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APPLICATION NOTES

PYROLYSIS

EFFECTS OF INCREASING PYROLYSIS TEMPERATURE ON THE BREAKDOWN OF N-BUTYLBENZENE

INTRODUCTION

An SGE Pyrojector system was used to study the pyrolysis products of n-butylbenzene. The n-butylnezene was dissolved in pentane and analysed using a range of pyrolysis temperatures.

DESCRIPTION AND COMMENTS

The SGE Pyrojector involves a heated chamber into which a sample is introduced, vapourised and pyrolysed. A flow of carrier gas is maintained through the pyrolysis chamber and then to the head of the capillary column. A splitter system was used so only a fraction of the sample was transferred onto the column, while the remainder was allowed to vent.

The flow through the pyrolysis chamber is controlled by a pressure differential between the head of the pyrolysis chamber and the head of the column. The greater the pressure differential the greater the flow through chamber.

The rate at which the sample travels through the pyrolysis chamber (transit time) may directly affect the extent of pyrolysis, i.e. the shorter the transit time, the lower the time during which the sample is subjected to the pyrolysis temperature. Pyrolysis may not occur if the transit time is too short. On the other hand, if the transit time is too long, secondary pyrolysis may occur. Peak broadening due to slow sampling onto the column may also result from low flow rates (long transit times).

A pressure differential of 2 psi was set between the head of the pyrolysis unit (7 psi) and the head of the column (5 psi).

DISCUSSION

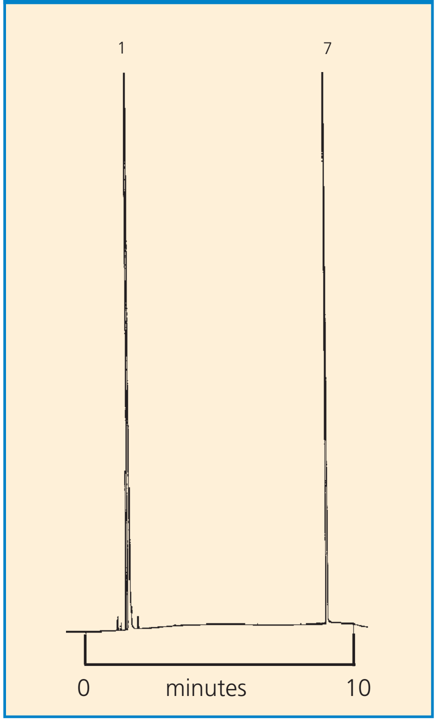
These results, together with those obtained in other studies, indicate that;

- Pyrolysis of liquids and solids can be studied simply and effectively. A high level of resolution and reproducibility is easily attainable.
- The degree of pyrolysis increases as the temperature increases as indicated by pyrograms 1-4.

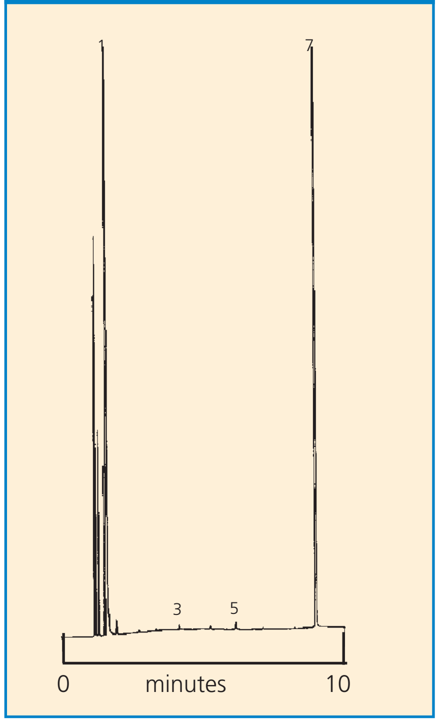
INSTRUMENTATION AND CONDITIONS

Pyrolysis Temperature:	600°C-900°C
Phase:	BP1, 0.5µm film
Column:	25 metres x 0.32 mm ID
	Initial Temperature: 40°C for 1 minute
Program Rate:	10°C/min
Final Temperature:	130°C for 1 minute
Detector:	Flame ionization
Carrier Gas:	Hydrogen
Linear Carrier Velocity:	35 cm/sec. at 40°C
Split Ratio:	100:1
Injection Mode:	Pyrolysis split
Sensitivity:	256×10^{-12} AFS
Sample:	n-Butylbenzene in pentane (2.5% v/v)
Injection Volume:	0.4µL
Pressure Differential:	2 psi

