

NEW ADVENTURES IN THERMAL ANALYSIS

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Abstract

This paper describes recent advances in thermal analysis instrumentation which combine the high resolution imaging capabilities of the atomic force microscope with physical characterisation by thermal analysis. Images of the surface may be obtained according to the specimen's thermal conductivity and thermal expansivity differences in addition to the usual topographic relief. Localised equivalents of modulated temperature differential scanning calorimetry, thermomechanical and dynamic mechanical analysis have been developed with a spatial resolution of a few micrometres. A form of localised thermogravimetry-evolved gas analysis has also been demonstrated. The same instrument configuration can be adapted to allow IR microspectrometry at a resolution better than the optical diffraction limit.

Keywords: evolved gas analysis, localised thermal analysis, near field IR spectroscopy, scanning thermal microscopy

Introduction

The past twenty-five years have seen considerable developments in the area of thermal analysis instrumentation and techniques. In the late 1970's the microelectronics revolution heralded the arrival of desktop computing. The ubiquitous personal computer was soon interfaced to thermal analysis equipment for instrument control, data collection, storage and analysis. This freed the scientist from the need to continuously monitor experiments and then perform laborious data reduction on the output from a chart recorder. During this time, robotic sample changers became commercially available, thus increasing productivity further. The 1990's saw this new found power used to change the way that instruments were operated. Although, sample controlled thermal analysis (SCTA or controlled rate thermal analysis) and AC calorimetry are not new techniques, their use was limited until the advent of computer controlled equipment [1, 2]. Constrained Rate or 'High Resolution' TG (as form of SCTA) and modulated temperature DSC (MTDSC) are modern methods which have built upon these earlier approaches in order to derive enhanced resolution and sensitivity for detecting mass and heat capacity changes respectively [3, 4]. Modulated temperature

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programs have now been used in thermogravimetry, thermomechanical and dynamic mechanical analysis [5–7]. Modulated temperature TG (MTTG) being a modern counterpart of the temperature-jump methods proposed by Flynn [8].

Despite these advances, thermal methods still largely operate on samples in the milligram (or larger) scale. Even though sensitive microbalances and calorimeters have been described, it is usual to make measurements on relatively large amounts of material. The results of such measurements therefore represent the sum of all of the constituents in the specimen. The thermal response is often dominated by the higher concentration of the matrix or substrate material. It is difficult to gain detailed characterisation of dilute components, contaminants and less dominant phases without physically altering the sample. In addition, the experiments are often time-consuming – particularly for thermomechanical and dynamic mechanical tests.

The invention of the scanning probe microscope (SPM) has opened up many new ways of visualising surfaces to very high resolution. The original development relied on measuring the tunnelling current between a sharp tip and a conductive sample. This was used to control the height of the tip and thus track the surface topography as the tip was scanned over the surface [9]. In 1986, Williams and Wickramasinghe described a scanning thermal profiler in which the temperature difference between a heated tip and sample was used to control the fly height of the probe (in this case a miniature thermocouple) [10]. By this means electrically insulating materials could be imaged. The major breakthrough in the field of scanning probe microscopy came the same year when Binnig *et al.* described the atomic force microscope (AFM) [11]. Again, this instrument is based on old principles, the forerunner of the AFM being the Edison phonograph [12].

A schematic diagram of a modern AFM is shown in Fig. 1. This consists of a sharp tip mounted on the end of a cantilever which is scanned across the specimen by a pair of piezoelectric elements aligned in the x- and y-axis. As the height of the sample changes the deflection of the tip in contact with the surface is monitored by an optical lever formed by reflecting a laser beam off of the back of the cantilever into a segmented photodetector. The tip is then moved up and down by a feedback loop driving a z-axis piezo so as to maintain a constant force on the sample. The voltage applied to the z-piezo provides the height of the sample at each x,y position. Besides the topographic information provided by rastering the tip across the sample, other

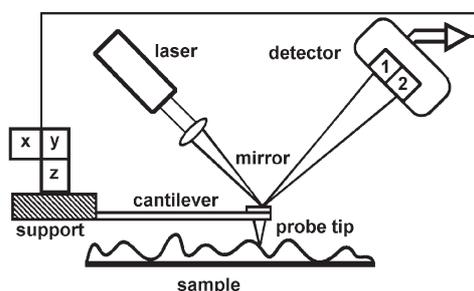


Fig. 1 Schematic diagram of an AFM

properties can be obtained by measuring the twisting of the cantilever as it is moved across the sample (lateral force microscopy) [13]. This provides image contrast based on the frictional forces generated from the sample-tip interaction. Other imaging modes, such as force modulation and pulsed force modes can indicate the stiffness of the sample [14].

