bonds that give the detector response, and since each of the individual components contains acyl chains of varying unsaturation, quantification by UV is only approximate. The ELS detector is rapidly becoming standard for this analysis. Since this detector is tolerant of solvent gradients, other normal-phase columns, notably the DIOL column, may be used instead of bare silica. These give better reproducibility but do not have sufficient resolving power for lecithin analysis in the absence of gradient programming.

Separation by acyl chain length is accomplished by reversed-phase LC of fractions separated by the normal-phase methods. LC–MS is an obvious way to simplify the characterization of unknowns. Precise phosphatide analysis is very much an activity of specialists and the field is advancing rapidly.

Conclusions

LC is the only practical method to characterize many surfactants according to their oligomer or homologue distribution. It is also the best way to determine quantitatively many surfactants, particularly ionic surfactants.

However, in spite of improvements in instrumentation and in stationary phases, LC is not easy. It demands more time and training of the operator than most analytical techniques. Preliminary sample preparation is very often necessary for mixtures and environmental samples, making an LC analysis an expensive analysis.

Continued development in the areas of detection (especially in element-selective detectors, detectors specific for chemical functionality, and LC–MS interfaces) will make LC even more useful in the future. For example, the ELS detector, even though suffering from problems in linearity in its present incarnation, has already greatly expanded the utility of LC for analysis of lecithin and ethoxylates.

See also: **II / Chromatography: Liquid:** Mechanisms: Ion Chromatography; Ion Pair Liquid Chromatography; Mechanisms: Reversed Phases. **Extraction:** Solid-Phase Extraction.

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SYNTHETIC POLYMERS

Gas Chromatography

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Introduction

Successful gas chromatography (GC) requires that the sample be volatile at the operating temperature. The majority of synthetic polymers are of substantial molecular weight, i.e. in excess of 20 kDa, and not amenable to direct chromatographic examination.

Figure 1 shows the molecular weight limitations of compounds suitable for gas and liquid chromatography. Monomers with molecular weights in the range 50–100 Da are particularly suitable for direct GC.

Performance-enhancing or compounding additives in polymers are also usually amenable to direct examination. The major difficulty with these materials is separation or extraction from the polymer matrix, which generally accounts for over 90% of the product. Plasticizers form a major part of many polymer compounds and monomeric plasticizers may frequently be examined directly or after extraction. Polymeric plasticizers, and polymeric additives after separation, require examination by pyrolysis or by spectrometric tools. The finely divided polymer is subjected to thermal desorption or extraction or digestion with solvents. Extraction with supercritical fluids is finding greater use and has the advantage that the removal of extraction solvent is simplified.

To increase the volatility of polymers, a reduction in molecular weight must be achieved. This is most commonly carried out by pyrolysis or thermal degradation in the absence of oxygen, or to a lesser extent by chemical degradation, which is applicable to most condensation polymers. Both techniques are indirect methods of analysis where the polymer is characterized by analysis of the volatile products of the degradation. A recently developed technique, known as pyrolytic methylation, effectively combines both methods and is applicable to condensation polymers. To date this new technique has found its major application in forensic science.

Pyrolysis

Pyrolysis techniques possess several advantages. The sample preparation is negligible, while the time for analysis is relatively short in comparison with that needed for other instrumental techniques. In addition the sample required for pyrolysis is small.

Pyrolysis was originally carried out separate from the GC instrument, but *in situ* pyrolysis in a device directly attached to the GC was soon universally employed. The pyrolysers available are of two basic types:

(1) Furnace type. The polymer sample is introduced into a heated microfurnace attached to the injection port of the chromatograph and the volatile pyrolysis products are rapidly swept into the column by the carrier gas.
(2) Pulse mode type. The polymer is attached to the pyrolysis element, which is rapidly heated to a predetermined temperature. The volatile pyrolysis products are rapidly swept into the chromatograph as before. The pyrolysis element may be either a filament or ribbon device that is resistively heated or a Curie point device. With Curie point heating the polymer is deposited on a wire of ferromagnetic material. The wire is rapidly heated to its Curie point using induction. A range of wires with Curie points from 358°C for a nickel wire to 980°C for a wire consisting of 50 : 50 iron and cobalt are available. Ribbon and filament pyrolysers normally use materials of high resistance that are inert in nature, such as platinum or other noble metals; this reduces the possibility of reactions occurring with the degraded sample.

Both types of pyrolysers are used, each type having both advantages and disadvantages, but the two pulse mode instruments are most widely utilized.

