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Applications of simultaneous thermogravimetry-mass spectrometry in polymer analysis

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Abstract

Although thermogravimetric analysis is a powerful tool for polymer analysis its scope is limited as no information is obtained about the qualitative aspects of the evolved gases during polymer degradation. Both simultaneous and sequential techniques have been developed for identification of these gases and volatiles. Especially simultaneous TG-MS is a very powerful hyphenated technique combining the direct measurement of weight loss as a function of temperature with the use of a sensitive spectroscopic detector. In addition to the weight loss information, mass spectrometry permits temporal resolution of the gases that are evolved during thermal or thermo-oxidative degradation of a polymer in controlled atmospheric conditions. The characteristics of a broad variety of TG-MS instrumental solutions, which depend partly on the sample characteristics and the desired conditions of thermal degradation are considered, particularly in relation to polymer characterization.

Advantages and limitations of TG-MS with respect to other evolved gas analysis techniques are outlined. The paper discusses the application of TG-MS in relation to the various factors affecting thermal stability of polymeric materials, thermoplastics, thermosets and elastomers. The thermoanalytical technique is used for the structural characterisation of homopolymers, copolymers, polymeric blends and composites and finds application in the detection of monomeric residuals, solvents, additives, toxic degradation products, etc. Information is also obtained on the mechanism of solid-state reactions, chemical reactivity, curing; TG-MS is also beneficial in matters of product formulation and development. The sensitivity of mass spectrometry is high enough to derive additional information about the kinetics of formation of the gases evolved from the polymer sample. Illustrative examples are given. Future prospects are outlined. © 1997 Elsevier Science B.V.

Keywords: Thermogravimetry; Mass spectrometry; Polymer analysis

1. Introduction

Polymer characterization using the tools of thermal analysis, analytical chromatography and spectroscopy has developed primarily within the industrial analytical research community [1]. It is important to understand the thermal degradation pathways of polymers and the effect of additives (such as antioxidants, stabilizers, plasticizers, flame retardants, etc.) in commercial materials on this degradation in order to control, accelerate or retard the degradative process. Direct pyrolysis of polymeric matrices with a range of additives is rarely a successful exercise. Considerably more mechanistic information is usually obtained if the degradation is carried out at modest, controlled temperatures and heating rates. It is then most desirable to have methods at hand allowing for undelayed, qualitative and quantitative, automatic determination of gaseous decomposition products. The complexity of thermal degradative processes and the great variety

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of additives present in polymer formulations benefits from the combination of thermogravimetric analysis (TG) with other analytical techniques. This is particularly true if thermogravimetric analysis is coupled to an analytical method that will permit the identification of the products, such as mass spectrometry (MS) or infrared spectroscopy.

TG-MS is just one of many polymer characterization tools. Limitations in sample form and amount, coupled with the nature of the information needed, direct the researcher to the most appropriate tool(s). System selection factors comprise the sampling process, sample size and configuration, reproducibility, sensitivity, dynamic range, selectivity, versatility, reliability, efficiency, interfacing, development level, service, cost, data handling/analysis, etc. The various techniques, as well as the experimental designs for TG-MS, presented in this paper, differ in many of these respects.

The study of polymeric materials by a combination of thermal analysis and mass spectrometry has now become increasingly popular in the analytical laboratory.

Thermal analysis is a group of techniques in which a physical property of a substance is measured as a function of temperature when the sample is subjected to a controlled temperature program. Thermal events bringing about a change in the mass of the sample are given in Table 1. The coupling with MS adds chemical analytical features allowing the chemist to assign the evolved gases to the detected weight losses thereby correlating chemical information with the thermal event.

Table 1
Phenomena capable of study by TG [a]

Phenomenon	Change in weight	
	Gain	Loss
Adsorption and absorption	X	
Desorption (diffusion), outgassing		X
Dehydration or desolvation		X
Foaming		X
Vaporization		X
Sublimation		X
Decomposition [b]		X
Oxidation	X	X
Reduction		X
Solid-gas or solid-state reactions	X	X

[a] Ref. [252].

[b] Including run-away reactions.

The theme of this paper is to demonstrate the utility of TG-MS to help understand the thermal degradation pathway of the polymer, the underlying kinetics and the wealth of other information which may be extracted. This paper reports the advancement in equipment, compares modern TG-MS instrumentation systems with competitive techniques for polymer characterization, and outlines advantages and limitations of TG-MS methodology in polymer degradation studies.

In the context of product applications and problems, a variety of polymer samples, including thermoplastics, thermosets, elastomers and lacquers were analyzed using TG-MS. Illustrative examples are given.

2. Evolved gas analysis and detection techniques

Evolved gas analysis (EGA) is a technique in which the nature and amount of volatile product(s) released by a substance are measured as a function of temperature while the substance is subjected to a controlled temperature program [2]. While EGA involves both the characterization and quantification of the gaseous decomposition products, evolved gas detection (EGD) is limited only to the characterization. The most widely applied EGD techniques are mass spectrometry and infrared; the most common EGA detection is by GC-MS. Thus TG-MS is a TG-EGD system; if the MS ion current is calibrated in terms of the intensity of the parent ion detected TG-MS becomes an EGA system.

Mass spectrometry is frequently applied to the analysis of thermal decomposition products of polymers (Refs. [3,4,5], and references contained therein). Evolved gases may be analyzed simultaneously or discontinuously, with or without generating weight loss data. Examples of the latter are thermal volatilization analysis (TVA) [6,7], linear programmed thermal degradation mass spectrometry (LPTD-MS) [8,9,10] or temperature-programmed pyrolysis mass spectrometry (TPPMS) [4,11,12], and such closely resembling probe MS methods as thermal analysis mass spectrometry (TA-MS) [13], mass spectrometric thermal analysis (MTA) [14–20], direct pyrolysis-mass spectrometry (DPMS) [21,22], temperature-programmed fractionation (TPF) mass spectrometry [23] or packaged evolved gas analysis (PEGA) [24]. The latter technique uses disposable devices to collect the evolved sample gases, eventually from a thermogravimetric analyzer. Also, other methods appear in combination with TG, for example, TVA-TG. TVA gives access to all major product fractions of polymer degradation (non-condensable gases, condensable gases and volatile liquids, tars and waxes, and the solid residue) and yields information on stages of breakdown and threshold temperatures. In addition, the information obtained by DPMS can be used to assess the primary thermal degradation mechanism of a polymer (e.g. polyamides [25]).

In MTA (or PPA), which operates at m.s. pressure, pyrolysis gases are analyzed continuously with a (TOF)MS as polymer samples (or non-volatile or thermally unstable compounds) located within the ion source at a short distance from the ionizing electron beam, are heated through linear rates of temperature rise [15,20,26]. Its main benefits are that temperature is controlled directly and that all volatile reaction products are directly and immediately detected and identified upon liberation from the sample; a considerable drawback is the lack of loss data. MTA, as well as direct coupling TG-MS, is limited by the operational pressure (and atmosphere) requirement of the mass spectrometer. This may be overcome by the use of an external DTA sampling cell coupled to a pressure reduction device (MDTA) [27]. TG-MS development has faced and solved a similar operating pressure problem. Although many of the aforementioned approaches of EGA were advertised as being generally applicable to the study of stability and degradation, the determination of residual solvent, monomer and additives, the evaluation of contamination, compositional analysis, quality control, the investigation of kinetics and mechanism, studies on toxicity, and process control, there has often been little follow-up. The more practical approaches of thermal analysis using mass spectrometry have recently been reviewed by Morelli [4].