Recent innovations in this area have combined the high spatial resolution of AFM with the characterisation capabilities of thermal analysis. Thus, for the first time, it is possible to measure the thermal response of a specimen in a localised region rather than on a macroscopic scale. The ‘micro-’ equivalents of well-known techniques such as DSC, thermomechanical and dynamic mechanical measurements have been described by Reading *et al.* [15]. We call this approach ‘micro-thermal analysis’. In this paper we will summarise some of these developments and describe some of our new areas of research into novel imaging modes and the potential for localised chemical analysis using the same equipment.

Micro-thermal analysis

The starting point for micro-thermal analysis is a conventional AFM – similar to that described above – where the probe tip has been replaced with an ultra miniature resistive heater which also serves as a temperature sensor (Fig. 2). This type of device was first described by Dinwiddie *et al.* who used it purely in an isothermal mode to simultaneously map topography and thermal conductivity [16]. The probe is fashioned from Wollaston process wire which consists of a thin platinum core (*ca* 5 μm in diameter) surrounded by a thick silver sheath (*ca* 75 μm diameter). This provides a wire of sufficient thickness to be formed into a loop and attached to a carrier to produce a cantilever. Once properly oriented, the silver at the end of the loop is etched away to expose the core. When a current is passed through the probe, heating occurs primarily in the exposed platinum filament since this is the principal resistance in the circuit. A small wafer of silicon is cemented across the arms of the cantilever to act as a mirror for the optical height feedback circuit. The heat lost from the probe to the sample is monitored by operating the probe in a constant temperature mode whereby the power required to maintain the tip at a predetermined temperature is monitored during image acquisition. Regions of high apparent thermal conductivity lead to greater heat

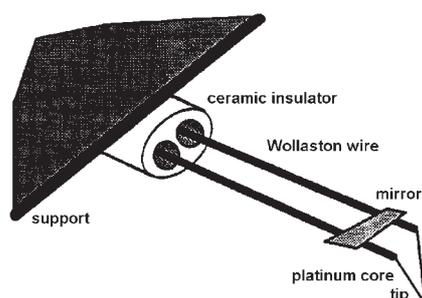


Fig. 2 Schematic diagram of thermal AFM probe

flow to the sample and subsequent image contrast against areas of lesser thermal conductivity. Thermal imaging of this type is universally applicable since all materials conduct heat. AC heating of the probe may also be employed in order to afford a means of obtaining depth specific information about the surface, since high frequency thermal waves penetrate to shallower depths than low frequency thermal waves [17, 18].

In the scanning thermal microscopy mode, topographic and thermal images are produced simultaneously as illustrated in Fig. 3. This shows the surface of a common analgesic tablet containing the drug 4-acetamidophenol (paracetamol or tylenol). The topography illustrates the rough surface of the compact but the thermal image suggests that two thermally dissimilar materials are present. Although Riuz has made absolute measurements of surface thermal conductivity of semiconductors, this is not routinely possible since the thermal signal is convoluted with the surface roughness of the sample [19]. Sharp changes in relief affect the contact area between the probe and the specimen, thus giving rise to changes in the amount of heat that is lost from the tip not arising purely from thermal conductivity differences. For very flat samples, the spatial resolution of thermal properties is of the order of 100 nm and we have successfully used this technique to obtain images of polymer blends of two or more components with different thermal conductivities [20]. Higher resolution probes based on a combination of an actively heated resistance thermometer and conventional AFM tip technology are under development.

For localised thermal analysis, the probe is placed at a selected point on the sample surface (using the topographic and/or thermal images as a guide) and the temperature of the probe ramped as in conventional thermal analysis. The z-axis deflection of the probe is monitored as a function of the probe temperature. Spatially-resolved thermal expansivity measurements can be made and the identification of softening temperatures can be performed [21]. This technique represents the microscopic equivalent of thermomechanical analysis (TMA). By comparing the power required to make the probe follow the temperature program with that of a reference probe isolated from the sample, calorimetric information regarding the nature of transitions can be obtained simultaneously. An AC temperature modulation can also be applied

