully described in previous papers[17–20]. It should be noted that the quantitative analysis of the detected signal allows a determination of the dichroic difference, ΔA, from a single measurement.

Results and discussion

The mid-infra-red spectrum of a PDMS film about 100 μm in thickness is shown in *Figure 3*. The bands associated with fundamental modes are very intense. Hence, in earlier investigations we have probed the dichroic behaviour of the band located at 2500 cm^{-1}, ascribed to the overtone of the CH_3 symmetrical bending vibration located at 1260 cm^{-1}. The transition moment associated with both vibrational modes lies along the CH_3–Si bond, which is a symmetry axis of the methyl group. As already mentioned, the determination of the local molecular orientation of polymer chains, reflected by the second moment of the orientation function, requires the definition of the angle β between the transition moment of the investigated band and a directional vector characteristic of a given chain segment. For the particular case of PDMS chains, the chosen directional vector is that joining two successive oxygen atoms. The angle β thus equals 90°.

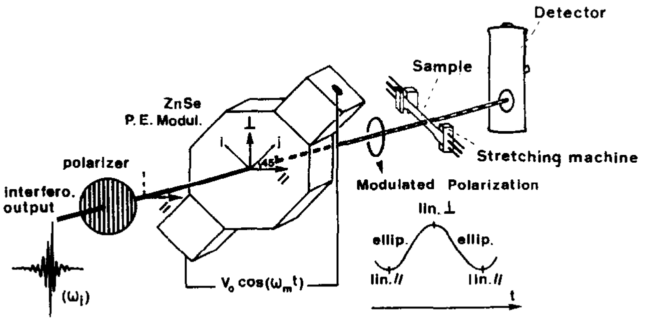

Figure 2 Schematic of the optical polarization modulation set-up

Figure 4 shows the n.i.r. spectrum of the same PDMS film. The reduced intensity of the n.i.r. absorptions makes a wide area of the spectrum available for evaluation of the dichroic effects.

Figures 5 and *6* represent the strain dependence of the dichroic difference, ΔA, for the band at 2500 cm^{-1} of the mid-i.r. region and for the spectral pattern between 4000 and 4500 cm^{-1} in the n.i.r. region, respectively, together with the proposed assignment for each band. In each case it can be seen that the absolute value of ΔA, and thus the anisotropy of the sample, increases with the draw ratio α. On account of its high sensitivity, this technique is able to detect precisely the onset of orientation and a dichroic effect can be measured for a draw ratio as low as 1.05, while the standard method leads to significant measurements only for $\alpha = 1.5$.

As shown in *Figure 6*, another advantage of the polarization modulation technique is the possibility of separating the bands on account of their different dichroic behaviour. In a conventional spectrum these bands overlap. In this case, the determination of the dichroic ratio requires the definition of an appropriate