2.1. Discontinuous mode

In the discontinuous method, sampling of the evolved gases is intermittent. In the past TG analysis was occasionally combined with cold traps (CT) for separate examination of residues and volatiles; examples are TG-CT-GC [28] and TG-CT-MS [29–34], but DTA-CT-MS has also been reported [35]. Chiu [36] has described direct TG-GC coupling as being particularly useful in the analysis of mixtures having components of different volatilities, study of decomposition mechanisms, determination of trace amounts of impurities, and characterization of molecular structures. In its capacity to analyze pyrolysis products, coupled TG-GC is equivalent to controlled py-GC plus weight loss. Chiu et al. [37] described thermal evolution-differential trapping mass spectrometry (TEA-DT-MS) for polymer characterization. The technique, essentially an extension of TVA to become a controlled Py-MS approach, involves heating of the sample under continuous vacuum at a programmed rate, condensing the evolved gases in traps maintained at different temperatures, continuously monitoring the pressure changes at strategic locations, and analyzing the trapped products by mass spectrometry; quantitative information was obtained on the basis of pressure change detection.

More recently more complicated systems have become operative, such as TG-CT-GC/MS [32,38,39], TG-Tenax-FTIR-MS [40] and TG-CT-GC-FTIR-MS [41], in parallel and tandem configurations. If cold traps are used and if products are to be stored prior to analysis great care must be exercised; chemical reactions between products are not to be excluded upon subsequent sample handling (heating). It is obvious that the aforementioned techniques are unsuitable for continuous monitoring of the weight change process/gas analysis.

2.2. Simultaneous mode

EGA allows determination of the nature of unknown compounds, where EGA of known compositions allows understanding of the thermal degradation mechanism in a particular atmospheric condition. Thermogravimetry can be uniquely used for qualitative and quantitative EGA based on prior knowledge of the sample. The capability of a thermal technique for materials characterization can be greatly increased if techniques other than thermal are connected to the thermal analyzer to identify further, either the residue or the effluence during a certain thermal event.

Simultaneous differential thermal analysis-evolved gas analysis (DTA-EGA) apparatus has been described long ago [42,43]. In TG-EGA, reviewed by Chiu [44], TG provides a means for precise heating conditions, and also information on mass changes and kinetic parameters, whereas the coupled technique identifies the nature of the mass change and thus the mechanism of such a change. For simultaneous TG-EGA, mass spectrometers, Fourier transform infrared spectrometers (FTIR) and gas chromatographs (GC) may be coupled, in which the latter are significantly slower in operation. It is now recognized that the detector offering the best combination of sensitivity and versatility is a mass spectrometer, although FTIR is also very popular. They enable the identification of the gaseous species emitted from a sample, according to their mass or their vibrational spectra.

Amongst the thermal analysis techniques combined to MS, DTA-MS or MDTA has already been described in 1960 [15,27,35]. According to Holdiness [45] relatively few instrumental developments and applications have been reported for this technique up to 1984. The method is being used in relation to the determination of physical and chemical phenomena (sublimation, degradation, volatility, etc.) and monitors thermal decomposition products and phase changes in one operation, at a 10^3 to 10^4 higher pressure than MTA. DTA-MS has been used to facilitate evaluation of toxicity of composites (e.g. textile fabrics) or products of their combustion, and can explain the synergistic interaction between individual components [46].

EGA-MS based methods of sample characterization have one main advantage over conventional MS analysis. Often the interpretation of mass spectra resulting from compounds of exceptionally large molecular weight is very difficult or impossible due to the complexity of such spectra. If however, the compound is thermally broken down in a controlled way to give a series of volatile products then structure elucidation is improved [47]. On-line TVA-QMS permits mass spectra to be recorded either during polymer decomposition or during product separation [7].

Murdoch and Rigby [48] used a thermal evolution-mass spectrometry technique for polymer characterization in which the sample was heated below the electron beam of a TOF-MS and the thermal evolution curve was obtained by plotting the total ion current vs. the sample temperature.

In the methodology of linear programmed thermal degradation mass spectrometry (LPTD-MS) [8,49] the (polymeric) sample is degraded in a chemical ionization source, which produces some advantages over the non-isothermal methodologies: no transport problems, less fragmentation due to the ionization process, possibility of relating results of temporal mass spectra to fundamental molecular energetics; TPPMS finds application in the analysis of involatile organic unknowns [11].

EGA-MS, reviewed by Dollimore et al. [47], has evolved in the last 30 years from a simple heating of samples deposited on an inert matrix and observing the decomposition products leak into an ion source [50] to automated simultaneous monitoring of three thermal analytical techniques (TG/DTG, DTA) by MS [51]. Amongst these the TG-MS coupling, first suggested but not implemented by Wendlandt et al. [52], and Gohlke et al. [53], has been the most popular.

Multiple methods of thermal analysis interfaced to mass spectrometry, such as TG-DTA-MS [54–60], TG-DTG-MS [61], TG-DTA/DSC-MS [62,63] or STA-MS [64], TG-DTG-DTA-MS [51,65–67] have recently been reviewed [45]; in this way complementary information on the same sample is obtained. Kaisersberger [54] and Redfern [58] have discussed some of the (dis)advantages of these instrumental methods. An important feature of these techniques is ease of interpretation in that the evolved gases can be identified in sequential order and a specific gas may be associated with a specific weight loss. It is equally important to notice that in TG-MS the products of degradation are flushed out with the purge gas, which greatly reduces the possibility of recombination, as opposed to sealed tube experiments.

Combined evolved gas analysis by mass spectrometry is not only based on controlled heating but also comprises (isothermal and non-isothermal) pyrolysis techniques, laser plasma excitation and laser ablation mass spectrometry, as reviewed by Holdiness [45]. Mass spectrometric evolved gas analysis (EGA-MS), essentially Py-MS in the absence of air, has already been described by Wendlandt et al. [52], and has been reviewed by Refs. [8,47,68–72]. Emphasis is on the use of such systems for kinetic studies.

Flash pyrolysis-MS or pyrolysis-GC-MS have been used very effectively to identify and analyze volatile products evolved following extremely rapid heating (eventually in air) [73,74]. The fingerprints of volatiles produced by polymers treated in this way are an excellent analytical tool: however, the kinetics associated with the rapid pyrolysis lead to a completely different distribution of volatile products; there is no time-temperature resolution of volatiles and no information is obtained about the rate of degradation. In the direct coupling systems [75] pyrolysis is performed directly in front of the ion source of the mass spectrometer; this prevents recombination reactions and/or secondary decomposition of reactive compounds and minimizes the loss of polar compounds through condensation. Determinations performed by Py-MS are rapid; they can be performed in less than five minutes, a significant reduction in analysis time when compared to Py-GC. Whether Py-MS actually represents an improvement over Py-GC in terms of reproducibility and discrimination are key questions yet to be addressed [76]. Py-GC-MS yields additional information due to different degradation conditions; the method allows quantitative analysis [41].

Liebman et al. [1] have recently described a variety of methods for the study of evolved degradation products from polymerics such as (pulse) pyrolysis FTIR, pyrolysis DIP-MS (to study time-resolved degradation), pyrolysis/concentrator/GC/MSD, etc. Yun et al. [75] have compared three different vacuum pyrolysis mass spectrometry techniques, viz. pyrolysis-field ionization mass spectrometry (Py-FIMS), thermogravimetry/low voltage electron ionization mass spectrometry (TG-LVMS), and Curie-point pyrolysis-low voltage electron ionization mass spectrometry (Py-LVMS). Although it is encouraging to note that time-resolved results from these three different vacuum pyrolysis MS techniques reveal that the distribution and the type of the primary pyrolysis products are largely independent of heating rate and of ionization methods, this may be determined by the nature of the sample. Finally, one should consider that non-isothermal degradations have greater likelihood of characterizing closely related species since the added dimension of temperature provides greater resolution. Use of various complementary analytical techniques, amongst which is TG-MS, show that the thermal degradation processes (e.g. in case of post-chlorinated PVC [77]) are often much more complex than reported previously. This illustrates the danger of relying on one method of investigation only. Complementary information, collected by means of TG-MS and Py-GC/MS, has been used by Jacab et al. [78] to determine the thermal stability and decomposition mechanism of polyimides.

Tables 2–4 summarize the main features of various thermochemical techniques.

