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Pyrolysis GC-MS: Acrylates and Methacrylates

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Keywords
Acrylates, methacrylates, consumer products, pyrolysis, gas chromatography, mass spectrometry

Abstract
Acrylates and methacrylates are two important classes of polymers used in a wide variety of products. Acrylates are polymers made from a family of monomers, which have a vinyl group attached to the carbonyl carbon of an ester group. Methacrylates have a methyl group attached to the alpha carbon.

Acrylates are used in the manufacture of printing inks, coatings and paints, sealants, adhesives, and textile fibers. The simplest member of this group of polymers, polyacrylate is a superabsorbent and is used in diapers.

Methacrylates are used in the manufacture of a wide range of medical equipment and many other medical and dental applications. They are also used in the manufacture of electronics and computers, extruded sheets for windows, lights, signs and molded resin for contact lenses, glasses and car parts.

This work will show the pyrolysis fragmentation patterns for a range of acrylate and methacrylate polymers along with the analysis of several consumer products containing these polymeric materials. The GERSTEL PYRO Core System in combination with gas chromatography mass spectrometry was used for the analysis.

Introduction
The GERSTEL pyrolizer heats the sample using an advanced dual coil platinum wire that allows it to operate in a variety of pyrolysis modes including standard pulsed, sequential, fractionated, evolved gas analysis, and smart ramped pyrolysis. In addition, lower temperatures can be used to perform thermal desorption before pyrolysis. The unique heating system provides uniform sample heating and unmatched reproducibility. The GERSTEL PYRO Core System has an integrated GERSTEL Cooled Injection System (CIS 4) inlet that can be used to cryofocus analytes in the inlet or be used as a hot split interface for direct transfer to the column. An also integrated GERSTEL MultiPurpose Sampler (MPS) allows for complete automation of the analysis.

This study describes the use of the GERSTEL PYRO Core System for analysis of acrylate and methacrylate standards and common consumer products containing these types of polymers.

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Experimental

GERSTEL PYRO Core System on Agilent 8890 GC with Agilent 5977B MSD

Analysis Conditions PYRO Core System

Thermal Desorption

Pneumatics mode	Splitless
Temperatures	80 °C, 300 °C/min to 300 °C (2.17 min)

Pyrolysis (Smart Ramp)

Lead Time	0.00 min
Follow up Time	0.50 min
Initial Time	0.00 min
Temperatures	300 °C, 5.0 °C/s to 800 °C (0.0 min)

CIS 4

Pneumatics mode	Split 50:1
Temperatures	300 °C isothermal

Analysis Conditions Agilent 8890 GC

Pneumatics	He, P_i = 7.1 psi (MSD) Constant flow = 1.0 mL/min
Column	30 m DB-5MS UI (Agilent) d_i = 0.25 mm, d_f = 0.25 µm
Oven	40 °C (1.0 min), 15 °C/min to 320 °C (5 min)

Sample Preparation

Acrylate standards included poly-methyl acrylate, ethyl acrylate, isopropyl acrylate, isobutyl acrylate, n-butyl acrylate, n-hexyl acrylate, n-decyl acrylate, and lauryl acrylate. Methacrylate standards included poly-methyl methacrylate, ethyl methacrylate, isopropyl methacrylate, isobutyl methacrylate, n-butyl methacrylate, cyclohexyl methacrylate, n-hexyl methacrylate, and lauryl methacrylate. The standards were purchased from Scientific Polymer Products Inc., Ontario, NY. The standards were neat or dissolved in toluene.

Samples analyzed by pyrolysis GC-MS included a plastic photo holder, acrylic nail hardener and acrylic latex caulk.

Pyrolysis – Approximately one milligram of sample was placed into an open-ended quartz pyrolysis tube with quartz wool. The quartz tubes were connected to pyrolysis adapters and placed into a 40-position pyrolysis tray. For the standards in toluene, 2 µL of standard were applied to the quartz wool in an open-ended quartz discharge tube using a 10 µL syringe. The standards were allowed to dry at room temperature for one hour.

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Results and Discussion

For the methacrylate polymers, the main polymer degradation mechanism is monomer reversion. The methacrylate polymers used in this study follow that trend. Table 1 lists the polymers and the area percentage for the monomer. Cyclohexyl methacrylate shows the lowest monomer reversion with only 40.6% peak area for the monomer. Other major peaks in the chromatogram are cyclohexene (26.9%), cyclohexanol (7.7%) and methacrylic acid (6.4%). Figure 1 shows a pyrogram for this polymer.

