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Planar Array Transient Infrared Spectroscopy: A New Tool for the Time-Resolved Analysis of Polymers

Christian Pellerin

Summary: Planar array infrared spectroscopy (PA-IR) was used for the first time to record transient infrared (TIRS) spectra. In proof-of-concept experiments, it was demonstrated that PA-TIRS can record high quality spectra of common polymeric samples. It was shown the this new technique allows acquiring spectra in as little as 17 ms, opening the door to high speed, real-time monitoring applications.

Keywords: planar array infrared spectroscopy; transient infrared spectroscopy; polymers; time-resolved studies

Introduction

Infrared (IR) spectroscopy is a powerful technique for the qualitative and quantitative characterization of polymers because it provides information about their chemical nature, concentration, structure, etc.[1] In particular, IR spectroscopy possesses excellent chemical selectivity because most functional groups absorb IR radiation at different frequencies. This feature is often used to identify materials non-destructively, but it also enables advanced studies such as the simultaneous characterization of the components of a copolymer,[2] the phases of a semi-crystalline polymer,[3] etc. Continuous-scanning Fourier transform IR (FT-IR) spectroscopy is by far the most widely used technique to record static IR spectra and to follow dynamic phenomena with time constants on the order of a second or more. However, its time resolution is adversely affected when long scanning times are necessary to provide an appropriate signal-to-noise ratio, for instance when measuring the reflectance spectrum of an ultrathin film.

The time resolution of FT-IR can also be a limiting factor for measurements in the emission mode because the emitted radiation is usually very weak, unless the species of interest are highly excited (chemically, thermally, or otherwise). Because absorption and emission of IR light involve the same energy levels, both techniques can, in principle, yield the same molecular information about a sample. According to Kirchhoff's law, the emittance (ε) of a sample at a given wavelength, ν, is equal to its absorptance (α) and is related to its transmittance (τ) and reflectance (ρ) through $\varepsilon_{(\nu)} + \tau_{(\nu)} + \rho_{(\nu)} = 1$.[4] A thick sample with a transmittance close to zero yields a featureless (saturated) spectrum in both the absorption and emission modes.

McClelland et al. have developed a technique that circumvents this problem, the so-called transient IR spectroscopy (TIRS).[5,6] In TIRS, a hot stream of air is directed on a moving sample in order to create a thin surface layer with a higher temperature than the bulk of the sample. This temperature gradient allows recording the emission spectrum of a transient "thin sample" that does not saturate even if the bulk sample is thick. Such surface measurements are often performed in the absorption mode, in particular trough the use of attenuated total reflectance (ATR) spectroscopy. The penetration depth in ATR can be easily controlled through selection of the crystal (index of refraction) and the incidence angle of the incoming radiation. In contrast, the thickness probed in a TIRS experiment depends on the time between

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Département de chimie, Université de Montréal, Montréal, QC, H3C 3J7, Canada
E-mail: c.pellerin@umontreal.ca

the exposure of the sample to the hot stream and its passage in the optical path of the spectrometer, as well as on the coefficient of thermal diffusion of the sample. For this reason, the use of ATR is much more convenient under normal sampling conditions. Nevertheless, the TIRS approach becomes advantageous for continuous, real-time, applications for which contact with the sample and/or immobilization are not acceptable. The interest of TIRS has been demonstrated both in the laboratory and in various industrial settings, for instance for the in-line characterization of polymer extrudates, wood chips, etc.[5–7] Time resolution is critical in TIRS because heat diffusion tends to homogenize the sample temperature, leading over time to a featureless grey body emission spectrum. The best option is often to circulate the sample very rapidly, but the spectrum then corresponds to an average over long distances or even to multiple samples.

In the last few years, we have coupled fast and sensitive focal plane array (FPA) detectors to IR spectrographs.[8,9] Such planar array IR (PA-IR) spectrographs allow recording broadband spectra with a time resolution typically between 17 ms and 100 μs, as limited by the frame rate of the camera. In a recent article, we have demonstrated for the first time that PA-IR spectroscopy can be used to record emission spectra of polymers in as little as 17 ms.[10] In this paper, we present our first attempt to perform TIRS measurements using a PA-IR spectrograph (PA-TIRS).