3. Development of TG-MS

Quite obviously, combined, simultaneous techniques offer considerable advantages over sequential methods, especially in a quantifying and identifying combination. Typically, such advantages are speed, reduced sample handling, unique sample, absence of retention times, etc.

In the past some 100 institutions worldwide have reported the use of simultaneous TG-MS equipment, with roughly an equal share for industrial R&D laboratories, governmental research centers and university departments. Literature survey shows some 190 TG-MS developments and applications. Due to the advances in instrumental developments a conspicuous fraction of the TG-MS papers deals with methodology and instrumentation. Already at an early stage major industrial U.S. companies explored the potentials of this hyphenated technique although the commercial instrument development has largely been a European issue. Table 5 summarizes the main developments in TG-MS history.

Amongst thermogravimetric analysis instruments in combination with a mass spectrometer, initially especially Mettler, later Du Pont, Perkin–Elmer, Netzsch and Stanton Redcroft equipment has been quite popular; coupled mass spectrometers mainly originate from Balzers, Du Pont, VG, Finnigan and Sciex. A number of instrument companies have actively pursued TG-MS hyphenation: from Mettler Instruments [79,80] starting already in 1968, to Balzers [71,81], Linseis/Leybold-Heraeus [82], Netzsch [62,65,83–89], Du Pont [31,90–92], Sciex [93] and more recently Stanton Redcroft [56,60] / PL Thermal Sciences [57] and Setaram [94]. Netzsch has reported most instrumental developments. Quite clearly, the lead for coupling is taken mainly by TG instrument

Table 2
Comparison of TG-MS with related techniques

Method [a]	Thermal effects		Evolved gas analysis			Ref.
	with mass change	without [b] mass change	quant.	semiqual [e]	qual. [f]	
TG	+	–	–	–	–	[253]
TG-DTA	+	+	–	–	–	[253,254]
TG-DSC	+	+	–	–	–	[255]
TG-MS	+	–	+[c]	+	–	This paper
TG-MS/MS	+	–	+	+	+[g]	[93,124]
TG-GC-MS	+	–	+[d]	+	+[g]	[38,178]
TG-(FT)IR [h]	+	–	+[c]	+	–	[256,257]
Py-MS [i]	–	–	–	+	–	[21,22,258–261]
Py-GC-MS	–	–	+[m]	+	+	[22,73,260]
PEGA [j]	+[k]	–	+[l]	–	+	[24]

[a] All combined techniques measure various effects on the same sample.
[b] Energetics of phase transitions or reactions (melting, crystallization, TG, crosslinking, etc.).
[c] With appropriate calibration the system is suitable for quantitative determination.
[d] Can be made quantitative.
[e] Structural assignment on the basis of molecular ion mass, fragmentation pattern or vibrational mode (verification).
[f] Identification.
[g] Molecular structure can be elucidated by examining mass spectral fragmentation patterns.
[h] TG-(FT)IR permits a complete sample analysis of materials in terms of thermal stability (quantitative weight loss data) and identification of evolved gases (not in mixtures).
[i] Method has disadvantage that the thermal degradation processes occur simultaneously and therefore cannot be analysed selectively.
[j] PEGA (Packaged evolved gas analysis) detects selected components in (thermally) evolved gases using disposable devices.
[k] Using thermogravimetric analyzer to produce the gaseous products.
[l] Elemental analysis of evolved gases (SO_2, HCl, etc.).
[m] A quantitative Py-GC-MS method was developed [41].

Table 3
Classification of some techniques for the measurement of polymer degradation reactions

Technique	Substance measurement		Analysis	
	Substrate	Volatile product	Analytical	Aggregate
Thermogravimetry (TG)		+		+
Spectroscopy	+		+	
PyGC/MS		+	+	
MS		+	+	
TG-MS		+	+	
TG-FTIR		+	+	

firms with some notable exceptions [81,93]. Table 6 lists TG-MS instruments which supposedly have been or are still commercially available, whereas Table 7 shows a great variety of TG-MS systems configured from skilled coupling of commercially available analytical instruments and components. On the one hand, this situation has hampered rapid expansion of the technique, while on the other, the limits of technical development have actively been explored.

TG-MS development is characterized by great ingenuity, in which all aspects of design and application were considered, such as:

performance and cost (from low budget – Ref. [95] – to highly sophisticated systems – Refs. [93,96])
versatility of interface (also in relation to sample characteristics)
control of atmosphere (in TG part)

Table 4
Qualifying features of some analytical methods in the study of polymer degradation

Feature	Technique			
	TG-MS	TG-FTIR	Py-GC	EGA [a]
Real time analysis	+	+	−	−
Batch analysis	−	−	+	+
Quantitative analysis	+	+	+	±
Temporal resolution	+	+	−	−
Degradation pathway	+	+	−	−
Compound specificity	+	−	+	+

[a] Sealed tube, head-space.

Table 5
History of thermogravimetry-mass spectrometry up to 1996

1965	Usefulness of MS to TG coupling suggested by Wendlandt et al. [52] and Gohlke et al. [53]; (Friedman [262] describes Py-TOFMS for plastics thermal decomposition studies)
1968	Zitomer [97] designs unique TG-TOFMS instrument; first application to polymers
1968	Wiedemann et al. [80] develop Mettler-Balzers TG-QMS instrument with direct vacuum coupling
1969	Stanton et al. [69] describe a TG-CT-MS arrangement
1975	Advanced coupling systems for TG-QMS [81]
1977	Critical review of simultaneous TG-QMS couplings [71]; introduction of TG-CIMS by Baumgartner et al. [118]; development of Linseis-Leybold-Heraeus TG-MS instrument [82]
1979	Introduction of commercial Netzsch high temperature TG/DTG/DTA-MS equipment [65] with two-stage pressure reduction system (quantitative interface); coupling of TG to magnetic sector instrument [61]
1980 [a]	First Du Pont-Du Pont TG-MS apparatus [31,92]
1982	Development of TG-APCI QMS [263]
> 1982	Strong improvement in data collection; software development [51,151]
1983	Commercially available TG-MS interface [63,85,89,264]
1984	Shushan et al. [93] describe TG-APCI MS/MS; Holdiness [47] and Dollimore et al. [45] review TG-MS instrumental developments
1986/87	Introduction of Stanton Redcroft-VG commercial apparatus [56,60]
1987	Development of simultaneous TG-modulated molecular beam mass spectrometry apparatus (STMMBA) by Behrens et al. [115]
1987/88	Reviews of application of TG-MS for polymer characterization by Chiu [44] and Jones et al. [102]
1988/91	Optimization of capillary sampling system [109,110]
1991	TG-MS,-FTIR Conference in Würzburg [101]; application of TG-LVMS by Yun et al. [75]
1993	Hi-Res TG-MS coupling by Lever et al. [107]
1994	Development of high sensitivity commercial Netzsch-Balzers instrument with improved orifice-skimmer coupling [83]
1997	Special issue of Thermochimica Acta on TG-MS

[a] Uncertain attribution.

mass spectrometer design and ionization type
complexity of the reaction
allowance for quantitative analysis (total vs. selective gas sampling, trapping)
automation.

This implies that one cannot properly speak of a standardized TG-MS coupling technique. This is apparent from Table 7 which gives instrumental details for a selection of instruments. There are good reasons to expect that a variety of TG-MS coupling techniques will eventually survive and co-exist depending on scope and application. Similar experiences have already been reported in the field of chromatography–MS interfaces.