The first application of pyrolysis and gas chromatography was in 1954, when vinyl polymers

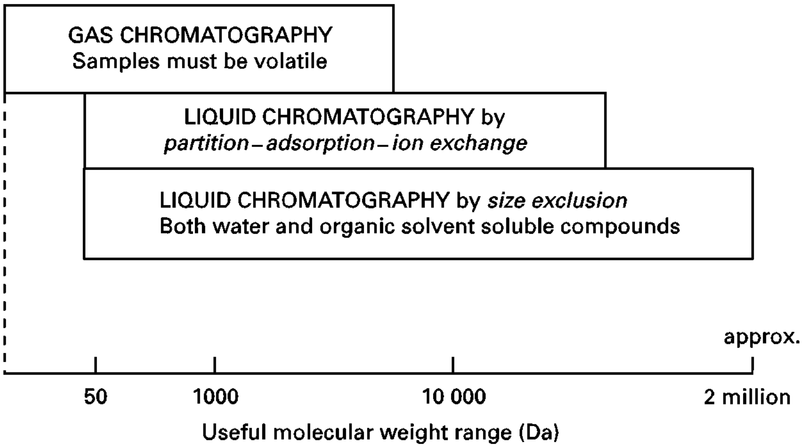

Figure 1 Approximate useful ranges of common chromatographic procedures. (Reproduced from Haken JK (1990) *Trends in Analytical Chemistry* 8:14 with permission of Elsevier Science Publishers.)

and copolymers were heated at 650°C in a stream of nitrogen. The volatile products were condensed and subjected to gas chromatography. *In situ* pyrolysis quickly followed with the use of a filament device, which was little different to that which has subsequently found extensive usage with almost every conceivable type of polymer.

Early workers used large samples, which resulted in poor heat transfer, the occurrence of combination reactions of the volatile fragments and the production of nonreproducible results. Bibliographies of papers and compilations of pyrolysis results, both as pyrograms and bar charts, date from the 1960s, but the early literature is of limited value as the reproducibility is often poor, and the techniques used do not always represent current practice. Libraries of pyrograms have appeared in texts, but the experimental conditions are frequently omitted and it is difficult to reproduce the results.

It has long been recognized that small samples, typically much less than 1 mg, good heat transfer, rapid heating of the pyrolysis element and rapid removal of the degradation products from the heated zone are essential in achieving reproducible results.

Packed chromatographic columns were widely used in the early work, but capillary columns that offer enhanced separation are now almost universally employed. The detection limits of the flame ionization detector, the mass spectrometer and the Fourier transform infrared detectors in current use are orders of magnitude better than that required by the smallest possible pyrolysis sample. In the 1980s a sample of 800 ng of acrylic polymer would produce a mass spectrum of about 30 compounds when pyrolysed. More recently samples of 1 μg have been used for forensic casework, while sample sizes of 2 μg have been generally used, the major difficulty being in handling and weighing these small samples. With such quantities a chromatogram containing dozens of peaks can be obtained and a mass spectrometer attached to the GC will provide a mass spectrum of each peak. The spectra may be interpreted offline or in many cases may be identified by simultaneous online matching with an inbuilt computer containing a library of spectra, which shows the degree of probability of the match.

Pyrolysis Temperature and Heating Time

The temperatures used for pyrolysis are variable and depend to some extent on the nature of the polymer. Polymers of high thermal stability or which are highly crosslinked obviously require a higher temperature than a simple thermoplastic. The bond strengths of the constituent atoms and the association of atoms influence both the ease and type of degradation that occurs, as rupture of the weakest bonds will predominate. The formation of stable free radicals generally occurs. Little pyrolysis of polymers occurs with the lowest available Curie point wire, i.e. 358°C and temperatures of 500–600°C might be considered as lower limits. The optimum temperature is considered to be near 800°C. An excessively high pyrolysis temperature is to be avoided, as with increasing temperature fragmentation of the pyrolysis products occurs, with an increased amount of very low molecular weight gaseous products being formed. These products are not helpful in achieving identification as they are typical of organic compounds generally rather than of a particular polymer.

The heating time, while variable, is short and may range from seconds to a fraction of a second. With Curie point pyrolysis the heating period is usually less than with filament or ribbon types. In either case the time to achieve the final temperature must be short. Pyrolysis under the conditions selected must be essentially complete, a situation that is readily checked by reheating the element after pyrolysis and determining if further pyrolysis products are separated. The flow rate of the carrier gas that passes through the pyrolyser should be such that the pyrolysis products are readily swept from the heated pyrolysis zone into the column, minimizing the recombination of reaction products. Such secondary products may be more characteristic of the apparatus than of the polymer. The unreactive carrier gases normally used can be conveniently employed. Gases that react with the reaction products are used in special circumstances, the most common being oxygen for use in oxidation studies or hydrogen with a suitable catalyst for hydrogenation.

An advantage of the resistively heated pyrolyser is that stepwise pyrolysis, where the same sample is pyrolysed at increasing temperatures, may be carried out. This technique has been used with low temperatures to remove the majority of additives and monomeric plasticizers, and also with higher temperatures to study the ease of polymer degradation. A disadvantage of resistively heated pyrolysers is that the resistance of the heating element may vary over time owing to corrosion and thinning of the wire. With a variation in the resistance of the wire, the nominal temperature is not achieved when the same current is applied and the pyrolysis results are variable.