Experimental Part

The PA-IR spectrometer and TIRS setup used in this work are shown schematically in Figure 1. The main instrumental difference between the usual absorption configuration and the emission configuration is the absence of an infrared source, which is replaced by the emitting sample. The spectrometer was custom-built around a Czerny-Turner monochromator equipped with a 300 μm slit and a 50 grooves/mm planar reflection grating. The diffracted radiation was dispersed on a 256 × 256 mercury-cadmium-telluride (MCT) FPA (Santa Barbara Focalplane, Goleta, CA) equipped with a Ninox compound lens

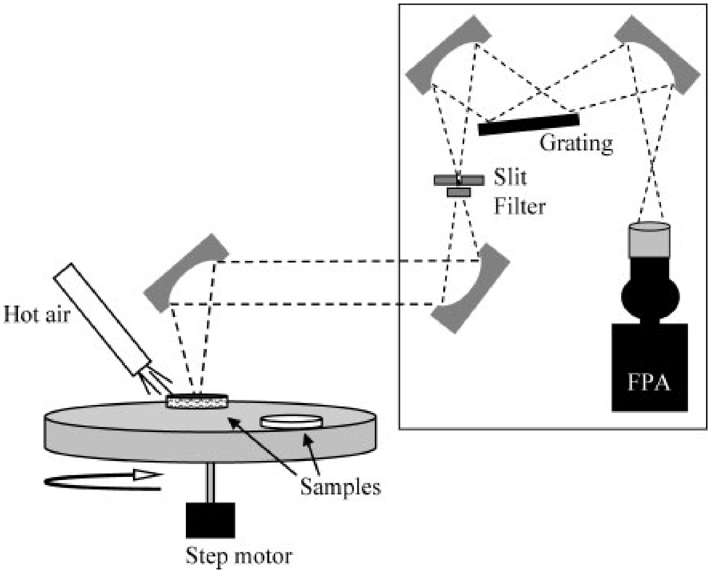

Figure 1.
Schematic representation of the planar array infrared spectrometer and transient infrared spectroscopy sampling accessory.

(Janos Technology, Keene, NH). Under such configuration, the spectral resolution varies from 7 cm^{-1} at 1100 cm-1 to approx. 14 cm^{-1} at 1600 cm^{-1}. The integration time and frame rate were fixed at 99 μs and 114 Hz, respectively. A 1950 cm^{-1} low-pass filter was used to block eventual unwanted high-order diffraction of the grating. PA-TIRS measurements were performed using a custom-built device to simulate on-line monitoring conditions. Polymer samples were deposited on an aluminum-covered stage rotating at a controlled speed using a stepper motor. A stream of hot air was funnelled onto the sample, upstream but as close as possible to the field of view of the spectrometer (radius ~6 mm), using a commercial temperature-controlled heat gun. A rheostat was used to control the flow rate and limit the stream temperature to approx. 150 °C. The emitted IR radiation was collected using a downward-looking off-axis parabolic mirror and focused on the entrance slit of the monochromator. The spectrometer was not purged.

TIRS emittance spectra were calculated by normalizing the luminance of the sample, L_S, by that of a blackbody source, L_B, at an elevated temperature.

$$\varepsilon(\upsilon) = \frac{L_S(\upsilon) - D_S(\upsilon)}{L_B(\upsilon) - D_B(\upsilon)}$$

Blackbody spectra were approximated by recording the emission from a metal plate covered by a thick layer of flat black paint. The blackbody plate was heated to different temperatures in a static mode, and the most appropriate blackbody spectrum was selected to match the luminance of the sample using the procedure described by McClelland et al.[6] All spectra were corrected by subtracting a dark background spectrum, $D(\nu)$, recorded with a closed monochromator entrance slit. This spectrum eliminates the contribution of stray light and corrects for residual pixel-to-pixel intensity variations. The absorption spectrum of a thin polystyrene film was recorded in transmission, using the blackbody plate as a source, to calibrate the frequency axis of the TIRS spectra. The procedure described by Pelletier et al. was finally used to correct the spectral images for slit curvature.[9]

Results and Discussion

Figure 2 shows the spectral images recorded for the blackbody source and for an inch-thick slab of expanded polystyrene. The horizontal axis corresponds to the frequency of the emitted radiation, while the vertical axis corresponds to the height along the field of view of the spectrometer. The useful frequency range, for which significant radiation can be observed in Figure 2, ranged from approx. 1850 to 1050 cm^{-1}. The spectral images were corrected for the dark background emission. Such correction is of utmost importance for PA-TIRS or emission measurements because the FPA is a DC-coupled detector that is sensitive to non-modulated radiation such as the IR emission from the environment. In fact, the maximum intensity for the dark background-corrected images in Figure 2 is 250 counts, as compared to a raw signal on the order of 5000 counts. Dark background spectra were thus recorded frequently to compensate for any drift originating from a slight variation in the laboratory temperature. This can easily be performed using a shutter inserted behind the slit in the monochromator.