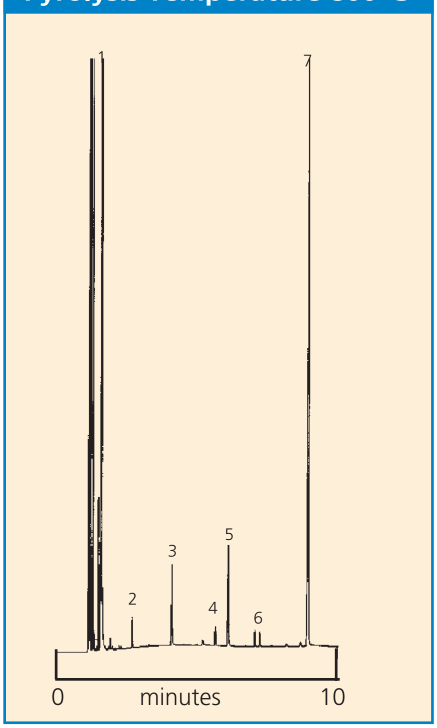
PYROGRAM 1.
Pyrolysis Temperature 600°C



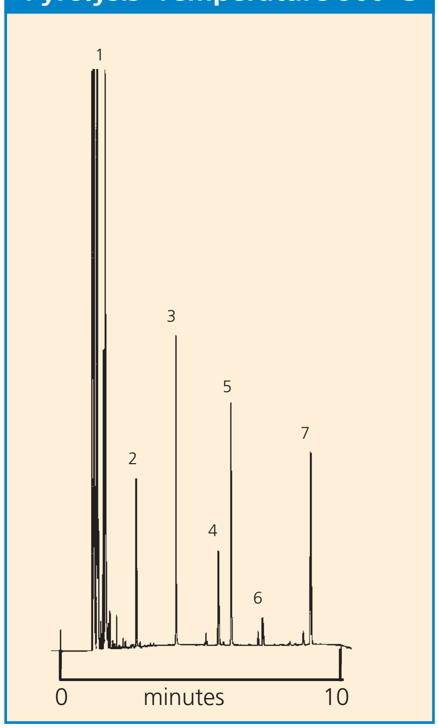
PYROGRAM 2.
Pyrolysis Temperature 700°C



PYROGRAM 3.
Pyrolysis Temperature 800°C



PYROGRAM 4.
Pyrolysis Temperature 900°C



- Transit times within the pyrolysis chamber (under the standard conditions listed above) are sufficient to achieve primary and secondary pyrolysis which can be controlled by the temperature setting. This is exemplified by the pyrograms obtained at 800°C and 900°C. At 800°C there is a pattern of pyrolysis products at which 900°C is not reproduced in the same ratio. Peak 5 (styrene), at 900°C has decreased relative to the other major pyrolysis products, indicating secondary pyrolysis.

- There is no loss of peak shape or resolution over a wide range of temperatures, as shown in pyrograms 1-4.

- It is possible to observe rearrangement reactions as indicated by the presence of styrene (peak 5) in the breakdown (pyrolysis) of n-butyl benzene.

Components	4. Ethylbenzene
1.Pentane	5.Styrene
2.Benzene	6.n-Propylbenzene
3.Toluene	7.n-Butylbenzene