Enclosed Curie point pyrolysis (ECP) has been described where the sample is deposited on the Curie point element and sealed in a capillary tube, with pyrolysis taking place in the tube. The tube is subsequently broken in the carrier gas flow. The method has been used for the study of the oxidation of polyisobutylene. A comparison with conventional resistive pyrolysis and ECP shows that a method for distinguishing gas phase versus melt phase secondary reaction is possible.

Polymer Degradation

Degradation may occur by a variety of mechanisms, or combination of these. The common mechanisms are described below.

Most addition polymers incorporate a carbon–carbon backbone. With a polyolefin such as polyethylene, the bonds are equivalent and the rupture is random. The strength of the C–C bond is approximately 349 kJ mol^{-1} (83 kcal mol^{-1}) and that of the C–H bond is approximately 393 kJ mol^{-1} (94 kcal mol^{-1}), so that rupture of the former bond occurs. In these circumstances a large number of fragments result and the mechanism is termed random scission. The hydrocarbons with terminal free radical ends require to be stabilized. The fragment with a free radical end may extract a hydrogen atom from an adjacent fragment and become a saturated end. In extraction a free radical is created on the adjacent fragment. This fragment commonly stabilizes by β-scission, where the induced free radical site becomes an unsaturated molecule end. This process continues and produces a sequence of three hydrocarbons, the first saturated, the next with a double bond at one end, and the third with a double bond at both ends, a series of *n*-alkanes, α-olefins and α,ω-diolefins being formed from methane to hydrocarbons of near 40 carbon atoms.

Where the carbon atoms are not equivalent, such as in polyvinyl chloride where the bond strength of the C–Cl bond is 305 kJ mol^{-1} (73 kcal mol^{-1}), random scission does not occur – rather aromatic compounds are formed. Hydrogen chloride is eliminated and the free radicals on the adjacent sites form a sequence of double bonds to make an unsaturated backbone. This then fragments to form a series of aromatic compounds.

A third mechanism that occurs with a few polymers containing α-methyl substitution, i.e. polymethyl methacrylate and polymethyl methacrylamide, is unzipping or reformation of monomer. Here fragmentation of the C–C backbone occurs with the free radical fragments formed undergoing β-scission with the elimination of a molecule of monomer and formation of a new free radical fragment. Repeated β-scission leads to the formation of more monomer, which is frequently in excess of 95% of the original monomer concentration. The yields of monomer vary greatly with the polymer. The lower polyalkyl methacrylates yield essentially all monomer, but as the substituent alkyl chain becomes larger the monomer yield decreases. With polylauryl methacrylate the monomer yield is approximately 70%, as some degradation of the alkyl chain occurs.

Polystyrene degrades by a combination of mechanisms, and the monomer yield is approximately 40%. Unzipping reactions are of little importance in the degradation of polyacrylates, where the monomer yield is in the order of 5%.

Microstructure

Pyrolysis GC of polymers allows determination of the microstructure in addition to the chemical composition. The polymer of simplest chemical composition, polyethylene, is prepared by polymerization under different conditions and with a variety of catalysts to produce products with greatly differing physical properties, dependent on the microstructure. Short- and long-chain branching occurs, as does stereoregularity.

First to be analysed were polymers produced by high pressure processes. These contain a significantly branched structure with both short-chain branching (C1–C6) and long-chain branching, as illustrated in **Figure 2A**. The introduction of low pressure processes using metal alkyl catalysts has allowed the production of products with structures as shown in Figure 2B and 2C.

The low density polymer produced by high pressure processes undergoes random scission and produces a strong sequence of triplet peaks corresponding to α,ω-diolefins, α-olefins and *n*-alkanes of each carbon number, with weak multiple peaks of isoalkanes, isoalkenes and isoalkadienes between the triplets.

A technique that has been used in polyolefin pyrolysis for decades is *in situ* simultaneous hydrogenation of the pyrolysis products, hydrogen being used as the carrier gas with a pre-column containing

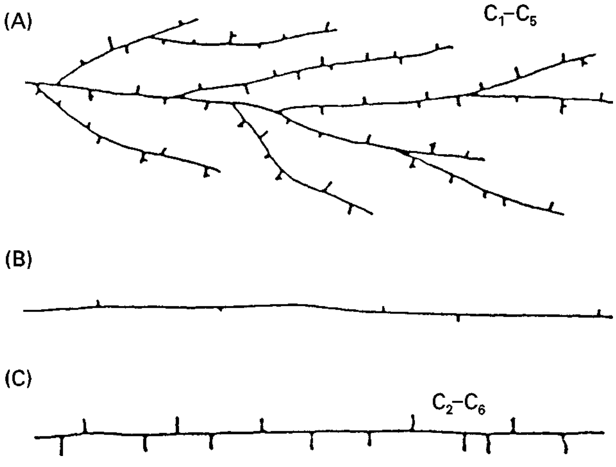

Figure 2 Structures of various polyethylenes. (A) Low density polyethylene (LDPE); (B) high density polyethylene (HDPE);(c) linear low density polyethylene (LLDPE). (Reproduced from Wampler TP (1995) *Applied Pyrolysis Handbook*, p. 81 with permission of Marcel Dekker.)

a hydrogenation catalyst inserted between the pyrolyser and the injection port. With this technique the triplets become single peaks of the *n*-alkane and the intermediate peaks are reduced in number and increased in intensity, with iso compounds of comparable structure forming single isoalkane peaks.