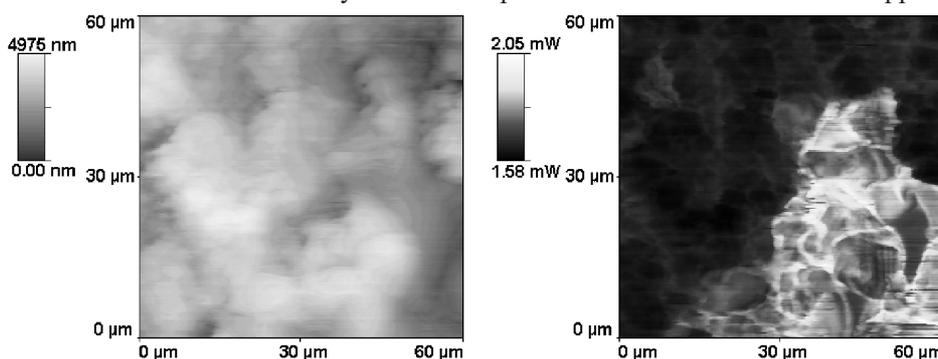


Fig. 3 Topographic (left) and thermal conductivity (right) images of the surface of an analgesic tablet

during the heating ramp and the changes in power required to keep the modulation amplitude constant can be measured, thus providing the microscopic analogue of modulated temperature differential scanning calorimetry (MTDSC). Although the calorimetric signals are not currently quantitative in terms of measuring transition enthalpies (even though the probe only heats a small volume of material, the sample size is undefined), very often simply measuring the temperature of a transition is sufficient to identify a phase [22].

Figure 4 shows the localised thermal analysis of two selected areas on the surface shown in Fig. 3. A temperature scan on the low thermal conductivity region detects the melting of the drug whereas no transitions were observed over the temperature range studied for the region of high thermal conductivity. The high thermal conductivity inclusion (invisible in the conventional topographic image) is probably composed of inert filler such as micro-crystalline cellulose or calcium carbonate. Due to the high heating rates than can be employed in this type of experiment, these measurements took only a few minutes and consumed only a small amount of material (less than $100 \mu\text{m}^3$). In addition to the ability to perform spatially resolved thermal analysis, there are obvious advantages for this approach in the area of new product development and forensic analysis.

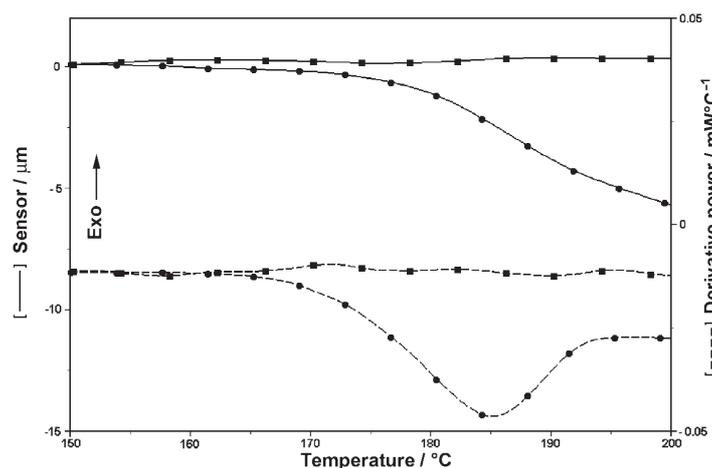


Fig. 4 Localised thermomechanical (solid line) and calorimetric (broken line) curves for different locations on the images shown in Fig. 3 (• – 0 represents data from a region containing the drug located at $9.8 \times 27.2 \mu\text{m}$, ■ – represents the filler at $41.2 \times 39.4 \mu\text{m}$)

The temperature range which may be studied is limited by the temperature of the bulk sample (at the lower end) and thermal endurance of the platinum tip. We have recently developed a versatile temperature stage for the instrument which enables measurements to be carried out down to liquid nitrogen temperatures. As will be demonstrated, at the other end of the temperature scale, the heat generated by the probe is sufficient to pyrolyse organic materials.

We have also used a force modulation to provide two additional signals, the AC amplitude and phase for the position sensor during heating of the tip (this is a micro-equivalent of DMA, but this is not currently routinely available [23]).