Table 1: Methacrylates and monomer area percent.

Polymer	Monomer Area Percent
Methyl methacrylate	90.5
Ethyl methacrylate	88.5
Isopropyl methacrylate	75.0
n-Butyl methacrylate	78.6
Isobutyl methacrylate	92.8
Cyclohexyl methacrylate	40.6
n-Hexyl methacrylate	95.1
Lauryl methacrylate	90.2

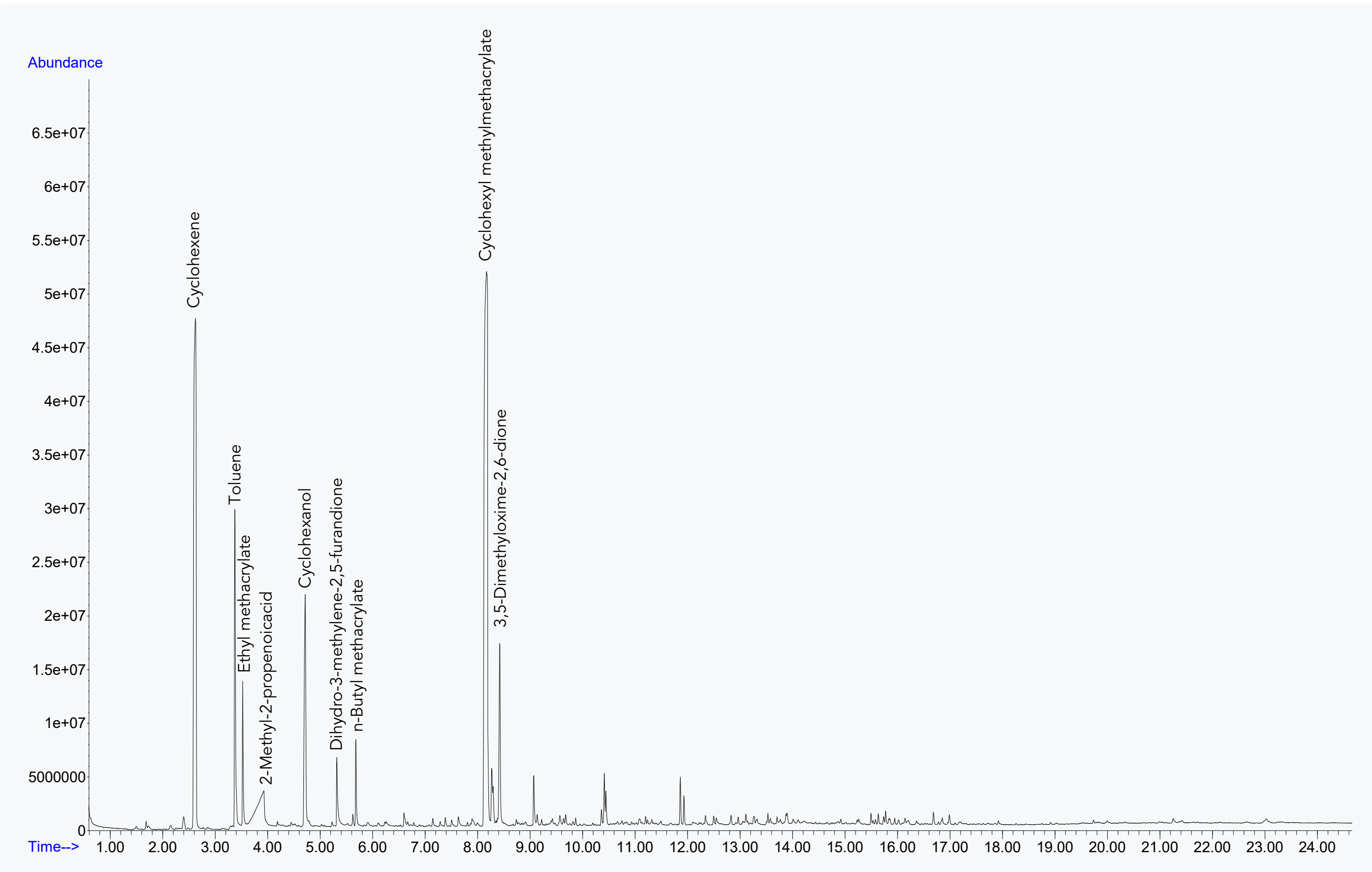

Figure 1: Pyrogram for polycyclohexyl methacrylate.