The spectral image of the blackbody source (Figure 2a) shows a signal envelope typical of that measured for the background in an absorption experiment.[8] The multiple vertical dark stripes are due to absorption by water vapour, as the spectrometer was not purged. The image of the polystyrene sample also shows a broad intensity envelope and water absorptions but is dominated by polystyrene emission bands. For instance, the most intense band appears around pixel #93 (1450 cm^{-1}) and is attributed to a phenyl semi-circle stretching and CH_2 deformation.[11]

Even if the image curvature appears limited in Figure 2, the spectral images were straightened before averaging 60 pixel rows

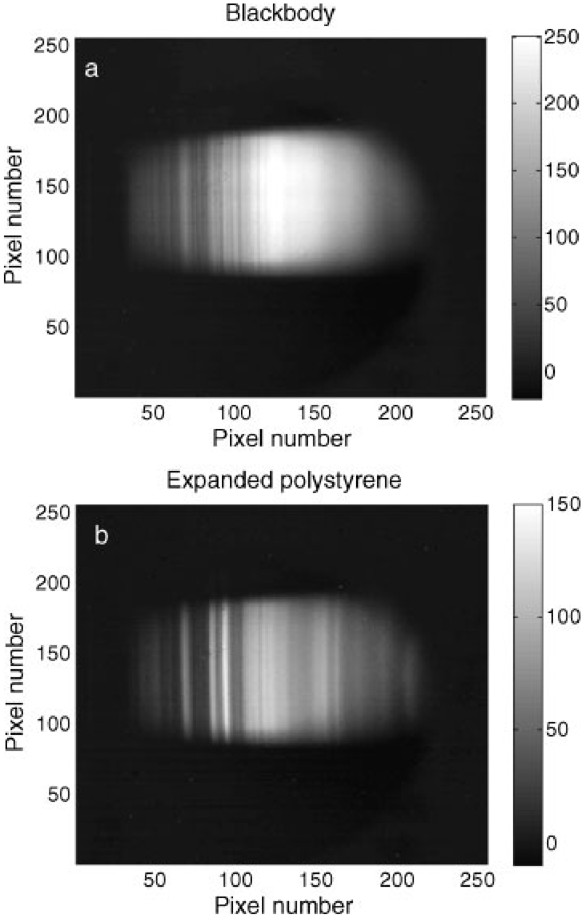

Figure 2.
Spectral images recorded for a) the blackbody source and b) the expanded polystyrene sample. The intensity scale is in counts.

to improve the signal-to-noise ratio.[9] Figure 3 shows the resulting spectra for the expanded polystyrene sample and for the blackbody source at two temperatures, as obtained by exposing the metal plate to the hot stream for different times. The shape of the blackbody spectra is due to the superimposition of a Planck's law distribution with the response function of the spectrometer, including the diffraction efficiency of the grating and the wavelength-dependent sensitivity of the FPA detector. The FPA cut-off precludes measurements below 950 cm^{-1}, while noise level considerations limit studies above 1800 cm^{-1} unless the sample can be heated to a high temperature without degradation. The blackbody spectra of Figure 3 also show water vapour absorption bands above 1300 cm^{-1} as down-going peaks.

In contrast, the sample spectrum shows multiple, chemically-specific, bands that are superimposed on a blackbody-type spectrum. The latter is due to emission from the greatest observable depth of the sample.[6] The heated surface layer of the sample can, in principle, produce bands with a maximum intensity determined by the radiance of a perfect blackbody emitter at the same temperature, as is the case in standard emission measurements.[4] The sample spectrum is thus sandwiched between two blackbody-type spectra, with the intense (weak) bands appearing close to the high

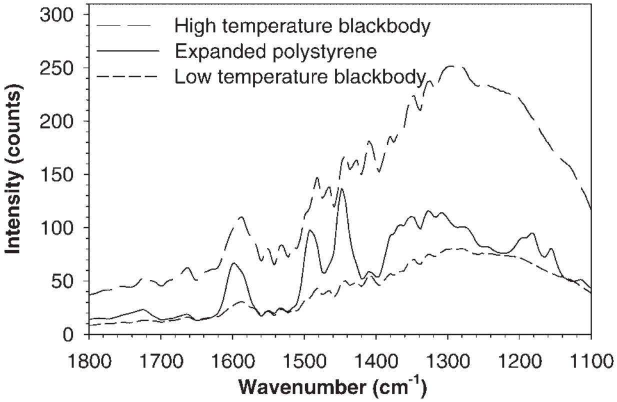

Figure 3.
TIRS radiance spectrum of a thick expanded polystyrene sample and of the blackbody emitter at low and high temperatures.