While ethylene is symmetric, propylene and other olefins are not, and the possibility of head to tail, head to head and tail to tail combinations exists; such differences are evident in pyrograms. With copolymers of polyethylene and polypropylene, pyrograms containing peaks associated with each monomer are observed; however, with different catalysts the intensity of the individual peaks vary. This is used as a measure of the sequence distribution of monomer units along the chain. Sequence distribution determination is not restricted to polyolefins, but has also been reported with many other important polymer systems.

The tacticity of various polymers, including polystrene, has been determined by pyrolysis gas chromatography. With polystyrene, fragments characteristic of the polystyrene chain, ranging from monomer to pentamer, were observed in the pyrogram. The relative intensities of the tetramer and pentamer peaks reflect the original tacticity.

Minor and subtle differences in the end groups of a particular polymer system frequently cause significant alterations of the properties of the polymer, particularly concerning thermal stability and transparency. It is well known in gas chromatography that the polysiloxane materials frequently used as stationary phases possess high thermal stability when appropriate end termination is employed. Details of end termination are also of value in determining polymerization mechanisms. The identification and determination of end groups is difficult owing to their low concentration. Pyrolysis-GC has been used to characterize many polymer systems. Examples are polymethyl methacrylate radically polymerized in toluene solution with benzoyl peroxide initiation under varying conditions. The peak intensities of some products characteristic of the end groups present have been interpreted in terms of polymerization temperature and solvent/monomer in the feed.

Methacrylate end groups in polystyrene samples have been determined by reaction with tetramethylammonium hydroxide where methyl methacrylate was split out and determined. The initiator used was *s*- or *n*-butyl lithium and on pyrolysis the main product was styrene monomer together with a considerable amount of dimers and trimers. Various minor fragments clearly showed the presence of *n*-butyl end groups. Similar analyses of end groups in other polymers have been reported, including end groups in polycarbonates.

Chemical Degradation

Alkyd resin constituents have been determined for decades, the method used being chemical cleavage followed by estimation by gravimetry, colorimetric or spectrophotometric means. The analysis of alkyd resins was revolutionized in the 1960s by US Government workers who determined the reaction products by GC.

The Zeisel reaction has also been extended by the use of GC; traditionally all alkoxy groups were estimated as methoxy groups. With GC, the alkoxy groups are converted to the corresponding alkyl halides by reaction with hydriodic acid in phenol prior to chromatographic separation of the individual halides.

Gas chromatography was early applied to the estimation of the hydrolysis products of polyurethanes, polyethers, polysiloxanes and polyamides.

In situ Chemical Degradation

The degradative analysis of many polymers with *in situ* GC was developed by scientists working on determination of the volatile degradation products in the 1970s. They conducted vigorous hydrolytic cleavage in a reactor constructed from a furnace pyrolyser attached to the injection port of a gas chromatograph. A 30 mol% excess of a prefused mixture of potassium hydroxide (85% KOH approximating to the hemihydrate) and 1–10% sodium acetate as flux was heated for 0.5–1.0 h at temperatures within the range 200–350°C. Volatile reaction products were examined by GC while the reaction products that formed alkanoate soaps remained in the reactor.

All the alkali metal hydroxides have been used for alkali fusion, although potassium hydroxide is preferred as its melting point is suitable and organic compounds have greater solubility in a potassium hydroxide melt than in a sodium hydroxide melt. **Table 1** shows the melting points of the common alkali metal hydroxides in both the anhydrous and hydrated forms.

Most acids, both organic and inorganic, have been used to effect hydrolysis and to achieve cleavage of ethers. They include phosphoric, hydrochloric, sulfuric, hydrobromic, hydroiodic and *p*-toluenesulfonic acids. Mixed anhydrides of *p*-toluenesulfonic and acetic acid or trifluoroacetic anhydride or trifluoroacetic acids have also been used. Some of the acids, particularly sulfuric acid and hydrochloric acid, produce by-products, while phosphoric and hydrobromic acids have often been used successfully. The ether groups in alkylene oxide polymers have been cleaved using a mixed anhydride of *p*-toluenesulfonic acid and acetic anhydride. The reaction is usually conducted by heating in a microflask with an appropriate condenser. The polymer may be converted to compounds suitable for GC or the reaction products may be worked up as derivatives.