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Figure 2 shows a pyrogram for isopropyl methacrylate. The main peak is the monomer. Smaller peaks include isopropanol, methacrylic acid, ethyl methacrylate, methyl methacrylate, and a couple of C5-C6 hydrocarbons.

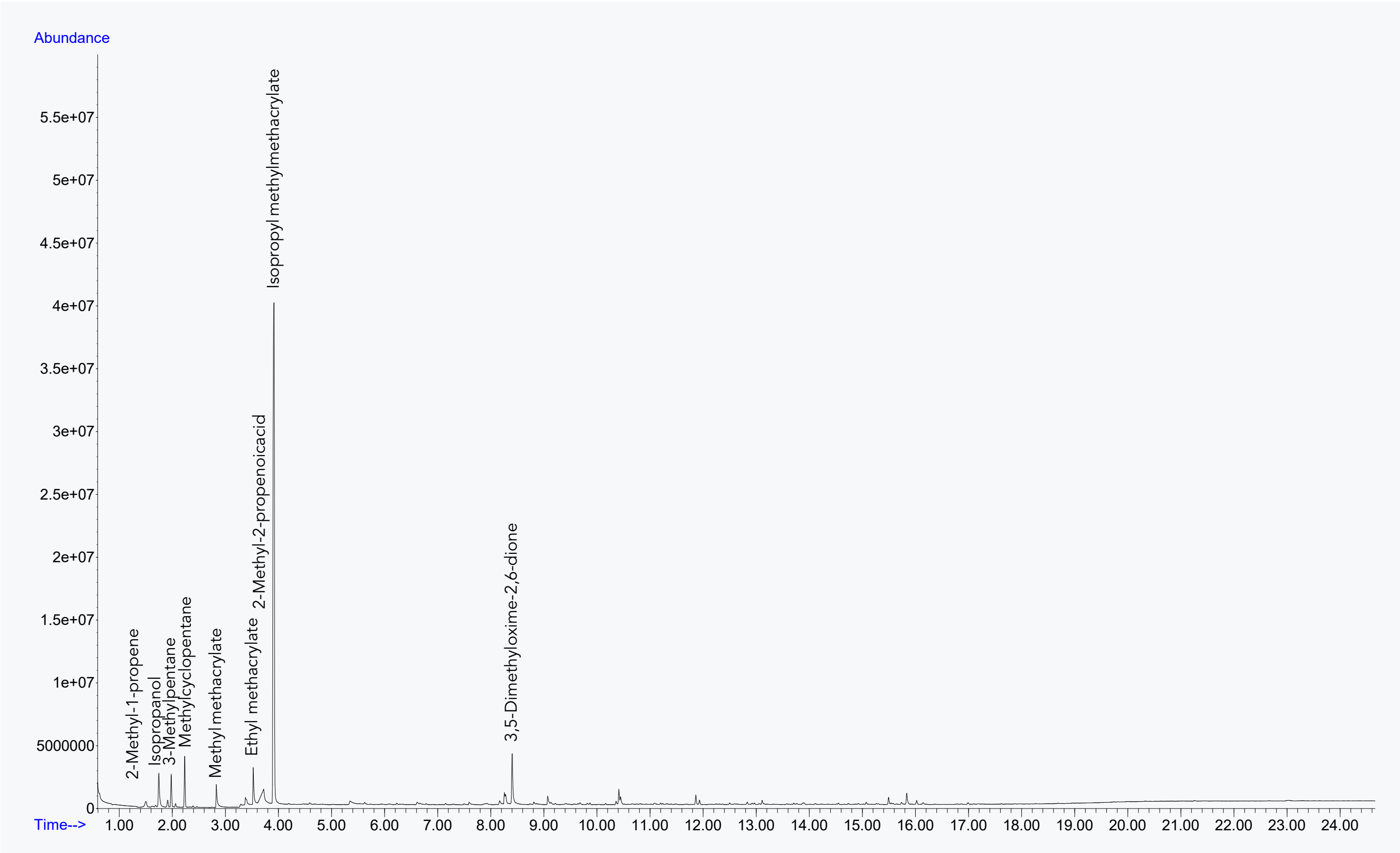

Figure 2: Pyrogram for polymethyl methacrylate.

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For the acrylate polymers, the pyrograms are more complex than those for the corresponding methacrylate polymer. Figure 3 shows the resulting pyrogram for polymethylacrylate. The monomer can be seen at retention time 2.16 minutes, but it is not the largest peak in the pyrogram. The largest peak corresponds to the trimer. A pattern of compounds from 2-7 monomer units is seen. Also identified in the chromatogram is dimethyl pentanedioate and the corresponding alcohol, methanol. A similar pattern was seen for the other acrylates analyzed in this study.