In early couplings with TG a time-of-flight mass spectrometer (TOF-MS) was preferred [30,97]. This work on mass spectroscopic analysis of gaseous

Table 6
Co-operative industrial TG-MS developments

TG manufacturer	MS manufacturer	Reference	Year
Mettler	Balzers	[79–81]	1968
Linseis	Leybold-Heraeus	[82]	1977
Netzsch	Balzers	[65,83–85]	1979
Du Pont	Du Pont	[31,90,92]	1980 [c]
Stanton Redcroft/	VG Quadrupoles	[56,60,282]	1986
PL Thermal Sciences	Fisons (VG Quads)	[57,58,64] [b]	1991
Setaram	VG Instruments	[94]	1991
Seiko Instruments	(Gas transfer system)	[150]	1994
ATI (Cahn)	ATI (Unicam)	—	1994
Rheometric Scientific	n.d. [d]	[265,319]	1995
Perkin Elmer	Balzers	[108,266]	1996 [a]

[a] Presented at Pittsburgh Conference (1996).
[b] Essentially STA-MS.
[c] Uncertain attribution.
[d] Rheometric Scientific STA 625 equipped with glass-lined stainless steel heated capillary coupled to a quadrupole mass spectrometer.

products evolved when organic or inorganic materials are heated at a linearly programmed rate has been carried out with low resolution, low sensitivity, high scan rate TOF-MS equipment based on the Wiley–McLaren design [16,17,98]. In fact, the very open geometry of the ion source of this design enables easy coupling to a wide range of ancillary techniques (GC, TG, etc.).

As in case of the GC-MS coupling [99], also in combination to TG in the 1970s TOF spectrometers were rapidly replaced by quadrupole mass spectrometers (QMS) [98,100] and are still the preferred coupling today (Table 7). Up to about 1975 the high vacuum necessary for m.s. analyzer systems had hampered frequent coupling with other instruments. It is not surprising that vacuum TG-coupling was then favoured. Indeed, the development of other hyphenated methods with similar problems, such as microwave-induced plasma (MIP) and inductively coupled plasma (ICP) techniques, operating at atmospheric pressure as an ion source for mass spectrometry, dates from about 1980.

Mass spectrometric thermal analysis cannot be done effectively without a computer. Software deals with the organization of the mass spectrometric measurement, the fast processing of the mass spectrometric peaks, the quick acquisition of time-averaged weight and temperature data. Better computing facilities have by far had the greatest influence on developments in the design of TG-MS instrumentation, leading to the upswing of interest in the TG-MS technique from around 1983 (Fig. 1).

Literature pertaining to TG-MS instrumentation is difficult to cover in depth because of the great variety of solutions adapted throughout (Table 7). Original research in the field is widely scattered in the literature. Although the technique has not generated a dedicated journal some 20% of all pertinent contributions are collected in *Thermochimica Acta.* At variance with ICP-MS or analytical pyrolysis no specific symposia have been centered around the topic, although recently a technical meeting in Würzburg has covered application of TG-MS and TG-FTIR couplings in industry [101]. Usually at mass spectroscopy meetings most of the attention is focused on the power of the MS technique, while TG-MS is merely considered as a method for introducing a sample into a mass spectrometer. However, in case of TG-MS this turns out to be a major problem.

Among the research papers concerning TG-MS overviews, Eppler et al. [71], Dollimore et al. [47], and Holdiness [45] deal with general and instrumental aspects of the technique; Jones et al. [102] and Chiu [44] have specifically considered applications to polymer research.

The industrial interest in TG-MS development stems from applications in the field of fossil fuels, fuel oil additives, catalysis, ceramics and ultrafine

Table 7
TG-MS equipment

TG	MS	MS type	Ioniz. type	TG pressure	Interface	Interf. type	Refer.
Du Pont Mod. 950	Bendix Mod. 12	TOF	(EI)	purge gas	Metering valve	II	[97]
	and Consolidated Electrodynamics Mod. 21–104	n.d.	n.d.	id.	id.	II	
Mettler	Balzers QMG-101	QMS	EI	vac.	—	I	[79,80]
Du Pont Mod. 950	AEI MS-9	(QMS)	(EI)	purge gas	Cold trap	TG-CT-MS	[29]
Mettler	Balzers QMG-511	QMS	EI	vac./purge gas	Direct/capillary	I, II	(28)[79]
Mettler	Finnigan 1015/SL	QMS	EI	vac.	—	I	[100,132,133]
Mettler TA-1	UTI 100 C	(QMS)	(EI)	vac.	Vacuum connector	I	[129]
Perk.-Elmer TGS-1	Finnigan 1015/SL	QMS	EI	purge gas	Heated copper tube	II	[134]
Cahn RH	Du Pont Mod. 21–491	(QMS)	(EI)	gas	Stainless steel capillary	II	[137]
Mettler TA-1	Balzers QMG-511	QMS	EI	gas	Orifice	II	[81]
Mettler TA-1	Balzers QMG-311	QMS	EI	vac./gas	—/Capillary	I, II	[14,105,267,268]
Mettler	Balzers	QMS	EI	gas	Leak valve	II	[140]
Mettler TA-2	Finnigan QMS 3200	QMS	EI-CI	reagent	Metering valve	III	[118]
Linseis L 81	Leybold-Heraeus Q 200	QMS	(EI)	purge gas	Capillary	II	[82]
Du Pont Mod. 950	Bendix Mod. 14101	(TOF)	(EI)	purge gas	Cold trap	TG-CT-MS	[30]
Setaram MTB 10-8	Riber QMM 17 D	QMS	EI	vac./gas	Diaphragm/capillary	I, II	[156,269]
Stanton Redcroft TG 750	VG Micromass 16F	Magn. sector	EI	purge gas	Capillary	II	[61]
Netzsch STA 429	Balzers QMG-511	QMS	EI	purge gas	Capillary-orifice/orifices	II	[65,66,85]
Du Pont Mod. 951	Du Pont Mod. 21–104	(QMS)	(EI)	vac./gas	Constant volume sampler	TG-CT-MS	[31,90,127]
Du Pont Mod. 951	Du Pont Mod. 21–491	(QMS)	(EI)	purge gas	Jet separator	II	[144]
Mettler	EAI Quad 300	QMS	(EI)	purge gas	Capillary/mol. leak	II	[148]
Stanton	Kratos MS 10S or Hitachi RMU-6D	Magn. sector	(EI)	vac./gas	Glass capillary or jet separator	II	[95]
Mettler TA-1	HP 5992	QMS	(EI)	inert/oxid.	Leak valve	II	[51]
Perk.-Elmer TGS-2	Sciex TAGA 3000	QMS	APCI	atm.	Orifice	III	[96,136,263,270]
Netzsch STA 429	Balzers QMG 511	QMS	EI	gas	Orifices	II	[59,67,120,122,130,217]
Netzsch STA 429	Balzers QMG 511	QMS	EI	gas	Two-stage (CrNi)	II	[271]
Netzsch STA 409	Balzers QMG-511	QMS	EI	gas	Orifice-skimmer	II	[83,84]
Perk.-Elmer TGS-2	Riber QS 100 B	QMS	EI	gas	n.d.	II	[121]
Perk.-Elmer TGS-2 or Du Pont Mod. 951	Sciex TAGA 6000	MS/MS (QQQ)	APCI	reagent	Capillary/micrometer valve	III	[93,124]
Perk.-Elmer TGS-2	Finnigan mod. 3000	QMS	EI	purge gas	n.d.	II	[159]
Perk.-Elmer TGS-2/4	Balzers QMG 511	QMS	EI	purge gas	Capillary/valve	II	[78,151,210]

Table 7
(Continued)