External Chemical Degradation

The work described above has been extended, by employing external fusion, to allow all of the reaction products to be identified as volatile products or as derivatives amenable to GC. Hydrolytic reactions using alkaline or acidic catalysts are achieved, as is acidic cleavage of ether groups. In several cases polymers have been examined using simultaneous hydrolysis and alkylation.

The advantages of external fusion are listed below:

1. Fusion is more rapid, efficient and more readily controlled than *in situ* degradation as the water necessary for the reaction remains in the reaction environment rather than tending to be swept into the cold trap.
2. Multiple fusions can be carried out in an external heater without restricting the use of a gas chromatograph, or, more importantly, restricting examination to GC alone.
3. Materials that would ordinarily be retained in the reactor as soaps or other material of low volatility can be examined after appropriate chemical reaction and/or derivatization.
4. Hydrolytic degradation and cleavage of ether groups can be conducted simultaneously or separately.
5. Other analytical techniques can be used as appropriate.
6. All of the components of a polymer can be analysed rather than simply those sufficiently volatile for direct GC.

The quantitative nature of both acid and alkaline fusion reactions has been reported and a number of polymers have been studied with acceptable results.

Table 1 Melting points of alkali metal hydroxides

Alkali metal hydroxide	*Melting point*	
	Anhydrous	*Hydrate*
Potassium hydroxide	360	125[a]
Sodium hydroxide	318	64.3[b]
Lithium hydroxide	417	–[b,c]

[a] Commercial potassium hydroxide contains 15% water and is present as the hemihydrate.

[b] Present as the monohydrate.

[c] Decomposes to form lithium hydroxide and water.

Nitrogenous polymers Nitrogenous polymers have been widely studied. These include: polyamides such as the simple nylon materials; the condensation products of dicarboxylic acids and diamines and the condensation products of α,ω-aminoalkanoic acids; the dimer polyamids (using the C_{36} dimer dicarboxylic acids prepared from vegetable oils); the aramid fibres (using an aromatic diamine and a dicarboxylic aromatic acid); and the polyhydrazides produced using hydrazine. Polyimides produced by the polymerization of benzene tetracarboxylic acids and aromatic diamines and copolymers of amides and imides have also been analysed using alkali fusion.

Polyesters External chemical degradation has been used to analyse polyesters, both containing oils and oil-free, as well as silicone alkyds and crosslinked systems of polyesters with various aminoplasts. In a crosslinked system the aminoplast butylated ureaformaldehyde is itself cleaved, while with other aminoplasts only the butylated groups are removed.

Simple fibreglass-reinforced plastic (FRP) and vinyl ester laminates are cleaved by this method. With the laminates and silicone polyesters, the siliceous fibreglass (normally E-glass, a very low alkali borosilicate glass containing approximately 50% silica and 10% boron trioxide) or organic silicone is converted into an organic derivative amenable to GC examination. A chromatogram showing the trimethylsilyl (TMS) derivatives of the polyols, dicarboxylic acids and organic siloxane moiety produced from a silicone polyester is shown in **Figure 3**. Other reinforcement materials that are used in aerospace and other specialized applications include polyester or polyamide (Nomex^{TM}) reinforcements, both of which are amenable to hydrolytic cleavage.

Polyurethanes Polyurethanes are conventionally the reaction products of an isocyanate with an ether or ester and terminated with hydroxyl groups. While these materials are relatively resistant to hydrolysis, they can be readily cleaved by vigorous hydrolytic reactions. The polyurethane ether materials are more resistant to simple solution hydrolysis than are the polyurethane esters. Many polyurethane compounds have been studied using both alkaline and acidic hydrolysis. The simple condensation products – chain-extended materials produced using a short-chain polyol or an amine; polyether polyurethanes used in medicine; transparent polyurethanes that use polycaprolactone diols; isocyanate-based copolyamide resins; and a urethane crosslinking agent used in reversion-sensitive natural rubber – have all been examined using vigorous hydrolysis reactions. Determination of the tertiary amino groups allows the