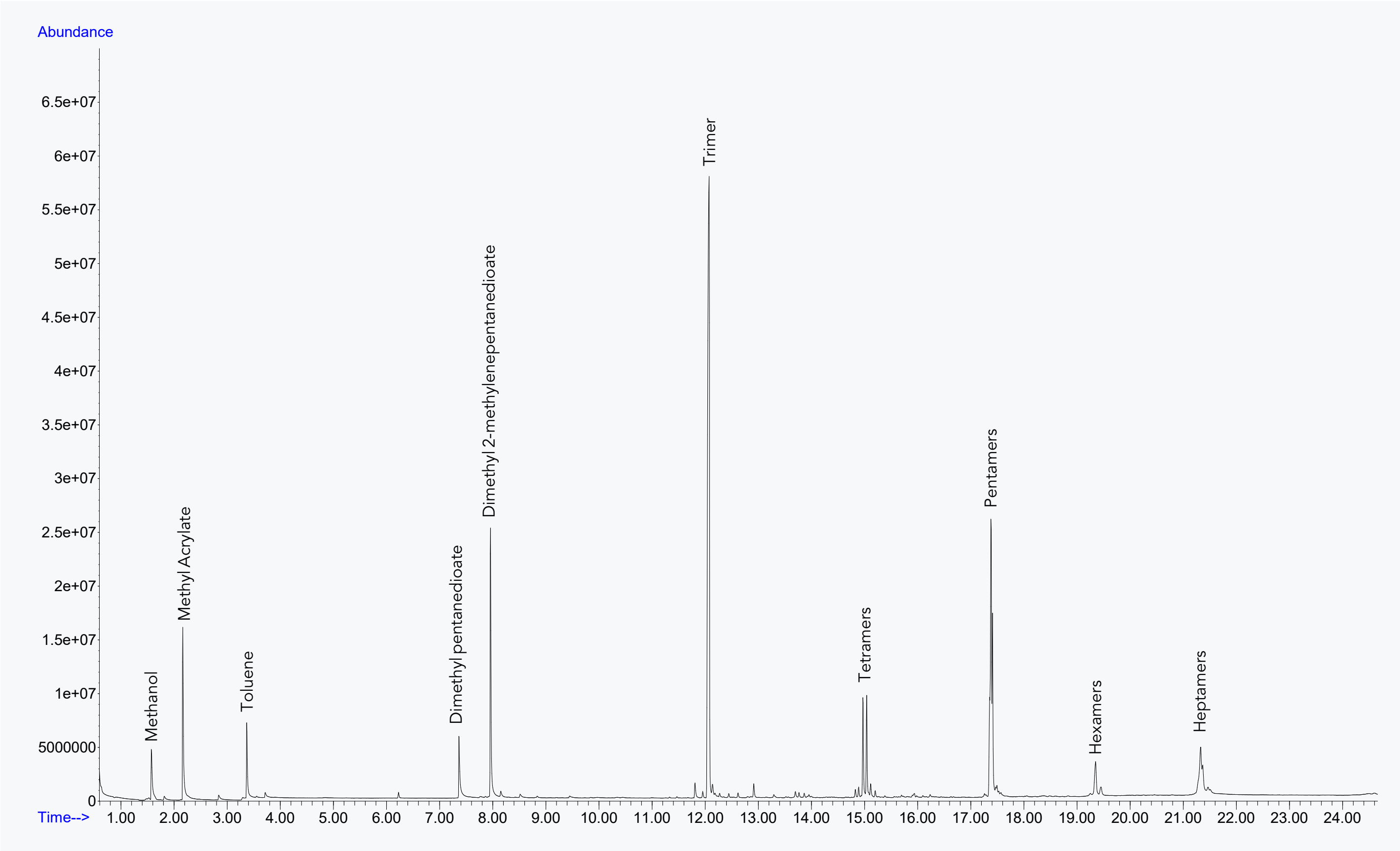

Figure 3: Pyrogram for polymethyl acrylate.

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For the longer chain alkyl acrylates, the corresponding alkene and alcohol peaks become more prominent as the alkyl chain length increases. This is seen in the pyrogram for n-hexyl acrylate in Figure 4. The peaks for 1-hexene and 1-hexanol are seen at retention times 2.02 and 4.45 minutes, respectively.