TG	MS	MS type	Ioniz. type	TG pressure	Interface	Interf. type	Refer.
Stanton-Redcroft STA 781	VG Micromass	QMS	(EI)	purge gas	Molecular leak/jet separator	II	[56,58,60]
Du Pont Mod. 951/1090	H.P. 5995-B	QMS	EI	purge gas	Jet separator	II	[141]
Mettler TA-1	n.g.	MMB MS	EI	vacuum	Orifice	I	[115]
Mettler 2000 C	UTI Mod. 100	(QMS)	(EI)	purge gas	Capillary/leak valve	II	[196,204]
Cahn RH	Finnigan	QMS	EI	vacuum	—	I	[102]
Perk.-Elmer TGS-2	Balzers QMG 511	QMS	EI	purge gas	Capillary	II	[109,110]
Du Pont Mod. 951	VG Micromass PC 300D	QMS	EI	purge gas	Heated steel capillary	II	[272]
Setaram	VG Instruments	QMS	EI	purge gas	Heated flexible quartz capillary	II	[94]
Du Pont mod. 9900/951	Balzers QMG 311	QMS	EI	gas	Capillary	II	[123]
Perk.-Elmer TGS-2/TGA-7	Balzers QMG 420	QMS	EI	purge gas	Capillary/valve	II	[108]
Mettler TA-1	Finnigan MAT 3200	QMS	LVEI	vacuum	—	I	[75]
Polymer Laboratories STA 1500	VG Micromass	QMS	(EI)	gas	Molecular leak/jet separator	II	[57,273]
TA Instruments Hi-Res TGA 2950	VG-300	QMS	(EI)	purge gas	No details	n.d.	[106,107]
Netzsch STA 409	Amagaz 200 Delsi Nermag	QMS	EI	purge gas	Capillary/mol. leak	II	[125]
Rigaku Denki Mod. 8112 BH	Shimadzu QP 1000	(QMS)	(EI)	purge gas	n.d.	TG-(CT-GC)-MS	[38]
Mac Science Mod. 2000	VG Anatech 560	QMS	(EI)	n.d.	n.d.	(II)	[274]
Du Pont Mod. 951	Extranuclear	QMS	LVEI	purge gas	Pt orifice	II	[117]
Shimadzu TG-30	Jeol DX-303	(QMS)	EI, CI	purge gas	Capillary	II	[119]

I	Mass spectrometer is included in the high-vacuum system of the thermobalance.
II	Thermobalance works under normal pressure.
III	Mass spectrometer operates at high pressure (up to 1 mbar).
APCI	Atmospheric pressure chemical ionization.
CI	Chemical ionization.
EI	Electron-impact ionization.
Reagent	Restricted choice of reagent type (to allow CIMS).

Results given in brackets are uncertain attributions, made by the present reviewers.

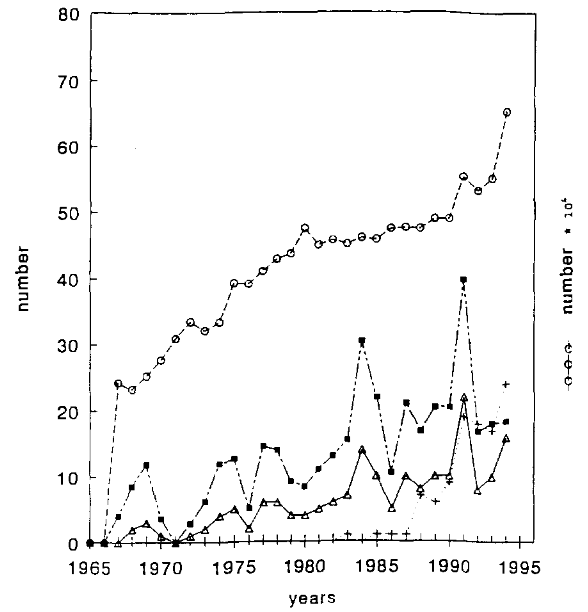


Fig. 1. Number of research papers reporting simultaneous TG-MS (Δ) and TG-FTIR (+) developments and use from 1968 onwards and total number of research papers ($\times 10^{-4}$, o). Normalized scores (fraction of TG-MS research papers $\times 10^6$; ■) take into account the increase in Chemical Abstracts entries over the same period.

microstructures, magnetic memory disk coatings, polymers, a.s.o. Amongst the academic institutions the Hungarian Academy of Science is outstanding with some 20 contributions over the last two decades [103,104] on a wide variety of subjects such as lignins, coal research, clathrates, polymers, phase determinations, catalysis, biomaterials and kinetics. On the whole the application fields for simultaneous TG-MS vary widely from coal, lignin and oil shale to carbon black and activated coke, minerals (clays, feldspars, silicates, bauxite), geochemical samples (meteorites), carbides, nitrides and mixed oxides, clathrates, glasses, catalytic materials, zeolites, nuclear reactor waste, organometallic complexes, organic air pollutants, polymeric materials, freeze-dried biological products, forensic science applications and fingerprinting of a bulk commodity such as coffee beans, and others.

As evidenced by the increasing number of publications in the field (Fig. 1) TG-MS is a growth area, though recently lagging behind in rate of progress to TG-FTIR. It is obvious, though, that the technique should no longer be considered a laboratory curiosity but rather a proven analytical tool. It is one that is widely applicable not only to analysis of polymers, plastics, and composites, but also to many organic and inorganic substances (not considered in this review). It is equally clear that two major drawbacks, namely, (1) the formerly unsettled state of instrumentation, and (2) method standardization, have long represented severe problems for potential users. The latter issue is still a point of major concern (see Section 5.3).

4. Instrumental

4.1. Thermogravimetric analyzer

Thermogravimetric measurements require a thermobalance. There are many different types of TG analyzers, varying in furnace (size, design and positioning), temperature range, sample quantity, sensitivity, degree of microcomputer control of the hardware, capabilities of the software etc. – all with typical specifications (Table 8). Depending on the problem a specific instrument may be preferred. For example, in ceramic applications furnaces up to 1500°C are frequently required [56,60,65,84,85]. Quality control, which can cope with different measurements, sets lower standards for balance and environment than more scientifically oriented measurements in which small details matter and indeed are the subject of investigation. In the case of expected and inherent inhomogeneity of the sample, large sample holders may be desirable (although there may be a problem from the point of view of dissipation of heat). Instead, when no internal memory effects can be tolerated the issue is to use small samples.

In TG-MS couplings both vacuum and gas atmosphere mass flow thermobalances have been used (Table 7). Various essential design principles are to be fulfilled using the high-vacuum working mode. Ref. [105] describes the requirements for furnace assembly for vacuum and atmospheric pressure TG. As the vacuum system is completely heated, all memory effects due to (water) vapour condensation can be avoided. It would appear (Table 7) that the concept of coupling a vacuum thermobalance to a mass spectrometer is gradually being abandoned (pos-

Table 8
Experimental TG-MS parameters

TG [a]
Instrument identification
Sample identification
Form and particulate size of sample
Sample quantity (initial and final) and packing
Preconditioning of sample
Configuration of microbalance and furnace (size, design and positioning)
Maximum balance sensitivity
Crucible geometry, size and chemical composition
Type and positioning of sample thermocouple
Atmosphere type (interactive or non-interactive), pressure, purge rate (turbulence, diffusion)
Mode of operation (isothermal, dynamic, quasi-isothermal, high resolution)
Heating rate (heat transport)
Calibration of temperature and weight signals
Accuracy (buoyancy corrections, electrostatic influences on balance mechanism; momentum effects; radiometric effects)
Degree of microcomputer control of the hardware
Interface
Internal or external microfurnace TG system
Type of pressure reduction system
Calibration of TG-MS connection
Nature of the gas flow
Selection of material, length and diameter
Temperature
Temporal correspondence between TG and MS data
MS
Analyzer type, ionization mode, electron energy
Mass range and mass resolution, sensitivity, detection limit
Optimum tuning parameters for ion source, mass filter and ion detector
Procedure for calibration of mass scale
Operating modes
Sample inlet temperature, operating pressure

[a] Cfr. also Ref. [154].

sibly because of the lack of any force directing the flow of evolved gases into the mass spectrometer) in favour of the indirect coupling type, whereby the TG operates at ambient pressure and the MS operates at high vacuum.

For almost all thermoanalytical experiments an exact control of the sample atmosphere is required. This is most desirable in the case of polymer characterization. In such conditions the top-pan sample arrangement enables an exact separation of the gas path towards the sample and balance, and facilitates the protection of the mechanic weighing system against thermal radiation of the furnace (especially at high temperatures) [65]. It would not appear that polymer samples set any specific requirements to the TG part of the TG-MS instrumentation.