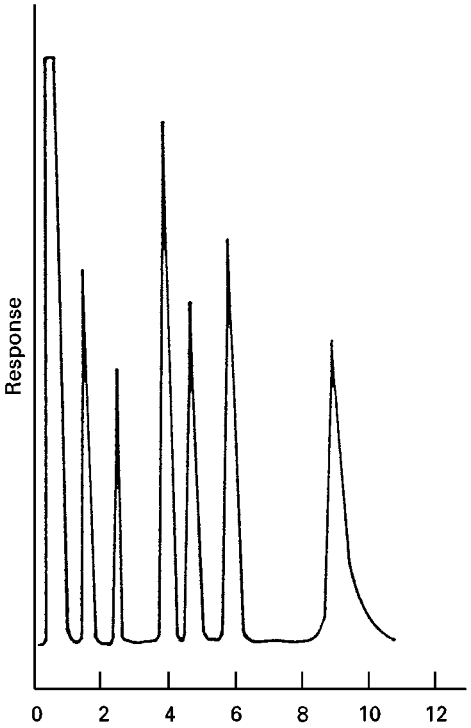

Figure 3 Gas chromatogram showing simultaneous separation polyols, dicarboxylic acids and silicate TMS derivatives of: 1, solvent peak; 2, neopentyl glycol; 3, silicate; 4, trimethylol ethane; 5, trimethylol propane; 6, adipic acid; 7, isophthalic acid. (Reproduced from Haken JK *et al.* (1985) *Journal of Chromatography* 441: 207–212 with permission of Elsevier Science Publishers.)

number of secondary amino groups in polyurethanes to be determined, and an estimate of the degree of crosslinking to be made.

Epoxy resins Only simple epoxy systems, either as the ether or crosslinked with amine compounds, can be cleaved by fusion. The majority of epoxy systems are complex networks that are sterically hindered and resistant to cleavage.

Polysulfones The aliphatic polysulfones are readily cleaved by vigorous hydrolysis. However, the aromatic polysulfones that find application as high temperature polymers, either alone or frequently as copolymers with polyethers, are resistant to hydrolytic cleavage.

Liquid crystal polyesters Liquid crystal polyesters based on *p*-hydroxybenzoic acid, *p*,*p*-biphenol, terephthalic acid and 2-hydroxy-6-naphthoic acid, which are also used as high temperature polymers, are readily cleaved by vigorous hydrolysis.

Summary

Systems that have been successfully subjected to chemical cleavage include polyacrylates, polyamides, polyimides, polyurethanes, polysiloxanes, polyurethanes, polyesters (containing vegetable oil and vegetable oil-free), liquid crystal polyesters, polyhydrazides and silicone polyesters. **Table 2** shows polymers and additives that have been examined using both *in situ* and external pyrolysis. Copolymers that include more than one functional class have been examined; these include polycarbonate–polydimethylsiloxane block copolymers and isocyanate-based copolyamides.

With a completely unknown sample alkali fusion is recommended, followed if necessary by acid reaction. This ensures that some reactants, such as polyethers, are not cleaved into such small fragments that their initial composition is not apparent. For some purposes acid reaction is more rapid. For routine purposes some of the extraction steps, which simply serve to separate functional classes, may be eliminated. The reduction or elimination of extraction steps increases the quantitative nature of the analyses. It has been shown that the cleavage reactions are essentially quantitative and that errors are introduced by the extraction steps.

Pyrolytic Methylation

The term pyrolytic methylation was first used in 1979 to describe the coinjection of tetramethylammonium hydroxide with free carboxylic acids and phenols into the injection port of a gas chromatograph, resulting in the formation of methyl derivatives. The application to polymers did not occur until a decade later. Simultaneous pyrolysis and alkylation was conducted by the use of tetramethylammonium hydroxide or tetrabutylammonium hydroxide mixed with the polymer in a pyrolyser. Typically a 5 μg sample of polymer and 2 μL of the derivatizing reagent is subjected to Curie point pyrolysis at 770°C. Separation is by capillary GC with confirmation using mass spectrometric detection.

The reaction mechanism has been discussed and the evidence suggests that reactions occur by the following mechanism. When intimately mixed with tetramethylammonium hydroxide and heated to temperatures above 400°C, the polymer undergoes hydrolysis with the strongly basic agent forming salts of the hydrolysed products. These then undergo thermal fragmentation to the methyl derivatives. The term SPM, or simultaneous pyrolysis methylation, has been acknowledged to be something of a misnomer and the process has been renamed ‘thermally assisted hydrolysis and methylation’, with the abbreviation THM.

Applications

Alkyd and polyester resins The use of THM has largely been directed towards polymers that find

Table 2 Polymers and additives examined using *in situ* and external pyrolysis

Material	*Product/s of reaction*	*Unidentified products*
In situ pyrolysis		
Nylons	Diamine	Alkali metal soap of acid
Phthalate esters	Corresponding alcohol	Alkali metal soap of acid
Polyacrylamide	Ammonia	[a]
Polyacrylonitrile	Ammonia	[a]
Polyamides	Diamine	Alkali metal soap of acid
Poly(amides-imides)	Diamine	Alkali metal soap of acid
Polycarboranesiloxanes	Amine and diamine	Nil
Polychloroacrylate esters	Corresponding alcohol	Alkali metal soap of acid
Polyimides	Diamine	Alkali metal soap of acid
Polymethacrylate esters	Corresponding alcohol	Alkali metal soap of acid
Polysiloxanes	Aliphatic or aromatic hydrocarbon	[a]
Polyurethanes	Diamine	Alkali metal soap of acid
External pyrolysis		
Alkyd resins	Acids and polyols as derivatives	Nil
Alkyd resins, crosslinked	Acids and polyols as derivatives	[b]
Butylated urea formaldehyde	Carbon dioxide and *n*-butyl trifluoroacetate	Nil
Epoxy resins	Diamines and acetate derivatives	[b]
Nylons	Diamines and diacids as derivatives	Nil
Phthalate esters	Alcohols and acids as derivatives	Nil
Polyacronitrile	Ammonia	[a]
Polyacrylamide	Ammonia	[a]
Polyamides	Diamine and acids as derivatives	Nil
Polyhydrazides	Hydrazine and diacids	Nil
Polyamides	Diamines and acids as derivatives	Nil
Polysiloxanes	Hydrocarbons and silica derivatives	Nil
Polyurethanes	Diamines and ester or ether derivatives	Nil
Silicone polyesters	Silicone, acid and diol derivatives	Nil