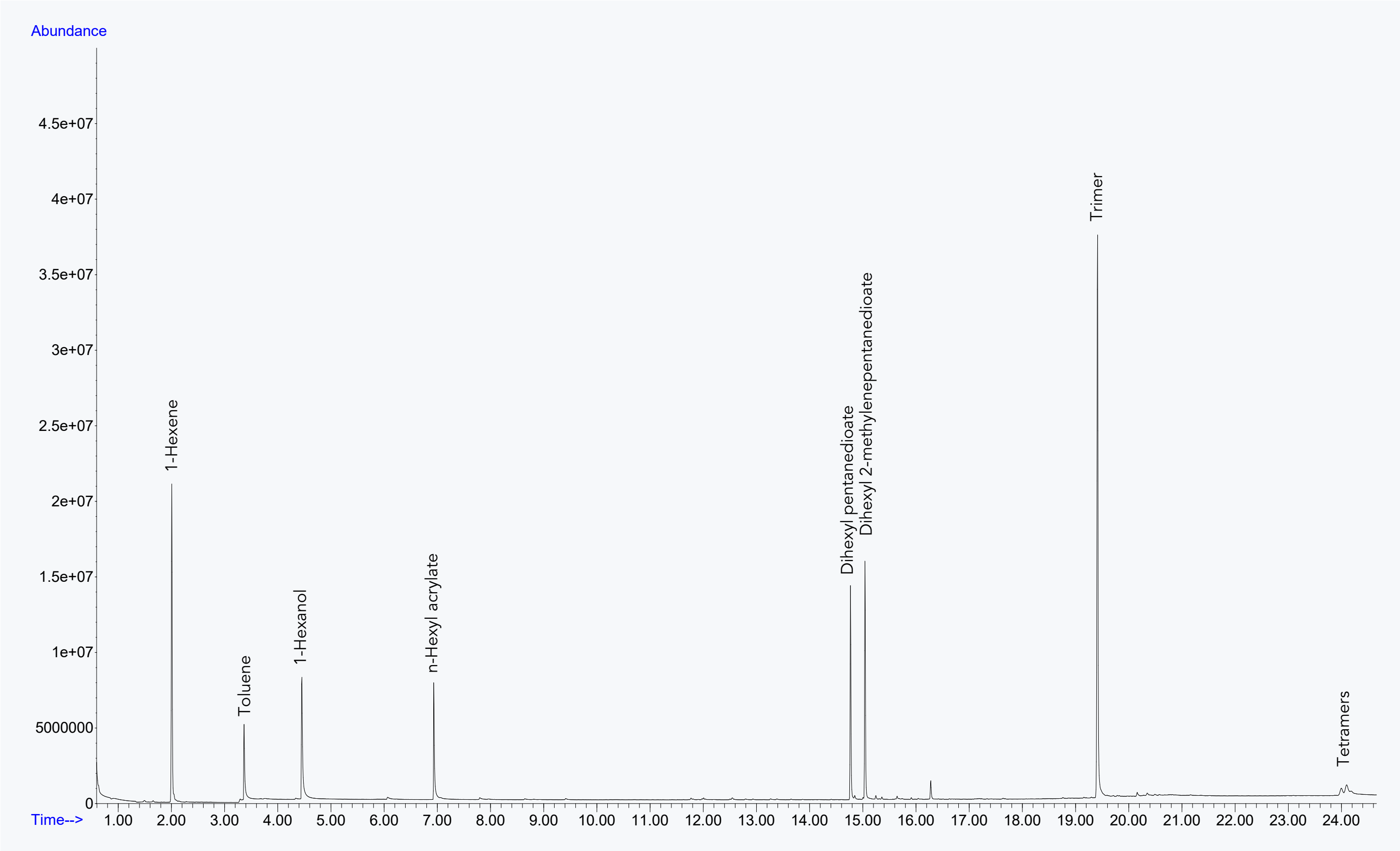

Figure 4: Pyrogram for poly-n-hexyl acrylate.

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Figure 5 shows a pyrogram for a sample from a clear plastic stand used to hold photos. The sign is made from polymethyl methacrylate (PMMA) as the major peak in the pyrogram is the monomer. A small peak for ethyl acrylate is seen along with groups of dimers and trimers of MMA.