The use of mass spectrometry in evolved gas analysis is compatible with oxygen as the purge gas through the thermobalance, clearly within the limits of the allowed pressures (max. 20%). There are certain advantages in the use of helium as a purge gas (Table 9). For reduction studies, an intrinsically safe gas mixture (5% H_2/N_2) is recommended.

In thermal analysis, the variables affecting resolution for a specific hardware design are typically sample size, heating/cooling rate, purge gas composition, flow rate, etc. Generally, smaller sample sizes, slower heating/cooling rates, and high thermal con-

Table 9
Helium as a purge gas in TG-MS

Advantages:
- Easy stripping from the gas stream
- Recommended carrier gas for the jet separator path
- Difficult to ionize
- Inert to charge exchange
- Inert to ion/molecule reactions with the target
- Low mass; no interference with m.s. spectra of volatiles
- High thermal conductivity
- High heat capacity (Cp)
- Low density (buoyancy)
- Low viscosity in comparison to other noble gases

Disadvantages:
- Cost
- Higher viscosity than N_2
- Unfavourable mixing with large molecules

ductivity purge gases (e.g. helium) result in improved resolution. TA Instruments [106] uses a controlled rate approach in which the programmed temperature ($\Delta T/\Delta t$) is regulated by the rate of reaction so as to maximize weight change resolution. The recent description by Lever et al. [107] of the coupling of a Hi-Res TG system to MS, which gives improved resolution and reduces analysis time, is of interest to the study of polymer blends and fibres. Resolution not only affects the ability to obtain accurate, quantitative effects but is also important in obtaining component identification in the evolved gases by MS, which is, in fact, the main asset of HR TG-MS. Although the enhanced peak separation aids in characterizing volatilization/decomposition processes and in the stoichiometric assessment of degradation mechanisms the technique also introduces unwanted artifacts; reproducibility is likely to be a problem. In case of simultaneous degradation and rest monomer evolution the observation of the degradation process is greatly disturbed. Temperature profiles of an extruder cannot readily be simulated with an HR TG. Therefore, in connection with MS it is also necessary to be able to use the instrument in an ordinary TG mode.

The device described by Dufour et al. [108] claims an (intralaboratory) precision of the weight change measurements of 0.1 wt% with a reproducibility of better than 1%.

4.2. *Mass spectrometer*

Mass spectrometers of low-to-high performance, which scan by measuring one mass-to-charge ratio at a time, are used effectively for TG-MS. The maximum admissible pressure at the source of the spectrometer is 10^{-6} mbar in continuous regime and 10^{-5}–10^{-4} mbar during short time intervals. Inside the mass spectrometer, the ion beam is focussed and transmitted by a series of electrostatic lenses (the ion optics). Hereafter, the ion beam enters a quadrupole mass analyzer, which serves as a mass specific filter, stabilizing and transmitting only one specific mass (in fact mass/charge) that subsequently reaches the detector, while all other masses are deflected. The ion detector most commonly used in TG-MS, as in ICP-MS, is a secondary electron multiplier operating in the pulse counting mode.

The mass spectra of the products must be sorted. Due to ion fragmentation, the sorting of complex mixtures can be extremely difficult. With the current diversity of ion mode (positive, negative) and ionization method (electron impact, chemical ionization, atmospheric-pressure ionization, etc.), the analysis may be simplified. In the past, high masses ($m/z > 200$) were seldom studied by TG-MS (mass range of 1–800 a.m.u. is currently felt appropriate) since molecules of higher molecular masses are usually not volatile under atmospheric conditions. Wenz et al. [109,110] report the successful detection of the parent ion ($m/z = 447$) of Tinuvin 234 by TG-MS.

In most cases of polymer degradation using TG-MS, the slow, programmed heating (1 to 10°/min) results in the intrinsic separation of the products due to degradation kinetics. An example of such separation is reported in Fig. 2 of Ref. [102] with six major volatile products arising from the cure and subsequent degradation of a particular resin system. The unique temperature dependences of the products and the fact that these are common volatiles tend to simplify the analysis. If it is necessary to detect and identify trace levels of volatiles or, if the product temperature profiles are very similar, the use of auxiliary MS techniques such as collisional activation or a GC interface is recommended.

Table 7 shows that three types of mass spectrometers have been used in combination with TG, namely, TOF, QMS and magnetic sector instruments; Table 1 of Ref. [111] indicates some possible candidate analysers. Proposed designs use electron impact ionization (EI) and chemical ionization (CI), simultaneous or intermittent MS scanning techniques as well as coupling of simple quadrupole and more sophisticated tandem triple quadrupole (MS/MS) spectrometers with a variety of thermoanalyzers. Not all proposed systems are suitable for continuous monitoring during the weight change process or dynamic atmospheric work.

Although the first couplings of thermal analysis equipment involved TOF-MS [97,112] it would appear that TOF-MS is no longer preferred as a simple detector to TG (cfr. Table 7). In fact, single-stage TG-TOF MS is no longer an issue [113]. However, as TOF-MS provides a complete mass spectrum 10^4 times a second, it is ideal for the study of fast reactions and the detection of reaction intermediates, and it is the instrument of choice with pulsed ionization methods such as plasma desorption MS [98] and plays a significant role in the analysis of high molecular weight compounds.

Table 7 shows that QMS is now most widely used in coupling to TG. QMS has gained a major foothold in the field of mass spectrometry, partly because of its relatively small size and reasonable cost, sufficiently rapid scanning capability (100 ms per scanning unit), high tolerance for pressure and ease of interfacing to computers, which has facilitated hyphenation with TG (as well as GC). Except perhaps for run-away reactions, in which case TOF-MS is more adequate, QMS performs ideally for the detection of evolved gases from thermogravimetry and little or no information is lost in this time frame.

Koprio [114] has described the characteristics of QMS (sensitivity, reproducibility, calibration); the limitations of QMS in polymer research have been discussed by Wingfield [57]:

qualitative analysis of gas mixtures by means of QMS is limited due to low resolution;

QMS cannot be used directly for quantitative gas determination;

QMS cannot distinguish ions of equal molecular masses (e.g. N_2 and CO);

QMS requires careful choice of purge gas which should not interfere with the expected reaction products; for example, degradation of Cl containing polymers cannot be studied in an Ar atmosphere as Ar gives isotope peaks at m/z 36 (0.3%) and 38 (0.6%), coincident with the Cl isotopes (here He is the obvious choice);

complex gas mixtures as reaction products constitute a problem especially for gases with low molecular weight (< 40).

Balzers QMG-511 appears to be the most frequently coupled instrument in TG-QMS systems. Also a commercially available TG-QMS combination is based on QMG-511 [65,83–85]. Kaisersberger et al. [88] have published theoretical and instrumental studies on the TG-QMS coupling.

Quadrupole mass spectrometers have some advantage over electric sector instruments by virtue of their cylindrical symmetry, absence of very narrow splits, and relatively high transmission efficiency; however, mass discrimination effects may be larger than in other instruments.

As opposed to low-budget TG-MS [95] some highly sophisticated solutions have been worked out amongst which STMMBA (simultaneous thermogravimetry and modulated molecular beam mass spectrometry apparatus) [115], equipped with a QMS, and high resolution magnetic sector mass spectrometers [61,95], fitted with array detectors to allow simultaneous ion detection. The use of the magnetic sector mass spectrometer in combination with TG has now completely been given up (Table 7). The much greater mass ranges of magnetic sectors than quadrupoles are of little avail for TG-MS. On the other hand, quadrupoles are more easily controlled by computer than are magnetic sectors. This is especially true when peak hopping rather than scanning is desired.