[a] Reaction with pendant groups.
[b] Limited application.

application in surface coatings. Pyrolysis and methylation of alkyd resins gives methyl esters of the constituent acids and methyl ethers of the polyols. A soyabean oil-pentaerythritol-orthophthalic alkyd resin produced C_8–C_{16} methyl alkylanoates from the vegetable oil; tri- and tetramethyl ethers of pentaerythritol, dimethyl orthophthalate and methyl benzoate from the benzoic acid used as the chain regulator; and cyclopentanone from scission of C–O bonds of adipic acid, dimethyl isophthalate and methyl benzoate.

The fibre polyester, polyethylene terephthalate, gave benzene, a degradation product obtained on pyrolysis, dimethyl terephthalate and methyl benzoate as a combination product. It was evident in the analysis that no product attributable to the ethylene portion of the polymer was reported. This result is different from that obtained by hydrolytic degradation and chromatography, where a component peak attributable to the ethylene or butylene chains was identified.

The partial structure of alkyd resins may be elucidated; in addition to identification of the carboxylic acids and polyhydric alcohols as the appropriate esters and ethers, the drying oil type, degree of cure, the oil length and modification with rosin and epoxy resins may be determined. The most common polyhydric alcohols used in alkyd resins are glycerol and pentaerythritol, resulting in the formation of the di- and trimethyl esters and the tri- and tetramethyl esters, respectively. All three of the isomeric phthalic acids are readily separated on the low polarity capillary column used. Methyl benzoate is observed, which is a problem as some of this compound is due to decarboxylation of some of the phthalic acid and differentation of the use of benzoic acid as a chain terminator is not possible. All types of oils, both vegetable and the more highly unsaturated marine types, are readily characterized before autoxidative polymerization. However, after ‘drying’ or autoxidative polymerization, little unsaturation remains. The relative proportion of unsaturated to saturated fatty acid methyl esters gives an indication of the cure or age of the alkyd resin. A simple alkyd resin based on linseed oil-pentaerythritol-orthophthalic acid was examined over 5 months. The following conclusions were made:

1. Before autoxidative polymerization the ratio of linolenic acid (9,12,15-octadecatrienoic acid) to palmitic acid (hexadecanoic acid) was significant but the unsaturation rapidly decreased such that after 2 days all the linolenic acid had been removed by crosslinking.
2. After 2 weeks the ratio of oleic acid (9-octadecadienoic acid) to stearic acid (octadecanoic acid) slowly began to reduce with time. After 4 months the concentration of oleic acid had been reduced by approximately two-thirds of its initial concentration.
3. Nonanedoic acid began to appear after 3 days and increased to a maximum in 1 month. The oil length of an alkyd resin is the percentage of fatty acid acylglycerols present in the total resin solids. By considering the ratio of products from the drying oil to the aromatic compounds from the phthalic acids, an approximation of the oil length may be obtained. Some decarboxylation occurs however, and the value of the estimate is reduced. Naturally occurring modifiers, i.e. rosin (as methyl dehydroabietate), have been determined, as have epoxy resins.

Epoxy resins A simple epoxy ether, i.e. a bisphenol A epichlorohydrin condensate, on pyrolysis produced three component peaks – phenol, isopropenyl phenol and bisphenol A. However, on pyrolytic methylation a variety of components was produced including phenol, isopropenyl phenol, the monomethyl ethers of these compounds and bisphenol A. The diether of bisphenol A was also formed.

Polyvinyl acetate Pyrolysis butylation has been used with low molecular weight products such as vinyl acetate-containing polymers where the vinyl acetate formed by pyrolysis is advantageously examined as vinyl butyrate, the disadvantage being that by-products, i.e. *n*-butanol and tributylamine, are formed.

Polymethyl acrylates Pyrolytic butylation of a methacrylic copolymer produced *n*-butyl methacrylate. *n*-Butyl acetate and *n*-butyl butyrate were produced from a cellulosic acetate–butyrate copolymer and *n*-butyl cyanoacrylate was produced from a commercial cyanoacrylate adhesive.