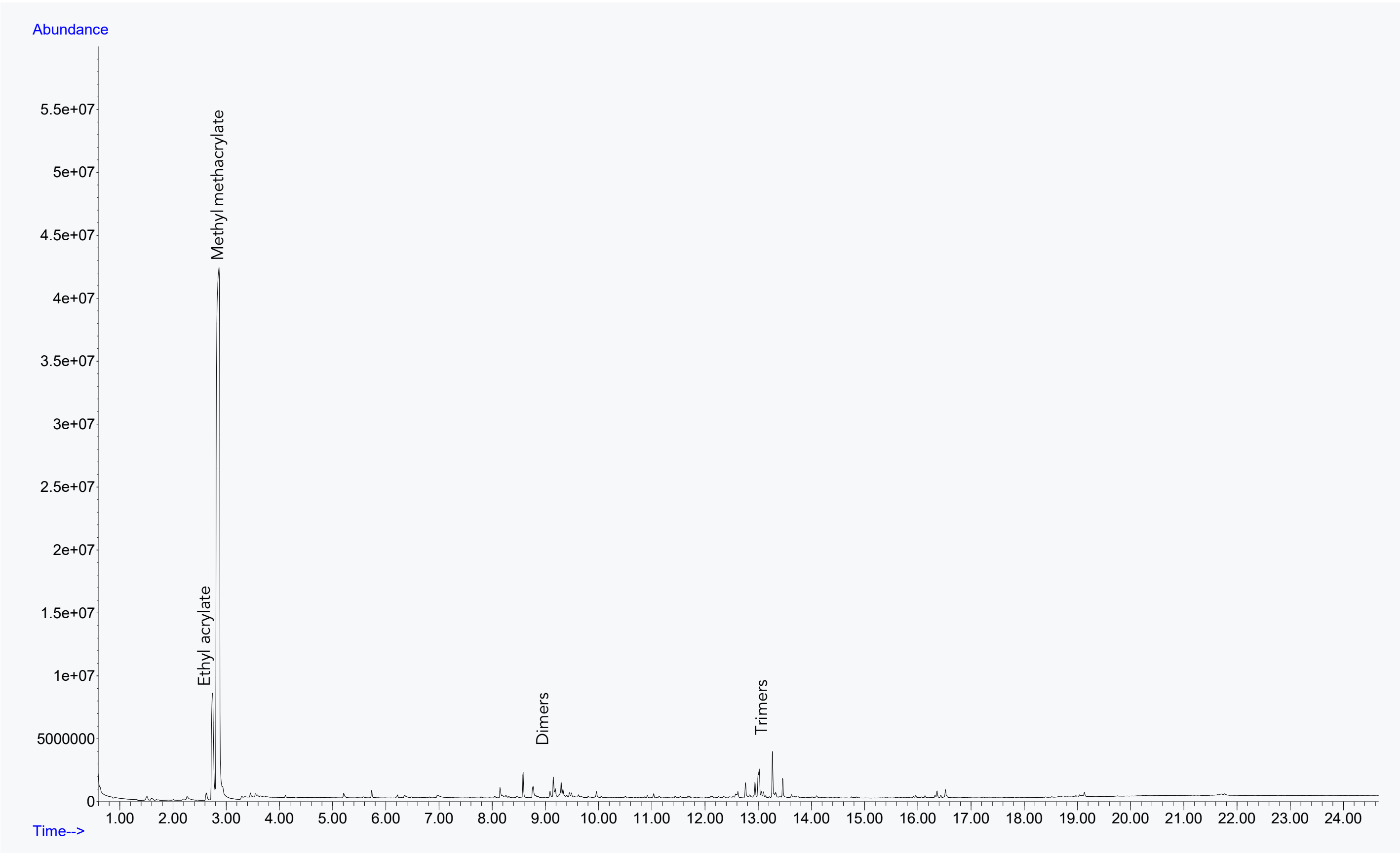

Figure 5: Pyrogram for plastic photo holder.

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Figure 6 shows a pyrogram for an acrylic nail hardener. The monomers methyl methacrylate and n-butyl methacrylate can be seen. Other compounds present in the pyrogram are butyl acetate (solvent) and tributyl aconitate and tributyl acetylcitrate, which are common plasticizers.