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APPLICATION NOTE

PYROLYSIS

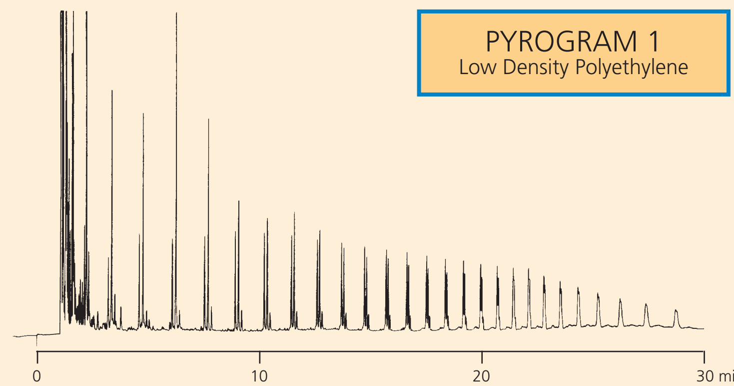
CAPILLARY GAS CHROMATOGRAPHY OF POLYOLEFINS

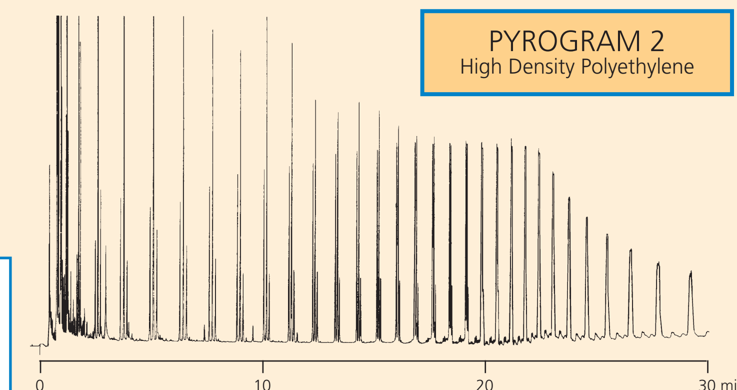
INTRODUCTION

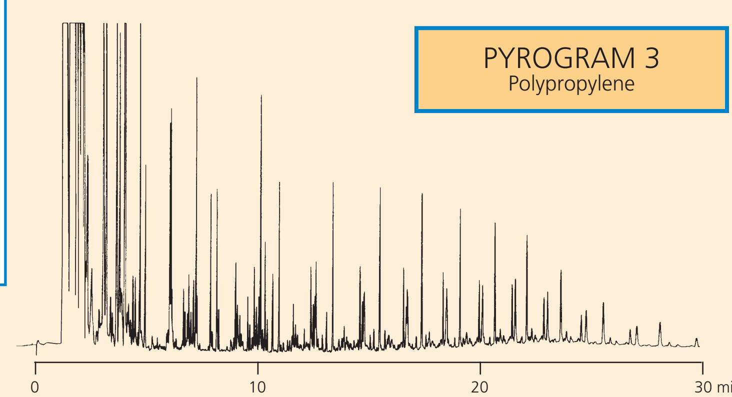
A rapid technique is available for the identification of polyolefins by pyrolysis — capillary gas chromatography.

Sample preparation is simple utilizing the SGE sample "Pelletiser P-1" and Solids Injector system.

Results display extremely high sensitivity and reproducibility is also excellent.







INSTRUMENTATION AND CONDITIONS:

Pyrolysis Temp.:	800°C
Column:	25QC3/BP1/0.5, 25m, 0.32mm ID
Stationary Phase:	Crosslinked methyl silicone, BP1
Film thickness:	0.5 micron
Initial Temp.	50°C for 0min
Program Rate:	10°C/min
Final Temp.:	320°C for 10min
Detector:	Flame Ionization
Carrier Gas:	Hydrogen
Linear Carrier Velocity:	40cm/sec @ 50°C
Split Ratio:	100:1
Injection Mode:	Pyrolysis Split