Thermal expansion imaging

The modulation of the probe caused by simply vibrating the sample in the z-axis leads to another imaging mode. In this case localised AC heating of the tip causes the surface to expand and contract according to its thermal expansivity. This change in dimension is detected using a lock-in amplifier and used to generate an image whose contrast is determined by the apparent differences in thermal expansivity of the surface components. Figure 5 shows an image of the interface between a steel spring (right) embedded in an epoxy resin matrix. The surface was carefully polished to avoid any artefacts due to surface topography. The thermal expansion coefficients of the individual components were measured by conventional TMA (steel: $15 \mu\text{m m}^{-1} \text{ }^\circ\text{C}^{-1}$, epoxy: $80 \mu\text{m m}^{-1} \text{ }^\circ\text{C}^{-1}$). The higher thermal expansion of the resin is depicted in Fig. 6 which shows a single line scan (left-right) across the mid point of the image. Similar measurements have been reported by Majumdar who employed a conventional AFM to detect the thermal expansion of Joule-heated elements as a means of mapping temperature distributions [24]. Some advantages of our approach are that electrically conductive substrates are not required and that topographic, thermal conductivity and thermal expansivity images may be acquired simultaneously. Localised modulated-temperature thermomechanical measurements have also been carried out [25].

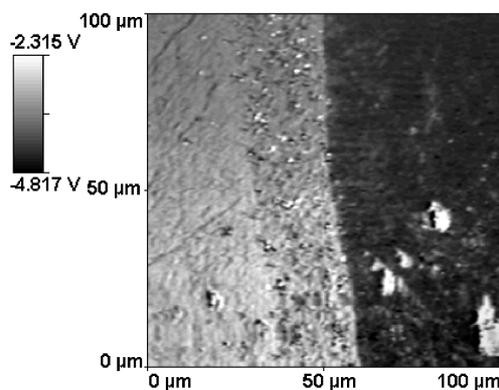


Fig. 5 Thermal expansion image of metal (right) embedded in epoxy resin (left)

Thus we have a means to map a surface by its topography, thermal conductivity and thermal expansivity and then perform localised thermal analysis on regions of interest. These techniques afford a physical means to discriminate between phases, the potential for localised chemical analysis will now be discussed in the two following sections.

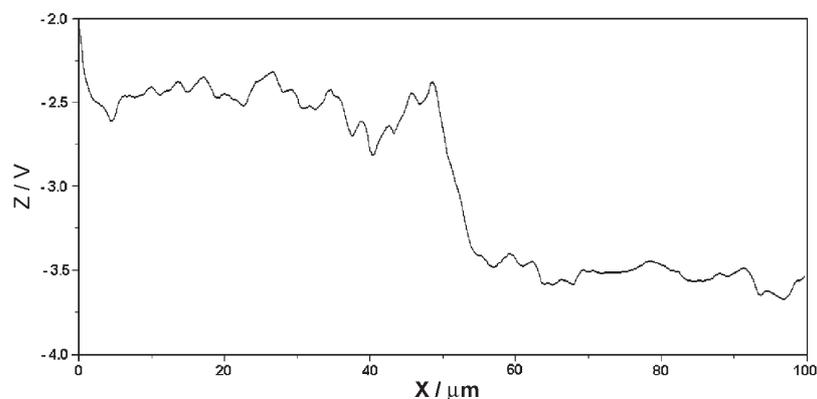


Fig. 6 Line profile across centre of image shown in Fig. 5 showing the higher thermal expansivity of the epoxy resin (left)

Localised infrared spectrometry

If the sample is irradiated with the focused beam from a conventional FTIR spectrometer the thermal probe can be used to detect any local temperature increase due to absorption of infrared radiation. In this way a photothermal IR spectrum can be acquired. Figure 7 shows the photothermal spectrum of pure 4-acetamidophenol and the conventional attenuated total reflectance (ATR) spectrum of the same compound. The great advantage of this approach over conventional IR microspectrometry is that the resolution is not limited by the wavelength of the radiation being used. Calculations show that sub micron resolution should certainly be achievable across the entire mid-IR range [26].

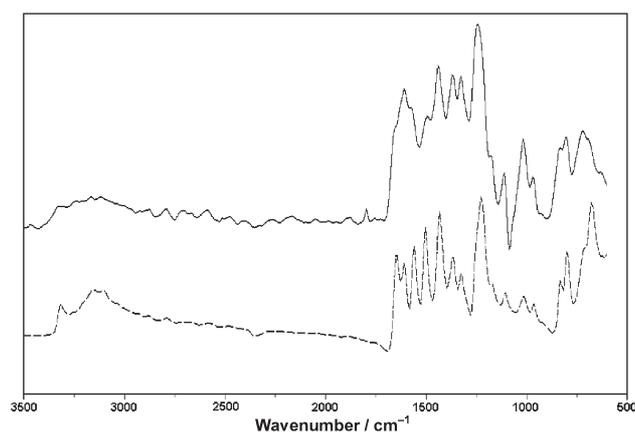


Fig. 7 Photothermal absorption spectrum of 4-acetamidophenol (solid line) acquired using the thermal probe – the conventional ATR spectrum is shown (broken line) for comparison