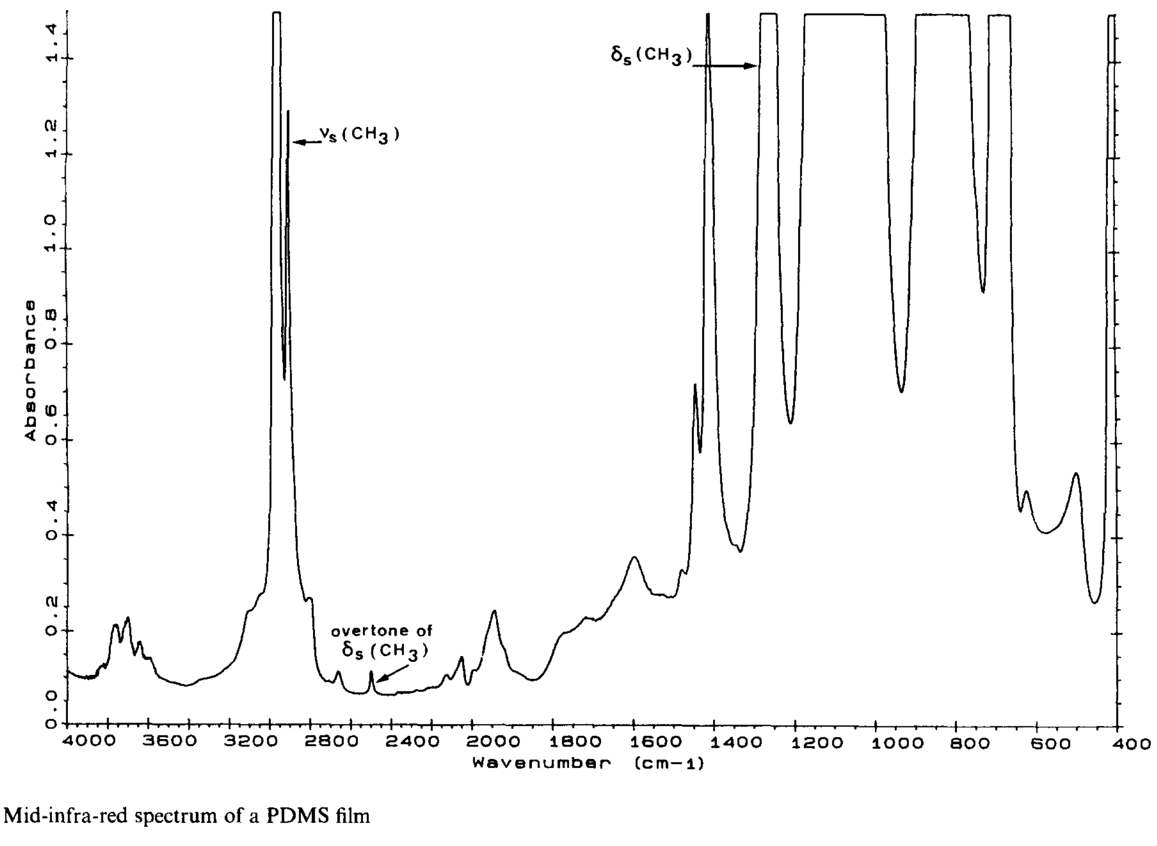

Figure 3 Mid-infra-red spectrum of a PDMS film

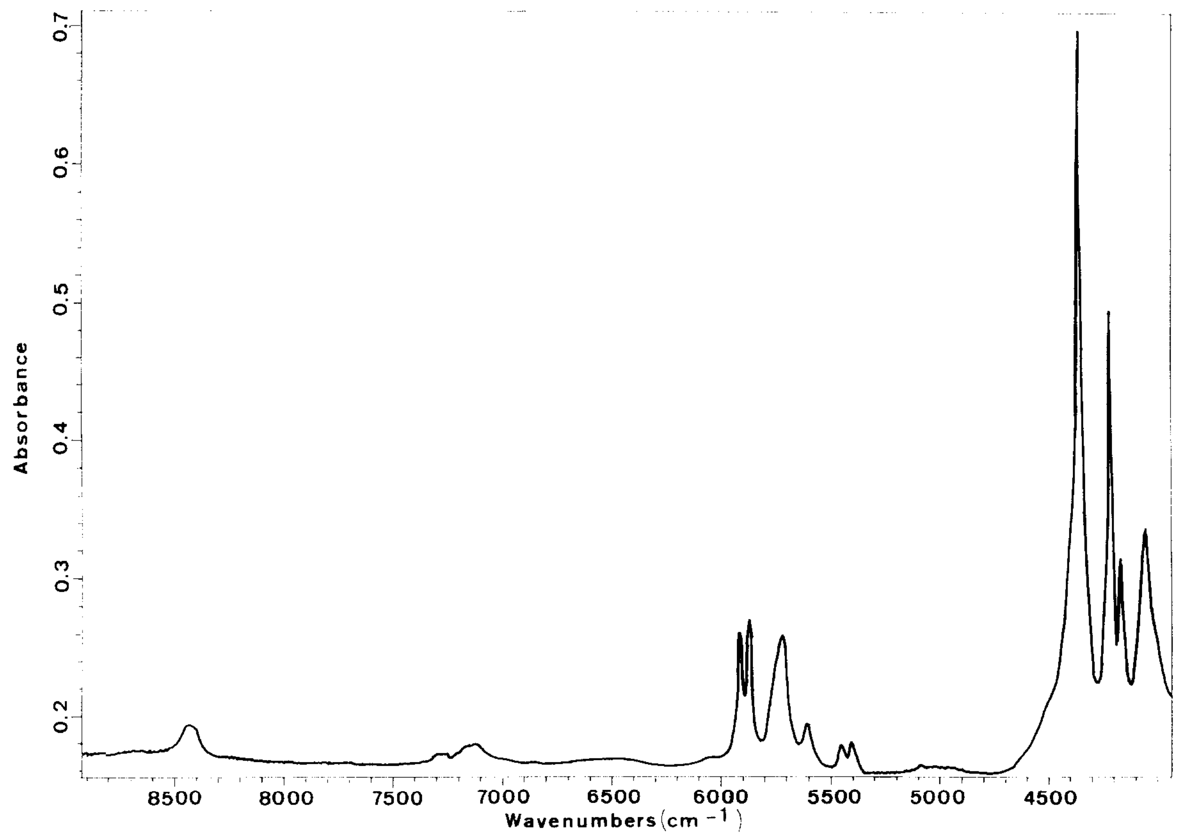

Figure 4 Near-infra-red spectrum of a PDMS film

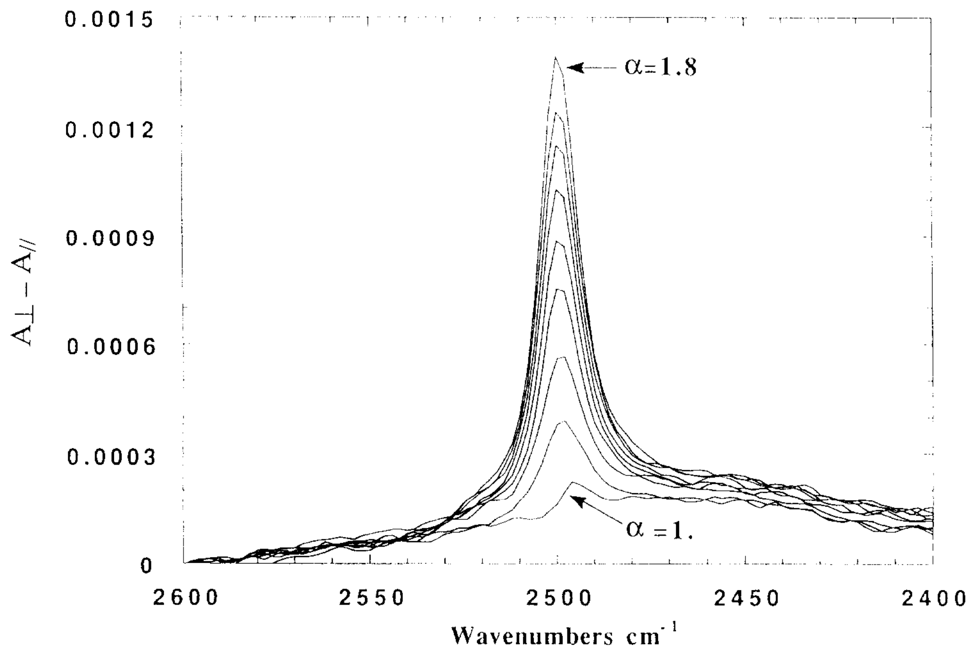

Figure 5 Strain dependence of the dichroic difference for the band at 2500 cm $^{-1}$

baseline. The polarization modulation approach obviates the need for defining the most suitable baseline.

Values of the orientation function $\langle P_2(\cos\theta)\rangle$, derived from the dichroic difference according to equation (2), are plotted against the strain function $(\alpha^2 - \alpha^{-1})$ in *Figure 7*. Two different measurements were carried out: one is related to the band located at 2500 cm $^{-1}$, and the other concerns the band at 4160 cm $^{-1}$ ascribed to a combination from the symmetrical stretching mode of the methyl group at about 2905 cm $^{-1}$ with the symmetrical bending mode of the same group at about 1260 cm $^{-1}$. The two sets of data exhibit, throughout the applied deformation range, a linear relationship between the experimentally observed $\langle P_2(\cos\theta)\rangle$ values and what we call the strain function $(\alpha^2 - \alpha^{-1})$. Such behaviour is predicted by the various theoretical models used to

