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THE COUPLING OF MICRO-THERMAL ANALYSIS TO LOCAL CHEMICAL ANALYSIS BY GC-MS FOR COMPOSITIONAL MAPPING.

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ABSTRACT
Micro-thermal analysis (micro-TA) combines the imaging capabilities of atomic force microscopy with the physical characterization capabilities of thermal analysis [1,2]. Specimens may be visualized by means of their topography and ability to conduct heat. The images so obtained can then be used as a means of selecting positions on the sample to carry out the spatially-resolved equivalents of such as thermomechanical analysis (TMA) and modulated temperature differential scanning calorimetry (MT-DSC). With some knowledge of the components in the sample and their likely thermal responses (e.g. melting point, softening temperature etc.) it is possible to use the results from such experiments to elucidate the nature and distribution of different phases within the bulk. Where the chemistry of the sample is unknown however, one may be forced to resort to the more traditional methods of surface analysis capable of providing localized compositional information (such as X-ray photoelectron spectroscopy (XPS) or secondary ion mass spectrometry (SIMS)) [3]. However, XPS and SIMS are often inconvenient techniques to employ since they require the sample to be analysed under high vacuum. The chemical information that they produce can be limited – especially in the case of complex mixtures.

Pyrolysis techniques are well-established methods for probing the chemical composition of polymers [4]. Samples are simply heated so as to decompose them into small fragments which are then analysed by mass spectrometry (MS) or capillary Gas Chromatography-MS (GC-MS). A number of systems have been described whereby the sample is heated in a thermobalance and the evolved gases trapped and analysed [5]. With micro-thermal analysis it is easy to use the resistively heated probe as a means of locally ablating material from the surface. In order to carry out such experiments the probe is placed in contact with the region of interest and rapidly heated to the pyrolysis temperature. The evolved gases are trapped in a specially designed tube packed with a suitable sorbent such as Tenax or Carbopak. The tube comes to a fine point which is placed immediately adjacent to the heated thermal probe using a micro-manipulator (figure 1). As the probe is heated, a syringe is used to draw gas through the tube which is then placed in a thermal desorbtion unit for analysis of the trapped volatiles by GC-MS. With this system it is possible to ablate a small (<10 x 10 μm) area of a sample (or a domain, feature or contaminant) and elucidate its composition under ambient conditions [6,7] (figures 2 & 3). Here were present the results of initial studies using this new technique on heterogeneous and homogeneous polymer systems.

Micro-thermal analysis promises to be a powerful new form of analytical microscopy, which is able to elucidate the organization and constitution of materials. The addition of a localized form of chemical analysis by pyrolysis-GC-MS to this technique provides an independent means of identification which is essential in cases where there is no *a priori* knowledge of the specimen's makeup or there is unclear discrimination between phases. This combined approach presents the possibility of visualizing a specimen's structure, characterizing its thermal properties and then analyzing its chemical composition.

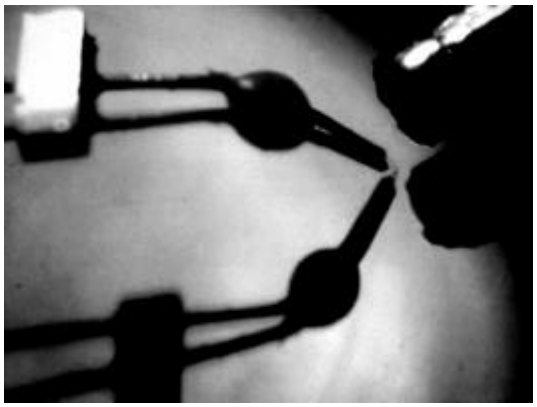

Figure 1. Thermal SPM probe (left) and end of sorbent tube.

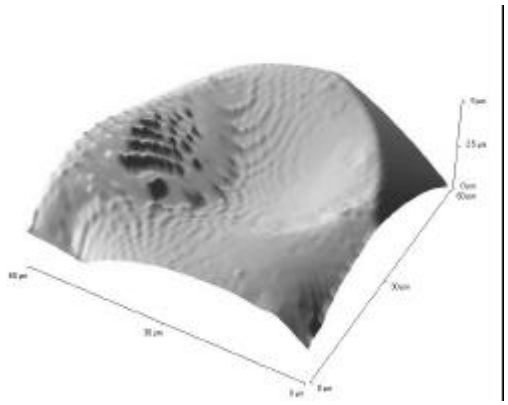

Figure 2. Pyrolysis crater (50µm across, 5 µm deep) in a 100 µm diameter polystyrene bead.

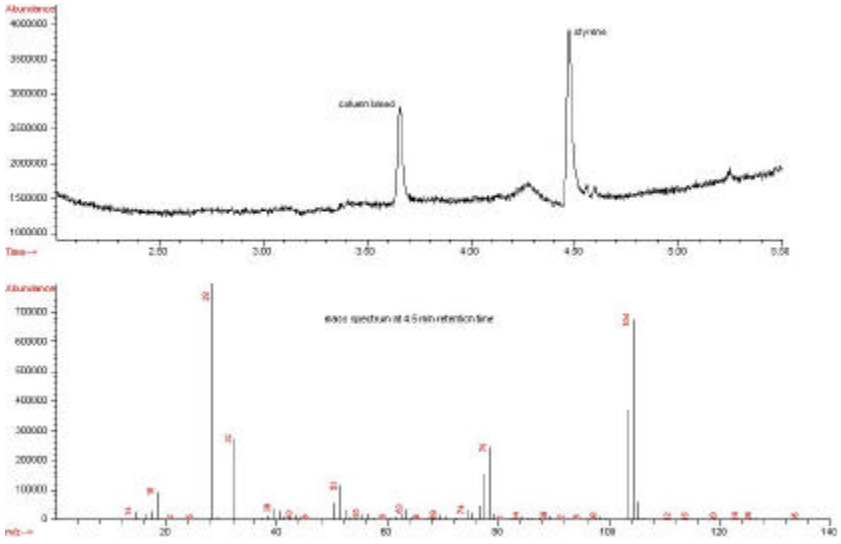

Figure 3. GC-MS analysis of evolved gases from the ablated area in figure 2 showing styrene monomer generated by pyrolysis of the polymer.

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