Localised evolved gas analysis, micro-sampling and micro-thermogravimetry

Rapid heating of the thermal probe in contact with the surface of a sample can be used to pyrolyse selected areas of the specimen. The evolved species can be captured and analysed by mass spectrometry (MS) or gas chromatography-MS. In our current implementation the gases are first trapped in a specially designed tube packed with a suitable sorbent such as Tenax or Carboxpak. The tube comes to a fine point which is placed immediately adjacent to the heated tip using a micro-manipulator. As the tip is heated a syringe is used to draw gas through the tube which is then placed in a thermal desorption unit for analysis of the trapped volatiles by GC-MS.

A further refinement of this technique is to use the probe to remove material from the surface by placing the hot probe on the specimen and pulling off a small amount of the material adhered to the tip. This could then be washed off the probe by immersing it in a suitable solvent. Chemical analysis of this 'micro-sample' might then be carried out by conventional chromatographic and spectrometric techniques (such as high performance liquid chromatography, matrix assisted laser desorption/ionisation spectrometry or nuclear magnetic resonance spectroscopy). Alternatively, the probe can simply be heated up in the usual manner in air (or inert atmosphere) and the evolved gases sampled as described above.

Figure 8 shows the effect of deliberately contaminating the thermal probe with poly(methyl methacrylate) and then heating it up at $10^{\circ}\text{C s}^{-1}$ in air. Two curves of the AC power required to modulate the probe by $\pm 5^{\circ}\text{C}$ at 5 kHz are shown: one run with a small bead (*ca* 0.5 μg) of polymer adhered to the tip and a baseline after the material had been pyrolysed from the probe. When the two curves are subtracted and integrated with respect to temperature the resulting trace looks very much like a conventional thermogravimetric curve (Fig. 9). This is because the AC calorimetry effectively detects the amount of material on the probe. The resulting evolved gases were

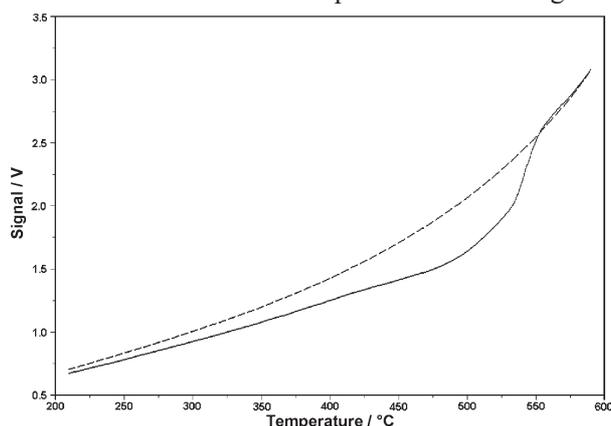


Fig. 8 AC signals recorded during for the pyrolysis of a bead of poly(methyl methacrylate) attached to the end of the thermal probe (solid line). A baseline post-pyrolysis is shown (broken line)

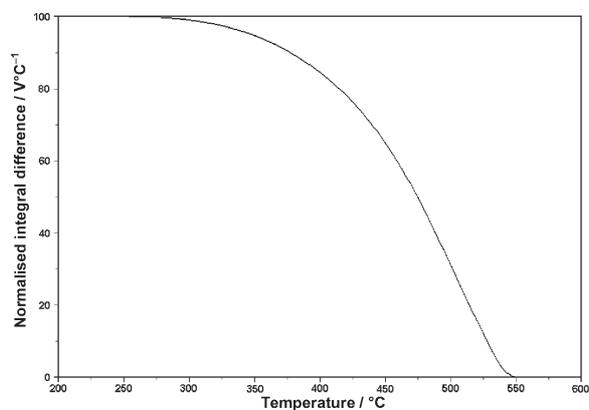


Fig. 9 Plot of cumulative integral of the difference between the two curves shown in Fig. 8