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APPLICATION NOTE

PYROLYSIS

CAPILLARY GAS CHROMATOGRAPHY ANALYSIS OF SOME MODERN PAINT FINISHES

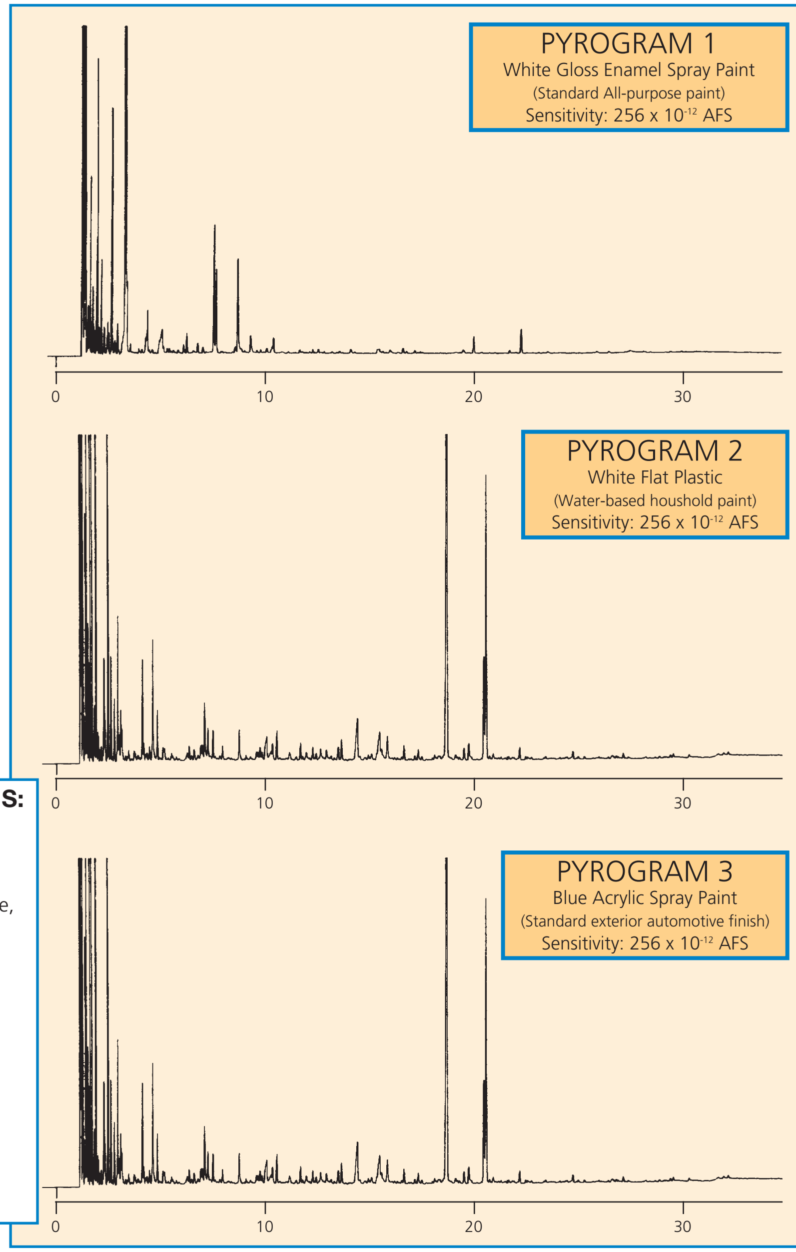
INTRODUCTION

Capillary gas chromatographic profiles of three commercially available paint finishes were obtained by a simple and rapid pyrolysis technique.

The samples run were a water based flat white plastic paint (houshold use), a white, gloss enamel (all purpose style) and a blue, acrylic paint (used in automotive industry). Sample preparation was simple using an SGE sample "Pelletiser P-1" and a "Solids Injector" system.

Results exhibit excellent reproducibility and extremely high sensitivity.

All samples were run under the following conditions.



INSTRUMENTATION AND CONDITIONS:

Pyrolysis Temp.:	800°C
Column:	25QC3/BP1/0.5, 25m, 0.32mm ID
Stationary Phase:	Crosslinked methyl silicone, BP1
Film thickness:	0.5 micron
Initial Temp.	50°C for 2min
Program Rate:	5°C/min
Final Temp.:	200°C for 10min
Detector:	Flame Ionization
Carrier Gas:	Hydrogen
Linear Carrier Velocity:	35cm/sec @ 50°C
Split Ratio:	100:1
Injection Mode:	Pyrolysis Split

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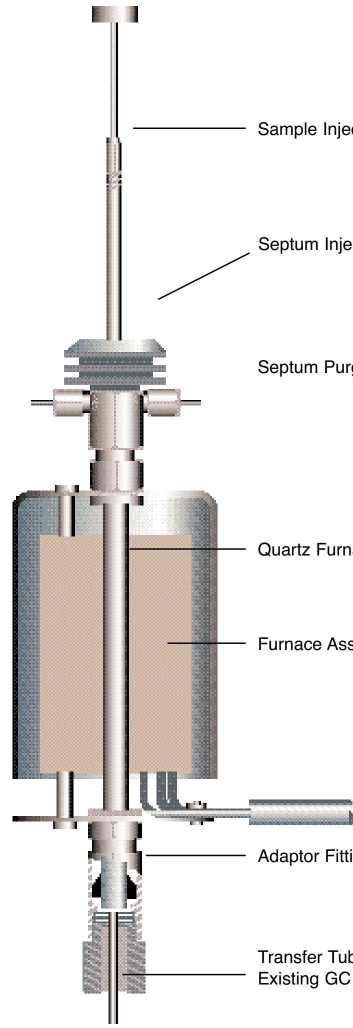
Pyrolysis of Paint Polymers

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.