(low) temperature blackbody spectrum. However, because the sample temperature is not uniform with depth (and even laterally because heating is not perfectly homogeneous), it is not possible to define a single temperature for the surface layer. As a consequence, the temperature of the blackbody to be used for calculating the TIRS emittance is not strictly defined either. The usual TIRS practice is to select a normalizing blackbody spectrum that only slightly exceeds the most intense feature of the sample spectrum.[6] Several blackbody curves were thus recorded at different temperatures in order to match the intensity of the sample curve and calculate the final TIRS spectra.

Figure 4 shows the spectra calculated using for the expanded polystyrene as well as for two other common packaging materials: an air cellular cushioning material (bubble wrap) and a second type of foam. These everyday products are meant to represent polymeric materials that could be found on a recycling unit. The spectra were not baseline corrected but were shifted for clarity. As expected, the three spectra show clear differences that allow easy distinction. The spectrum of the expanded polystyrene shows all the expected bands, in addition to a carbonyl band most likely due to additives. The second packaging foam shows the characteristic bands of polyolefins and is likely composed of polypropylene. The

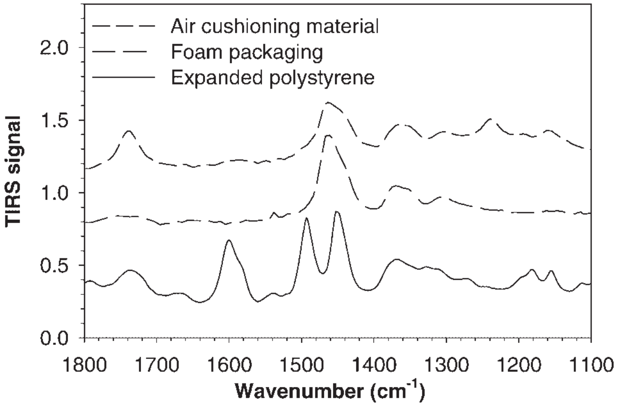

Figure 4.
TIRS spectra of various polymer samples.

spectrum of the cushioning material is more complex and also appears to contain a large fraction of polypropylene. Additional bands, which could help identifying the other component contained in this material, are visible at 1735 and 1235 cm^{-1}. The expanded polystyrene TIRS spectrum is qualitatively similar to an ATR spectrum (not shown) of the same material. Small differences in band shape exist because the spectral resolution varies as a function of wavenumber in spectra recorded with a dispersive spectrometer. The band intensities are somewhat different from those in conventional ATR or transmission spectra, with the weaker bands showing larger relative intensities in the TIRS spectra. This is due to the fact that the emitting layer was relatively thick in these measurements, leading to equivalent absorbance values beyond the linear (Beer law) range. It was shown that TIRS spectra can be used for quantitative analysis using bands of appropriate intensity.[7]

The results of Figure 4 demonstrate that good quality TIRS spectra can be recorded using a no moving part PA-IR spectrometer. This feature could be advantageous in the context of on-line monitoring, where the interferometer of an FT-IR spectrometer can be affected by strong vibrations. A rather large bandwidth was recorded in these experiments by using a grating with a low groove density, but at the expense of a spectral resolution limited to 7–14 cm^{-1}. Alternatively, a higher resolution could be obtained at the expense of bandwidth. This compromise does not have to be made when using FT-IR spectrometers, for which the two parameters are independent. Nevertheless, a potential major advantage of PA-IR spectroscopy over FT-IR spectroscopy for TIRS measurements is the possibility of performing faster time-resolved acquisition, as was demonstrated in absorption experiments.[8,12]

Figure 5 shows spectra of the expanded polystyrene sample recorded by averaging between 300 and 2 camera frames, corresponding to acquisition times of 2.6 s, 435 ms, 87 ms and 17 ms. The four spectra are almost identical, albeit with slightly different baselines. The signal-to-noise level is very good, even for the spectrum recorded in a mere 17 ms. Similar results were obtained with the air cushion sample, while the second foam became noisier in 87 ms acquisitions. In that case, however, the intensity of the most intense band was only 46 counts, as compared to 133 counts for the expanded polystyrene in Figure 3.