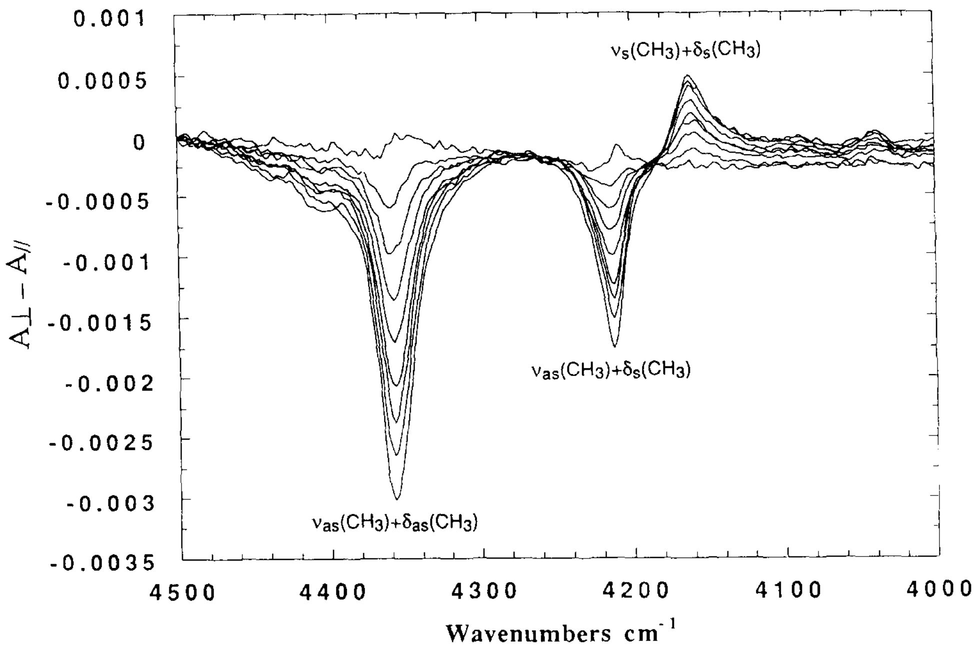

Figure 6 Strain dependence of the dichroic difference for the bands located between 4000 and 4500 cm^{-1}

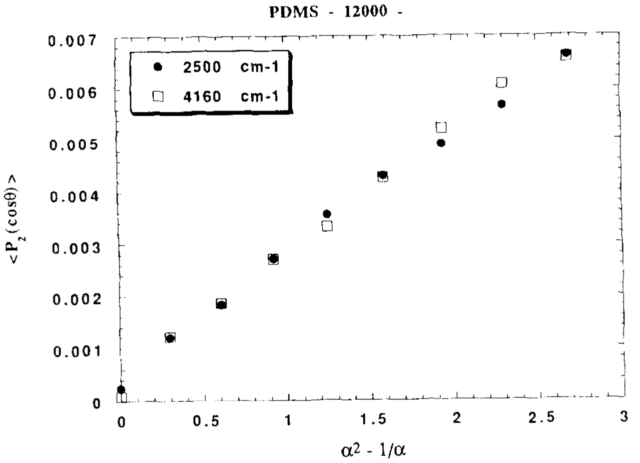

Figure 7. Strain dependence of the orientation function derived from experiments carried out in the mid-i.r. (2500 cm^{-1}) and n.i.r. region (4160 cm^{-1})

estimate molecular orientation under deformation. In the simplest form, $\langle P_2(\cos\theta)\rangle$ may be expressed as the product of two contributions[21]:

$$\langle P_2(\cos\theta)\rangle = D_0(\alpha^2 - \alpha^{-1})$$

The front factor D_0 incorporates the structural features of the specific network chain and the strain function $(\alpha^2 - \alpha^{-1})$, which reflects the effect of the macroscopic deformation on orientation.

The data plotted in *Figure 7* show that similar information can be obtained from mid- and near-infrared spectroscopies. The novelty of n.i.r. is the possibility of analysing thick specimens because of the relatively weak n.i.r. absorptions.

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