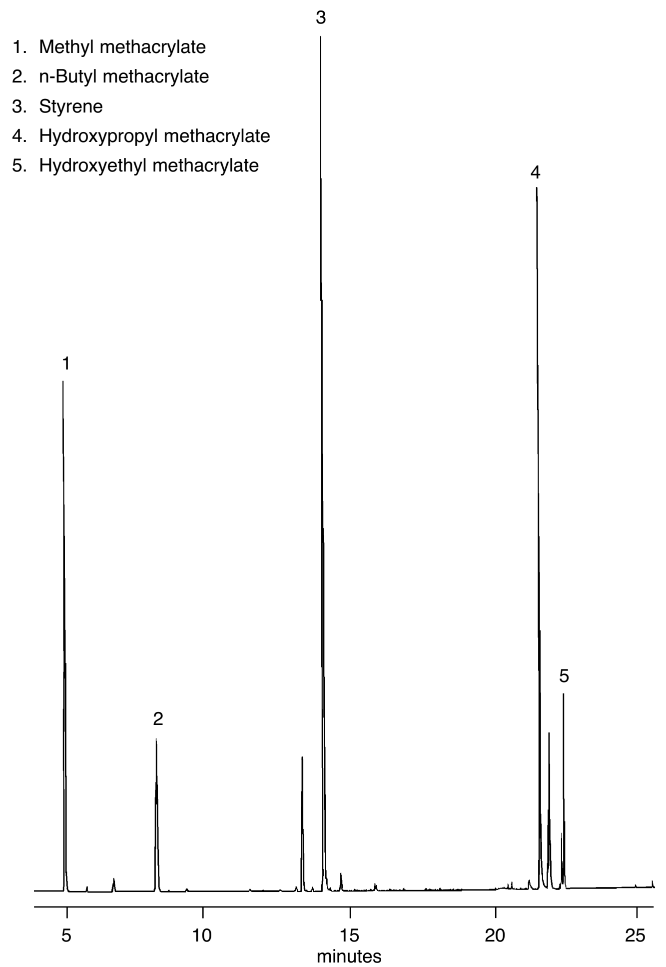


This article describes the analysis of acrylic binders which are commonly used in surface coatings. The polyacrylate is a free-radical polymer which will depolymerise or 'unzip' to its constituent monomers when heated. For example, a homopolymer of polymethyl methacrylate will unzip to yield methyl methacrylate (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.

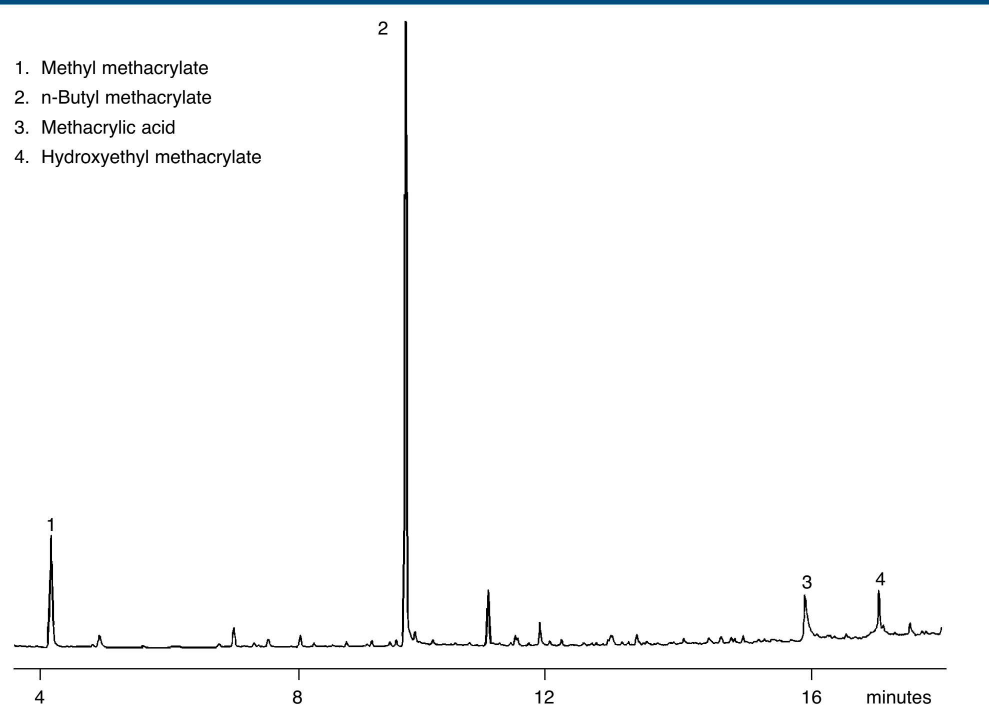
Figure 2 shows a pyrogram of another surface coating binder with a different composition to that shown in Figure 1. Note the ratio of the MMA to styrene is different in this case showing the mole ratio is not the same. This polymer contains methacrylic acid which can be used as an adhesion promoter. 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