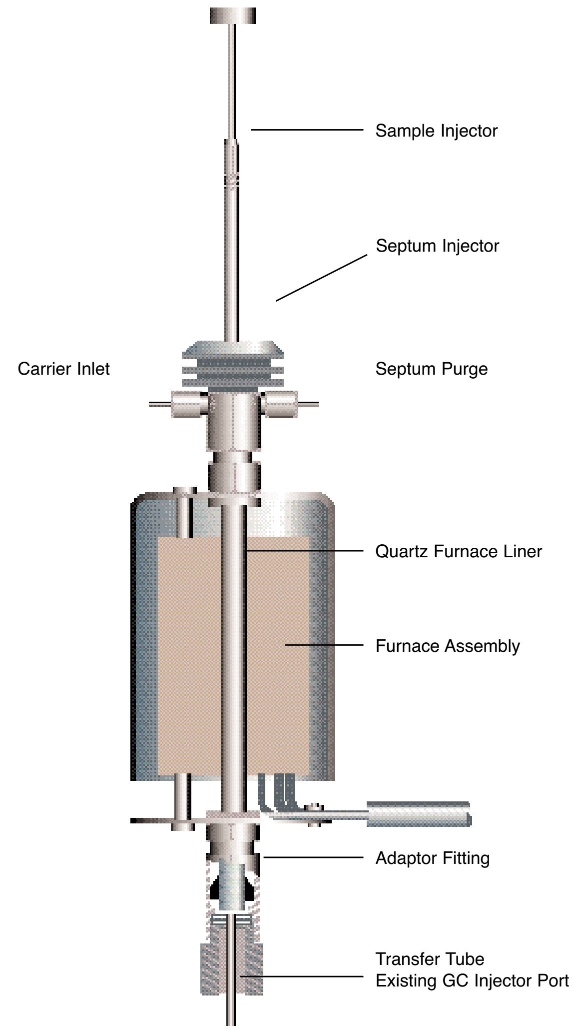
Pyrolysis of Paint Polymers

Paints or surface coatings are widely used for a variety of applications ranging from decorative or household paints to automotive and heavy duty coatings used in industrial environments. Paints generally contain pigments, solvents and a polymer known as the ‘binder’ which is the heart of the surface coating as this is the component that binds the pigments together and is responsible for adhesion to the substrate.

The type of binders used in surface coatings range from free radical formed polymers such as polyacrylates to epoxy resins and alkyl resins used in decorative enamels. Within a class of polymers, the individual monomers also vary. For example, an automotive clearcoat air-drying acrylic lacquer will have a different monomer composition to one that cross-links during the drying process. The monomer composition of the polymer is therefore important in the end-use application and properties. Various techniques can be used to understand the chemistry of the polymer. Gel Permeation Chromatography is a common molecular sizing technique while infrared spectroscopy can give valuable information on the functionality of the polymer. The main techniques used however for monomer analysis are Nuclear Magnetic Resonance (NMR) spectroscopy - both proton and carbon-13 and pyrolysis GC/MS. The latter technique is extremely powerful especially for qualitative analysis.

This article describes the analysis of acrylic binders which are commonly used in surface coatings. The polyacrylate is a free-radical polymer which will depolymerise or ‘unzip’ to its constituent monomers when heated. For example, a homopolymer of polymethyl methacrylate will unzip to yield methyl methacrylate (MMA) upon heating. MMA is volatile and can thus be analysed by gas chromatography. Coupling of a pyrolysis unit to a GC mass spectrometer can therefore be a powerful tool providing information about the monomer make-up of a polymer.

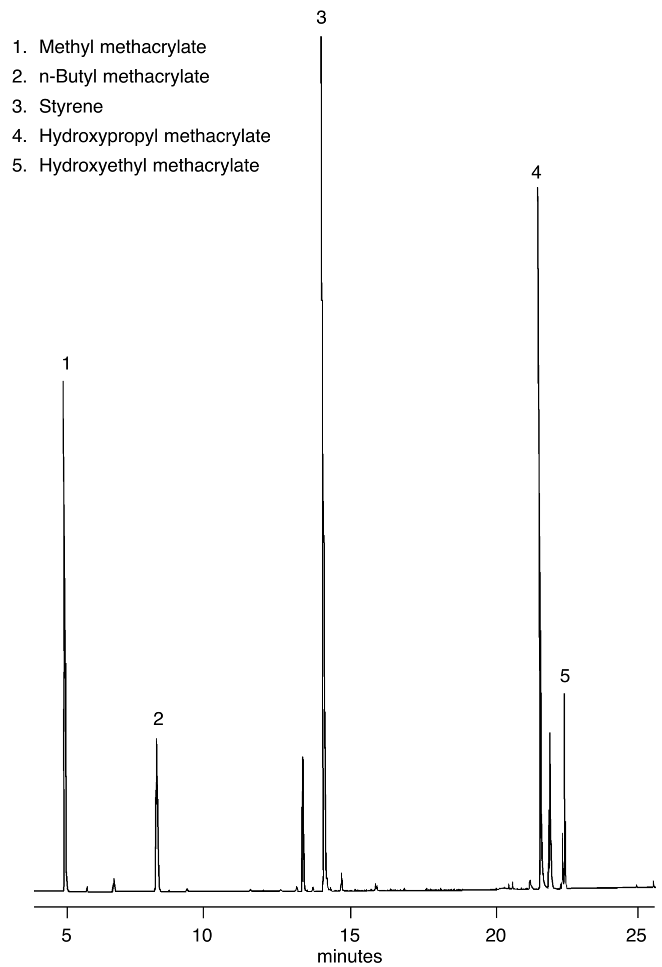
The SGE Pyrojector can be easily attached to any GC and comes with a variety of injection accessories. There are five in total, three as standard and two more as options for quantitative



work. Solids and liquids can be easily injected directly into the furnace and pyrolysis products swept into the GC injection port. This type of pyrojector is operated in a continuous furnace mode and the temperature and pressure of carrier gas through the furnace can be accurately controlled. These controls permit reproducible pyrolysis.