Also the type of ionization technique, either electron impact (EI) or chemical ionization (CI), has been varied in combination with TG (cfr. Table 7). Amongst other ionization methods (Table 10), it is noticeable that FI finds application in Py-MS [5,116]. The most common ionization method in TG-MS is electron impact using high energy electrons (70–90 eV). For the EI ion source, the generated total ion stream is directly proportional to the gas pressure in the impact field, which provides a basic condition for quantitative analysis. On the other hand, EI ionization at the normal ionizing voltage causes extensive

Table 10
Combinations of separation techniques and mass discrimination[a]

Separation/sample introduction	Ionization[b,c]	Mass discriminator
GC	EI[d]	Sector (B, E)
HPLC	CI[d]	Time-of-flight (TOF)
SFC	FI[d]	Quadrupole (Q)
CE	TI	Ion-trap (IT)
IC	Desorption[e]	FT-ICR
TLC	Nebulization[f,g]	
TA	Photon ionization	
Pyrolysis	ASGDI	
Probe		

[a] Most couplings are technically feasible, cfr. Ref. [275].

[b] Ionization methods are reviewed by Refs. [276,277].

[c] For ion activation processes in MS/MS cfr. Ref. [278] and Table 2 of Ref. [234].

[d] Ionization of molecules in the vapour state.

[e] Comprises fast atom bombardment (FAB), (liquid) secondary ion mass spectrometry (L-SIMS, SIMS), plasma desorption (PD), matrix assisted laser desorption (MALD), desorption CI (DCI) and field desorption (FD).

[f] Includes fluid introduction techniques like thermospray (TSP), electrospray/ionspray (ESP/ISP), heated nebulizer/atmospheric pressure chemical ionization (HNI/APCI).

[g] With HPLC-MS interfaces removal of eluent and ionization are combined in one step.

fragmentation of components entering the ion source from the TG producing an overlapping of fragment and molecular ion signals. This makes identification of individual compounds extremely difficult, especially when several complex compounds co-evolve, for example, during polymer degradation. In case of EI there are problems in differentiating between fragmentation in the TG and in the MS. Lower ionizing energies (10–30 eV) enhance the relative intensity of molecular ion peaks and reduce the number and relative abundancies of the lower molecular weight fragment ions as well as the fragmentation, ionically induced rearrangements, or ion–molecule collisions, as may occur in polymeric degradation. There is, however, a marked decrease in sensitivity with decreasing electron energy. Yun et al. [75] and Knümann et al. [117] have reported low voltage electron impact TG-MS.

The use of CI overcomes some of the limitations of EIMS. Various groups [96,118,119] have examined the feasibility of characterizing evolved volatiles by CI mass spectrometry. Chemical ionization MS (CIMS) has the advantage of ease of interpretation (due to better control on the complexity of the spectral fragmentation pattern) and of being able to operate at higher input pressures. A TG-CIMS system in which the thermobalance works under normal pressure, connected to a mass spectrometer working at elevated pressure ($p = 1$ mbar) offers the possibility of using the purge gas of the thermobalance as a reaction gas in the chemical ionization source [118]; the reaction gas is understood not to interfere with the volatiles. This reduces interface problems and restricts the fragmentation of released volatile compounds. This in turn leads to simple cracking patterns, intense molecular ions (or quasimolecular ions in case of hydrocarbons used as the reaction gas) and therefore easy-to-interpret spectra, especially useful in the analysis of mixtures with many hydrocarbons, which often occur in the course of thermal decomposition of polymers. Identification of individual components is clearly favoured by well-developed fragmentation patterns. Conventional mass spectrometry does pose some limitations on TG-MS analysis. The usual method of ionization, standard 70 eV electron impact, is vulnerable to the presence of oxygen, making TG-EIMS essentially less suited for studies of combustion and other thermo-oxidative processes or simulation of polymer processing under air. The problems of ion source filament lifetime with use of strongly oxidative atmospheres in the TG system remain though using conventional CI. Diluted oxygen [107,108,117,120–123] and other reaction and purge gases are used frequently.

TG-CIMS has found limited use so far (Table 7) and appears to be restricted to specific cases. Contrary to PyMS [5] no comparative study of electron impact and chemical ionization techniques in TG-MS has been carried out.

In single-stage TG-MS, in principle, only the molecular weight is easily derived; however, structural assignment on the basis of molecular weight only can be a tenuous proposition.

In order to *unambiguously* identify a component without forgoing direct TG-mass spectral integrity, MS/MS techniques are an obvious choice. Shushan et al. [93,124] have described a TG-APCI MS/MS system for evolved gas analysis. With the introduction of commercially available (triple–quadrupole) tandem mass spectrometers (MS/MS) real time structural identification of single components within complex evolved gas mixtures can be carried out rapidly under computer control (cfr. Section 10 also).

APCI ion source technology permits excellent temporal correspondence between TG and mass spectral data; ability to operate in a variety of oxidizing as well as inert atmospheres; ability to identify and resolve complex products, including isomers, emanating from the TG apparatus; compatibility with a variety of TG instruments; MS/MS library search and rapid identification of unknowns evolved from the TG system. Coupling of APCI-MS/MS to TG vastly increases the amount of chemical information one obtains from either method alone. The rapid identification of coevolving compounds by MS/MS, combined with weight loss data from TG, provides a means of delineating complex thermally activated processes such as decomposition and cure of polymers. The combination of atmospheric pyrolysis with APCI-MS/MS provides an ideal method for assessing the potential hazards of the oxidative degradation of polymer systems used, for example, in building materials or interior furnishings of homes, offices, aircraft, etc. This type of dynamic analysis allows important contributions to be made to the areas of polymer science, materials characterization, and combustion toxicology [124]. Such an analytical procedure is not only useful in the analysis of polymers, such as cellulose acetate, but is also of great value in the identification of copolymer substrates, and the various polymer additives such as antioxidants, stabilizers, and plasticizers.

4.3. Design criteria for efficient TG-MS coupling

The coupling interface between the thermoanalyzer and the mass spectrometer fulfills two functions. It operates simultaneously as a gas-input system for the mass analyzer and (usually) as a pressure reduction system.

In TG-analysis of polymers the handling of large quantities of material released during sample decomposition constitutes a difficulty. For example, in problems concerning outgassing, the components of interest are light molecular weight compounds (entrained solvents and plasticizers) in low concentrations, which evolve before the sample reaches its own anaerobic decomposition temperature. In other processes, large volumes of materials are expelled as a mixture of decomposition products and particulates. A properly designed TG-MS interface cell must therefore be capable of handling both trace components as well as any large quantities of material released during sample decomposition. Without proper precautions volatiles evolved from a sample are swept from the furnace by a stream of purge gas and condensation easily occurs given the low temperatures of the wall of the furnace tube, leading to fouling of the cell, of the hangdown wire of the thermobalance, the inlet system and ionization chamber of the mass spectrometer.

Design criteria for an ideal interface allowing routine application of TG-MS are given in Table 11. Quite obviously, it is difficult to meet all these criteria. The usual arrangements result in insufficient function in high temperature measurements or in the case of heavy volatile condensable gases and vapours. Some instruments have been reported to give problems with sample transport and long-term reproducibility [61,125]. Especially, compounds having low volatility are unfavoured in reaching the mass spectrometer. Condensation in the thermobalance has been mentioned as a main source of fouling and 'memory' effects [108]. Eppler et al. [71] have described the most desirable TG-MS couplings for low- and high-temperature furnaces with various evolved gas condensation temperatures. The effects of interface sublimation have been well illustrated by Jones et al. [102].