Such fast acquisition times could greatly improve the performance of TIRS in terms of sample resolution. Indeed, the samples are often circulated at a speed around 40 cm/s but which can be as high as several m/s.[6] In either case, recording an FT-IR spectrum in as little as 1 s would still mean averaging a sample (or several samples) over a long

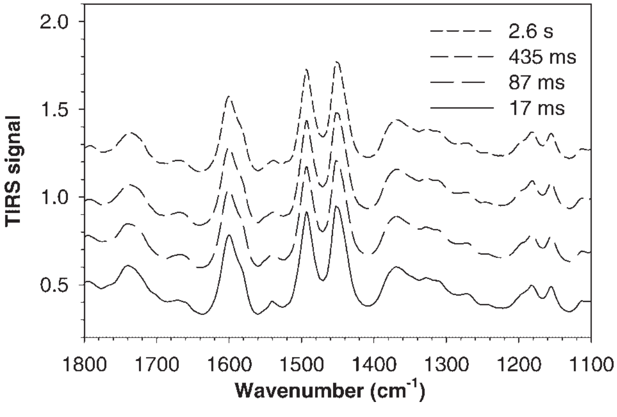

Figure 5.
TIRS spectra of expanded polystyrene recorded using different acquisition times.

distance. In contrast, a PA-TIRS setup with a time resolution of 25 ms could in principle provide a spectrum per cm, opening the door to true real-time TIRS monitoring.

An important limitation of our demonstration setup should be acknowledged. Because the PA-IR spectrograph was built on an optical table without any protection for the optical elements, it was necessary to keep the temperature of the hot stream relatively low, and the linear velocity of the samples on the rotating stage was restricted to 10 cm/s. Both aspects are detrimental because 1) they reduce the temperature gradient between the surface and bulk of the sample, leading to a decreased TIRS signal, and 2) the longer heat diffusion time creates a thicker surface layer that can lead to saturation of the signal. This was indeed a problem for dense samples with better heat diffusion properties, leading to ill-structured or even blackbody-type spectra. It should nevertheless be stressed that these limitations are of an engineering nature and that, under improved sampling conditions, the performance of the PA-TIRS technique is expected to match that of Figure 4 and 5 for such samples.

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[1] P. R. Griffiths, J. A. De Haseth, *Fourier Transform Infrared Spectrometry*, 2nd ed., Wiley-Interscience, Hoboken, NJ 2007.
[2] Y. Wang, C. Pellerin, C. G. Bazuin, M. Pézolet, *Macromolecules* **2005**, *38*, 4377.
[3] K. C. Cole, C. Depecker, M. Jutigny, J. M. Lefebvre, P. Krawczak, *Polym. Eng. Sci.* **2004**, *44*, 231.
[4] J. Mink, Infrared Emission Spectroscopy. In *Handbook of Vibrational Spectroscopy*, Vol. 2, P. R. Griffiths, J. M. Chalmers, Eds., John Wiley & Sons, Chichester **2002**, pp. 1193–1214.
[5] R. W. Jones, J. F. McClelland, *Anal. Chem.* **1989**, *61*, 650.
[6] R. W. Jones, J. F. McClelland, S. J. Bajic, Transient Infrared Spectroscopy. In *Handbook of Vibrational Spectroscopy*, Vol. 2, P. R. Griffiths, J. M. Chalmers, Eds., John Wiley & Sons, Chichester **2002**, pp. 1215–1230.
[7] R. W. Jones, R. R. Meglen, B. R. Hames, J. F. McClelland, *Anal. Chem.* **2002**, *74*, 453.
[8] C. Pellerin, C. M. Snively, D. B. Chase, J. F. Rabolt, *Appl. Spectrosc.* **2004**, *58*, 639.
[9] I. Pelletier, C. Pellerin, D. B. Chase, J. F. Rabolt, *Appl. Spectrosc.* **2005**, *59*, 156.
[10] C. Pellerin, I. Pelletier, J. F. Rabolt, D. B. Chase, *Anal. Chem.* **2007**, *79*, 2037.
[11] S. Krimm, *Adv. Polym. Sci.* **1960**, *2*, 51.
[12] C. Pellerin, S. Frisk, J. F. Rabolt, D. B. Chase, *Appl. Spectrosc.* **2004**, *58*, 799.