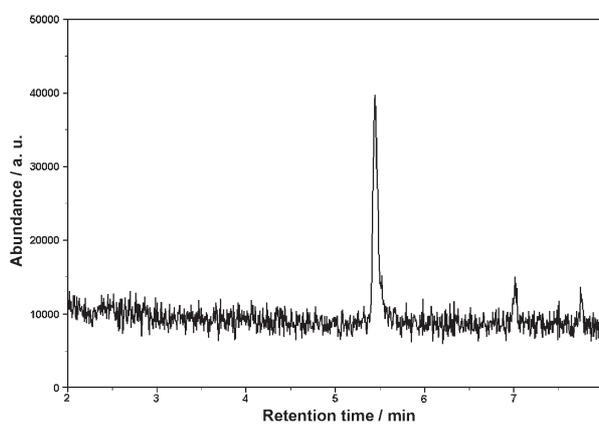


Fig. 10 Gas chromatogram of thermally desorbed species trapped during pyrolysis experiment

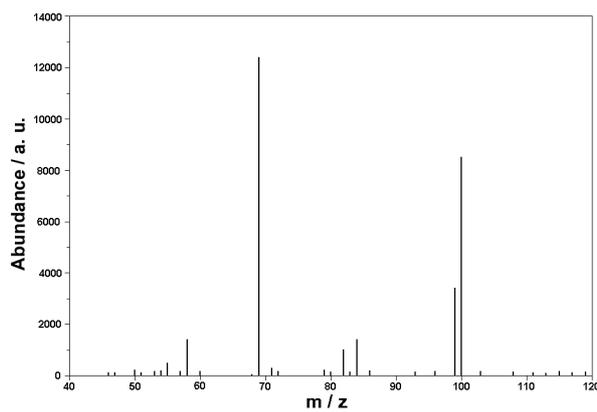


Fig. 11 Mass spectrum of peak at 5.45 min showing detection of methyl methacrylate monomer

trapped on an adsorbent tube and the resulting chromatogram shown in Fig. 10. The mass spectrum of the peak at a retention time of 5.45 min detects methyl methacrylate monomer generated by unzipping of the polymer chain (Fig. 11).

In addition to the ability to perform localised chemical analysis by sampling small areas of the specimen, workers at IBM have recently employed an approach related to micro-thermal analysis as a means of data storage [27]. An array of probes, similar in principle to that described, are used to melt small pits in a sheet of polymer. These are then read using the same configuration by detecting the change in temperature of the probes as they fall into the holes as they are scanned across the surface. Data storage densities exceeding that possible with conventional magnetic media are claimed. In effect, this amounts to the reverse of micro-thermal analysis, *i.e.* localised thermal analysis followed by scanning thermal microscopy. Our own modest efforts in this area are shown in Fig. 12.

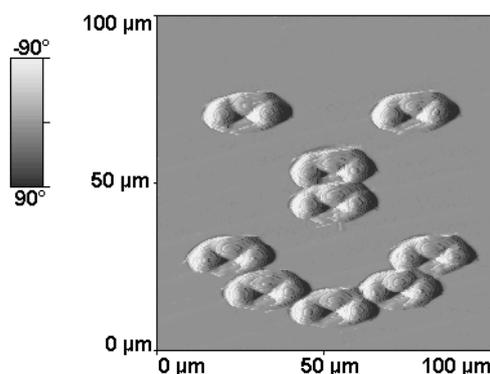


Fig. 12 Shaded topographic image of an array of nine craters on the surface of a poly(ethylene terephthalate) film. These demonstrate the reliability of positioning the thermal probe and the potential of this approach as a means of data storage

Conclusions

Micro-thermal analysis affords the means to image a sample and then obtain spatially resolved measurements on small areas thus overcoming the limitations of traditional thermal methods. It is possible to investigate sample heterogeneity or characterise the individual phases in multi-component systems. This approach can also be used to simply examine specimens that are too small to characterise by conventional methods (e.g. thin coatings or minority constituents in a matrix). This opens up a unique range of applications in polymer science, composite, catalysis and pharmaceutical research by providing a powerful new form of analytical microscopy. An important feature of this technique is that it enables very fast thermoanalytical measurements to be carried out since heating rates two orders of magnitude greater than those used in conventional methods can be employed. This gives the potential for the rapid analysis of a very large number of samples. Localised chemical characterisation by near-field IR spectrometry and pyrolysis-GC-MS adds a new (and smaller) dimension to the realms of chemical analysis.

The authors would like to thank the U. K. Engineering and Physical Sciences Research Council, Bruker U. K. Limited, T. A. Instruments and ThermoMicroscopes Inc. for financial support and the provision of equipment. The ATR spectrum of 4-acetamidophenol in Fig. 7 was kindly obtained by P. H. Turner.

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