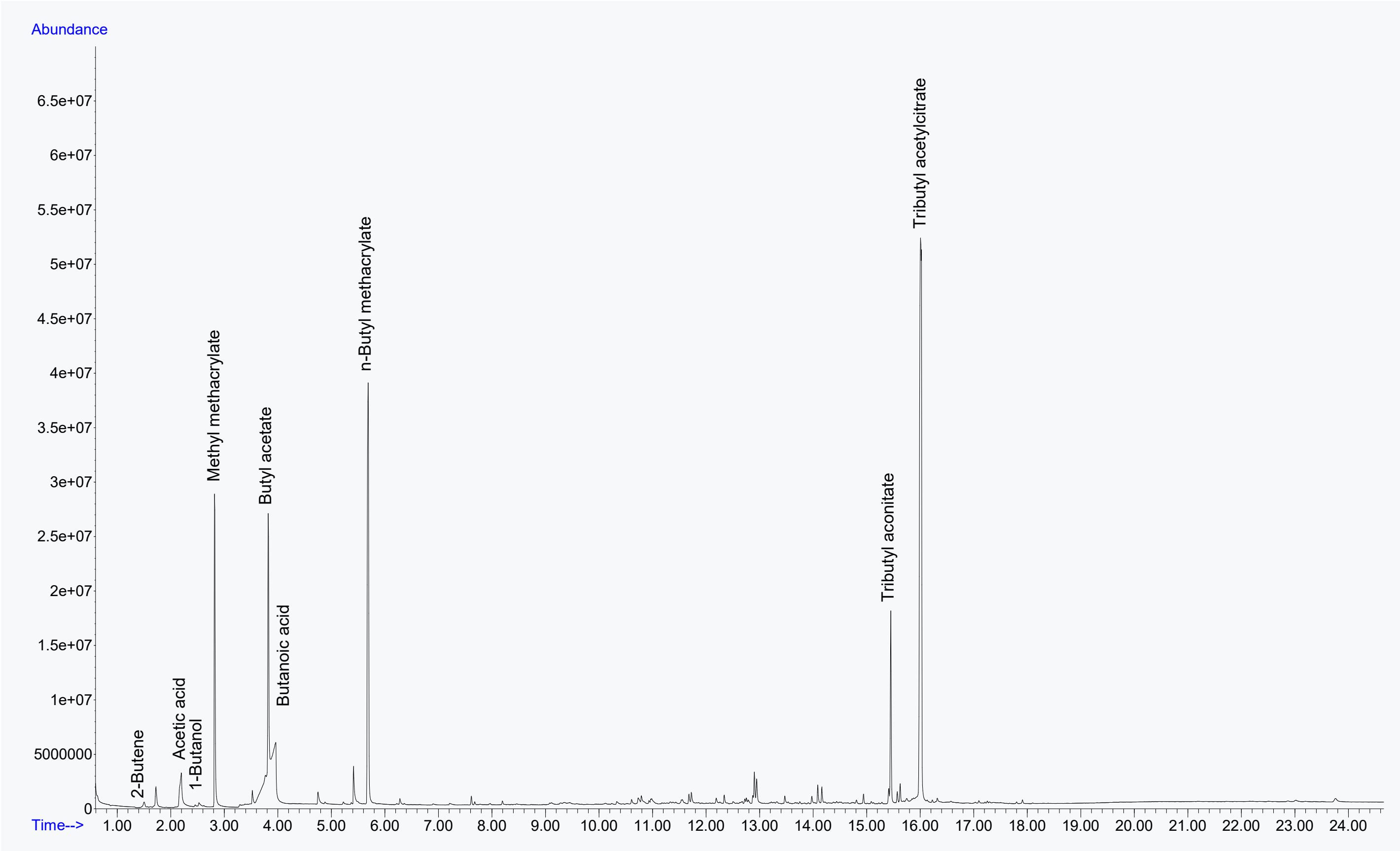

Figure 6: Pyrogram for acrylic nail hardener.

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The last example, Figure 7, shows the resulting pyrogram for an acrylic latex caulk. The sample contains a mixture or co-polymer of ethyl acrylate and 2-ethylhexyl acrylate. Both monomers are found in the pyrogram, along with peaks for the ethyl acrylate dimer, trimer, tetramer and pentamer. The retention times and spectra for these peaks were a match for those seen in the pyrogram for the standard of ethyl acrylate. The corresponding alcohol and alkene are seen for the 2-ethylhexyl acrylate. The unresolved hydrocarbon hump from retention time 14-21 minutes is most likely due to a "lubricating petroleum oil", listed in the MSDS for this product.