Figure 1 shows a program of a polyacrylate polymer containing MMA, styrene (Sty), n-butyl methacrylate (BMA) and two hydroxylated acrylate monomers, namely hydroxypropyl methacrylate (HPMA) and hydroxyethyl methacrylate (HEMA). All these monomers are clearly identified in the pyrogram and the peak heights correlate well with relative mole ratios. Other peaks are due to non-evaporated solvents. The temperature of 600°C was chosen to achieve complete pyrolysis of the

Figure 1. Pyrogram showing various acrylate monomers from an acrylic binder extracted from a refinish automotive coating.



acrylic binder but was not high enough to generate secondary pyrolysis products from the monomers themselves. The identification of the hydroxylated acrylic monomers shows that this refinish automotive coating is one that can be cross-linked and most likely part of a two-pack product. The hydroxy monomer could possibly be cross-linked with an isocyanate compound. The easy identification of n-butyl methacrylate via pyrolysis is much more difficult by carbon-13 nmr spectroscopy. While this technique is very quantitative and compliments pyrolysis GC/MS, it is difficult to distinguish between n-butyl acrylate and n-butyl methacrylate as the distinguishing functionality is the butyl group from the monomer. Pyrolysis GC/MS, on the other hand, will yield the monomer which can be identified by their respective retention time and mass spectra.

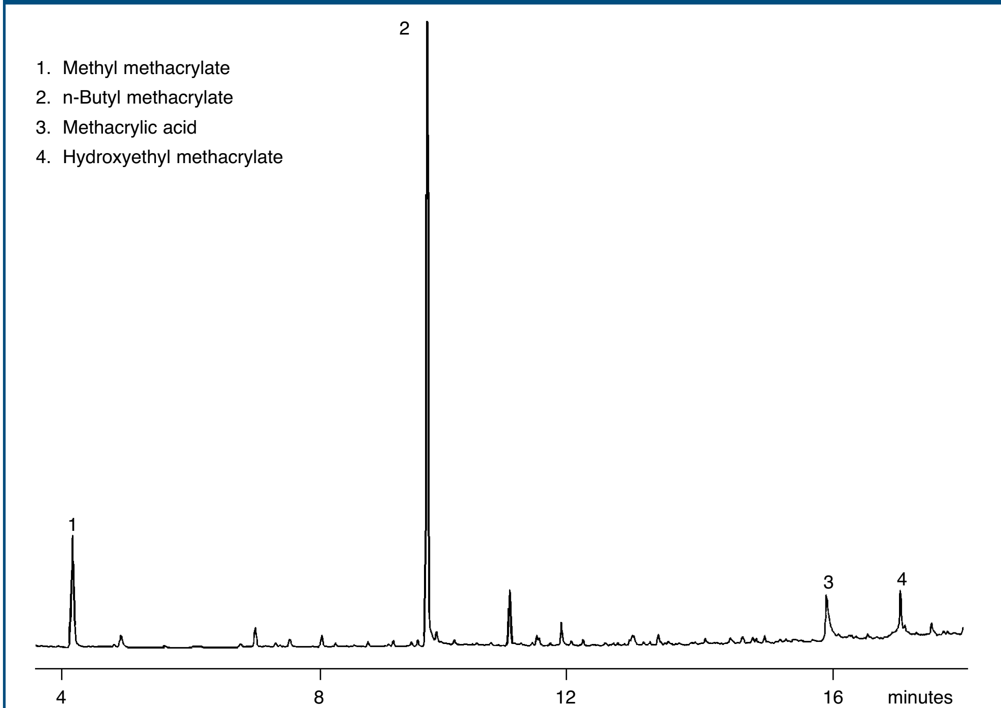
Figure 2 shows a pyrogram of another surface coating binder with a different composition to that shown in Figure 1. Note the ratio of the MMA to styrene is different in this case showing the mole ratio is not the same. This polymer contains methacrylic acid which can be used as an adhesion promoter. This monomer is very difficult to detect by NMR without derivatisation but easily stands out in the pyrogram.

PYROJECTOR ORDERING INFORMATION

Description	Part No.
Pyrojector (110-240V 50-60 Hz)	**095001**
Pyrojector (CE Marking)	**095004**

Note: Indicate GC make, model and injector when ordering to enable the correct adaptor fitting to be supplied.

Figure 2. Pyrogram showing various acrylate monomers from an acrylic binder containing a low amount of acrylic acid.



Column:
BP20, 25m x 0.22mm ID, 0.25μm

Pyrojector furnace temp: 600°C

Oven temperature:
50°C (hold 5 min), ramp rate @ 10°C/min to 200°C (hold 10 min)

Sample introduction:
A THF extract of the binder was allowed to dry on a solids injector syringe before manual injection.

Detection:
Mass spectrometric in full scan EI mode.

Injector temperature: 250°C