Rosin adducts The rosin-based resins have been extensively studied. While these are natural polymers, they are used in many modified forms. Abietic acid is the principal acid and it contains both a conjugated diene and a carboxylic acid, both of which are readily reacted on a commercial scale. Wood rosins contain a high proportion of diterpentine and mixtures of seven organic acids. Pyrolytic methylation has allowed the identification of (1) fumaric acid, (2) sandaraco-fumaric acid, (3) pallstric acid, (4) isofumaric acid, (5) dehydroabietic acid, (6) abietic acid and (7) neoabietic acid.

Para-substituted alkylphenol resins or modifications with rosin or its esters produce characteristic pyrograms when subjected to pyrolytic methylation. Tertiary butylphenol and *p*-nonylphenol are the tonnage phenols used. Traces of the free phenols result from both phenol modifications and methyl- and dimethyl-substituted phenols. Pentaerythritol rosin esters produce peaks due to the methyl esters of dehydroabietic acid and abietic acid in addition to the tri- and tetramethyl ethers of pentaerythritol. Modification of rosin with fumaric or maleic acids produce dimethyl fumarate. Rosin and reaction products with fumaric acid have been detected as a size on paper at the 1% level.

Polycarbonates Polycarbonates have been cleaved using alkaline reaction. Various phenolic compounds are formed by C–C bond cleavage as well as by cleavage of carbonate linkages. Almost quantitative degradation of the main chain occurs through reactive pyrolysis at the carbonate linkages to yield the dimethyl derivatives of the constituents.

Liquid crystal polyesters As in chemical degradation, reaction occurs with liquid crystalline polyesters, partial reaction occurring with products based on *p*-hydroxybenzoic acid and 2-hydroxy, 6-naphthoic acid. Quantitative results were achieved by varying the reaction conditions. Similar liquid crystalline polyesters based on 4-hydroxybenzoic acid, terephthalic acid and 4,4-biphenol produced almost quantitative results.

Conclusion

The application of GC to synthetic polymers has been outlined using three types of methods – pyrolysis, chemical degradation and pyrolytic alkylation. In all cases a considerable reduction in molecular weight is achieved before GC. Pyrolysis is applicable to both addition and condensation polymers and occurs by thermal degradation of the constituent chemical bonds. Chemical degradation and pyrolytic alkylation are applicable to condensation polymers with degradation at the location of constituent functional groups. Pyrolysis in some cases produces quantitative results, while chemical degradation usually produces quantitative results. Pyrolytic alkylation has to date been used only for qualitative analysis.

See also: **II/Chromatography: Gas:** Derivatization; Detectors: Mass Spectrometry; Pyrolysis Gas Chromatography. **Extraction:** Supercritical Fluid Extraction.

Further Reading

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Liquid Chromatography

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Introduction

The goals in the use of liquid chromatography for the separation of polymers and polymer oligomers include the determination of purity, the production of pure/purer polymer mixtures and for obtaining quality control data for polymer intermediates. There are fundamentally two partition mechanism options for such separations: size exclusion or sorption in the sense of surface adsorption or dissolution into a stationary phase. Size exclusion involves the partition of the molecules of interest from the mobile phase into the stationary mobile phase contained in the various pores of the solid support. The extent to which the stationary liquid is explored by the polymer molecules is determined by their Stokes' radius (dynamic size) and the volume of mobile phase in pores of a diameter large enough for penetration to be possible. Adsorption onto or sorption into a phase coated or grafted as a thin film on the surface of a solid support is dominated by solubility in the mobile phase and the chemical potential for sorption of the polymer molecules in a given mobile phase in contact with a given stationary phase. Because stationary phase supports used in modern liquid chromatography are themselves porous, mixtures of size exclusion in the presence of sorption and *vice versa* are known.

Size Exclusion

Historically, size exclusion has been the method most often used for polymer separation, purification and molecular weight determinations. The technique developed in parallel in the 'organic' polymer area and the biological polymer area. When used in organic polymer work, the term 'gel permeation' is used. In water soluble biopolymer work, it is called 'gel filtration'. There is no fundamental difference in the principles involved and both are size exclusion based. In liquid chromatography molecules move in the direction of development because of mobile phase flow. Most gel electrophoresis methods are, in reality, size exclusion based separations and that includes the gel methods used for sequencing of nucleotide fragments. There the driving force is electromigration of molecules with essentially identical ionic mobility which reptate through a porous polymer medium at rates proportional to size.

Sorption

Despite the potential attractiveness of a method which could introduce chemical selectivity in to the separation of polymers, sorption methods have seen little practical application until more recent times. The sole exception is the ion exchange purification of polyelectrolytes such as proteins. The history of the development of polymer high-performance liquid chromatography (HPLC) is an interesting one and is detailed in subsequent paragraphs. The reader should keep the following introduction in mind when