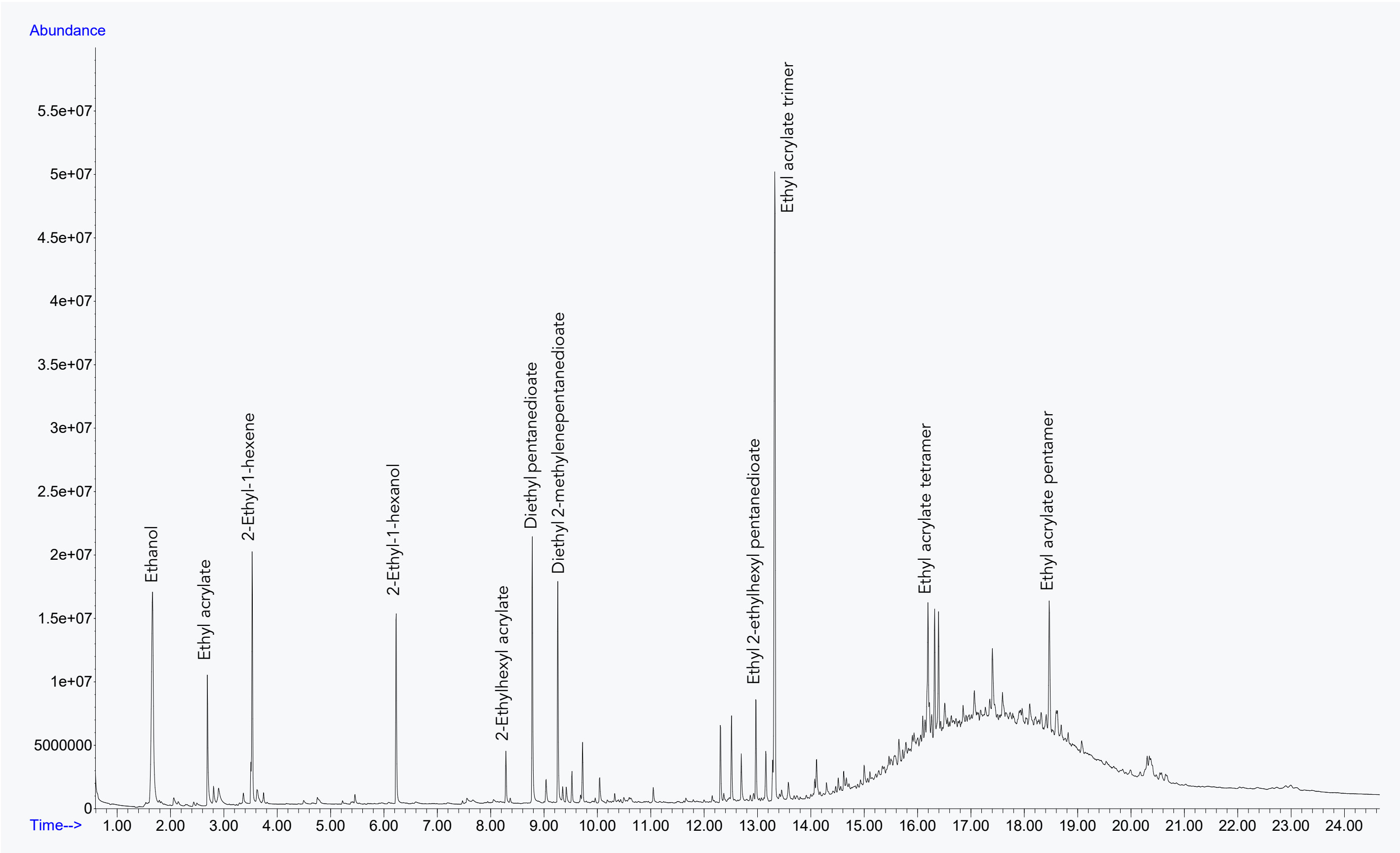

Figure 7: Pyrogram for acrylic latex caulk.

Conclusion

Pyrolysis of polymethacrylate standards showed monomer reversion as the main mode of polymer degradation. Pyrolysis of the polyacrylate standards resulted in monomer reversion accompanied by formation of dimers and higher number oligomers. As the chain length of the alkyl group increased for the polyacrylates, the formation of the corresponding alkene and alcohol increased.

Pyrolysis GC-MS was used to identify polymethacrylates and polyacrylates in several sample types.

Smart Ramped Pyrolysis combines a slow heating rate with a quick transport rate to apply a broad temperature range to a sample without overheating its components. This results in an optimized pyrogram for a sample without having to determine the optimal pulsed pyrolysis temperature. This is especially important for unknown samples or whenever the amount of sample is limited. It was applied in this study and greatly reduced method development time, while improving the accuracy of compound identification. The GERSTEL PYRO Core System enables highly flexible and efficient automated pyrolysis of solids and liquids up to 1000 °C combined with GC/MS determination of the thermal decomposition products. It provides an excellent tool for the analysis of polymers, polymer mixtures, and polymer additives.