It is obvious from the history of TG-MS that the interface is of crucial importance and poses several problems. Within the interface, conditions are converted from the high temperature and (usually) atmospheric pressure of TG to the room temperature and (usually) high vacuum conditions in the mass analyzer. Both the temperature and the geometry of the interface region influence the coupling. Upon proper design of both furnace tube and interface condensation and memory effects can be overcome [108,126]. The inlet system of the mass spectrometer usually consists of a flexible refractory (fused silica) capillary tube, where the length of the coupling is not too critical (10 m in Ref. [119]). The interface between the thermobalance (operating at near atmospheric pressure) and the ionization chamber of the mass spectrometer is able to withstand high temperatures. Kaisersberger et al. [63] report a capillary coupling that can be operated up to 2400°C, and an orifice coupling up to 1500°C. It

Table 11
Design criteria for an ideal TG-MS interface [a]

(a)	Quick transfer from TG to MS (< 100 ms); rapid response time
(b)	Absence of 'memory' effects (caused either by traces of a previous sample or originating from long residence times of high molecular weight components released during decomposition)
(c)	High yield and enrichment (no dilution of the sample of interest)
(d)	Quantitative introduction of sample into the mass spectrometer (neither condensation nor degradation)
(e)	No separation due to wall effects; unvaried gas composition for reliable qualitative and quantitative interpretation (i.e. low mass discrimination)
(f)	Flexible atmospheric control (free choice of vacuum or atmospheric pressure)
(g)	No mutual interference on the specifications of the hyphenated instruments
(h)	Continuous monitoring
(i)	Simplicity of construction
(k)	Easy (de)coupling of the component instruments (rapidly interchangeable inlet capillary and coupling device)
(l)	Short cleansing times of furnace, the furnace tube, TG-MS interface and mass spectrometer

[a] Cfr. also Ref. [58].

is equally important to avoid mutual influence of thermobalance and mass spectrometer. Fouling of the latter is achieved by stepwise build-up of the vacuum, usually in a two-stage process. In many experimental set-ups evolved gases are transferred in an inert atmosphere from the thermobalance to the mass spectrometer in ca. 100 ms.

Obviously high molar mass fragments are most likely to prove difficult to sweep from the thermobalance, through the interface, to the mass spectrometer without condensation at some point in the system, although the present authors have also unexpectedly experienced serious problems with some selected low molecular weight volatiles (notably benzoic acid and melamine) prone to sublimation. Provision should also be made to ensure that undesired condensation products are removed between TGA experiments. Data gathered from a blank run (no sample in the TG-pan) should indicate no sample residues from previous analyses. It may be mentioned that even in the harsh conditions of our application laboratory, in which a great variety of materials is investigated, the TG cell needs cleaning only a few times a year provided that the system is regularly flushed.

The effects of interface sublimation, showing weight loss, rate of weight loss, and total ionization current for the analysis in vacuum of a resin, have been illustrated by Jones et al. [102]. In the particular case the total ionization current displayed two peaks, a smaller one associated with the residual solvent and a larger one associated with the thermal degradation of the resin. The rate of weight loss (DTG) and total ionization current curves should always correspond well for mass-detected degradation products. In the reported example, a large peak in the dW/dT profile without counterpart in the total ionization current was found to be indicative of the monomer subliming in the high vacuum before curing. This monomer was condensed and was not detected by the mass spectrometer.

4.4. Interface techniques

All the interfaces operate on the principle that only a small portion of the TG effluence is leaked into the MS so as not to exceed the pressure tolerance level of the MS. In cases where analysis of small traces of some constituents is desired (e.g. in polymer additive analysis), or where the determination has to be performed over a long period of time, such techniques are not adequate. For such applications, STMMBA [115] or the condensation trap is probably a better choice [127].

The practice of intermediate stockage of fractions for subsequent analysis by spectroscopic or other methods poses several problems; secondary reactions can lead to the formation of products other than those initially collected; cross contamination can result if several products are liberated at short intervals; the most opportune time for collection is not always obvious. Some consider the condensation trap as the most sensitive and reliable interface for TG-MS coupling [31,91]. This is certainly true for isothermal systems, not for dynamic cases. The proposed method does not allow continuous monitoring of evolved gases.

Many TG-MS couplings for continuous monitoring have been described, as reviewed by Refs. [44,45,47,71,102], and are shown in Table 7. Direct connection of the two instruments is possible, but then the TG experiment can be performed only under high vacuum [14,71,75,79,80,88,100,102,115,122,128–133]; others make use of inert purge gases [97,107,134] or allow chemical ionization under certain types of reagent gas [93,96,118,124,135,136].

In the high vacuum systems the source of the mass spectrometer is practically inserted in the pumping circuit of the thermobalance. The pressure in the whole system may not exceed 10^{-4} mbar, not even during a burst-like decomposition of the substance, because of damage to the ion source and loss of linearity above this pressure limit. This requires a selection of samples with a low vapour pressure increase during heating. Various essential design principles are to be fulfilled using the high vacuum working mode [105]. As pointed out by Kaisersberger et al. [65,85,88], high vacuum coupling seems to be very easy with the ion source and m.s. analyser arranged in a straight way, but does not make maximum use of the sensitivity of the mass spectrometer and leads to adsorption of gas molecules on the walls. The main important disadvantage for low pressure TG-MS analysis is the lack of heat transfer by convection and in part by conduction. The simple construction in the high vacuum coupling is not possible at high temperatures (heat radiation) and in case of condensable vapours. Advantages of direct TG-MS coupling are the absence of gas transport and condensation problems and of time delays in the analysis of the released volatile components. Evolved molecules are ionized immediately. In many practical problems of thermal analysis of polymeric materials a restriction of the high vacuum as 'sample atmosphere' cannot be accepted, and therefore the possible applications of such a combined apparatus are limited.

The major problem in linking TG equipment to mass spectrometers lies in the transport of the volatiles without condensation. TG is ideally performed in an atmosphere as near as possible to the practical application conditions of the sample in a flow of a selected carrier gas of possibly 100 cm^3 min^{-1}, whereas MS must be operated below 10^{-5} mbar. Consequently, in variable pressure TG-MS there is a need for a complicated interface for pressure reduction, situated between the test space of the thermoanalyzer and the ion source of the mass spectrometer. On the basis of the equations for the molecular and viscous flow region, Kaisersberger [87] has shown that only with a two-stage pressure reduction a continuous gas inlet to the mass spectrometer is possible without mass discrimination. From a theoretical discussion [88] and a practical demonstration of a commercially produced instrument combination it has indeed become clear that a sensitive and exact gas analysis with a coupled mass spectrometer is feasible using such a system. To prevent condensation the transfer line is heated. Long transit times in the interface should be avoided; transfer of the evolved gas to the mass spectrometer is essentially instantaneous on the time scale of thermal analysis experiments.

Various ways have been implemented to solve the interface problem arising from the different operating pressure conditions of the hyphenated partners and the need for concentration enhancement. These interfaces (cfr. Table 7) include various restrictions, such as a capillary [47,61,81,91,137–139], orifice [71,81], molecular leak [51,140], capillary–orifice [65,71,87,137], orifice-skimmer [83,84], jet separator [23,60,95,141–145], jet separator–orifice [146], micro metering valve [51,60,97,142,147], metering valve–jet separator [142]; also constant volume samplers [31,90,148] and total condensation trap [127] are applied. In the case of sweeping with a fast-moving carrier gas dilution cannot be avoided, and pressure reduction is coupled with sample enrichment through either jet or membrane separators.

A successful interface for continuous monitoring under various atmospheric conditions is a leak valve [51]. The metering valve, introduced in 1968, remains a convenient solution even today. The molecular leak may be operated with any common purge gas, and thus the conditions of the thermal analysis experiment are not compromised [56].

From a theoretical point of view, molecular beam inlet systems are the 'cleanest' sampling devices, as, during the transport from the sampling position to the mass spectrometer's ion source, gas surface interactions and chemical gas-phase reactions can be avoided. However, they are complicated and expensive. While discriminating against lower molecular weight species, the use of a jet separator to reduce TG effluent pressure (ca. 1 atm.) to the low pressure necessary for MS operation (10^{-6} mbar) increases the relative concentration of thermal decomposition products in the flow by stripping a substantial quantity of the carrier gas from the stream. This leads to a major increase in sensitivity with respect to molecular leak systems; operation with a helium or hydrogen purge gas is necessary [60], (cfr. Table 9 also).

Typical interface parameters that require judicious choice include material selection, length and diameter, nature of the gas flow, temperature (Table 8). Criteria for material selection are: desired working temperature of the TG instrument (especially for the first pressure stage), oxygen and chemical resistance, embrittlement tendency, etc. The obvious choice is glass, preferally silanized, as opposed to any metal (stainless steel, copper or aluminium). The diameters of the capillaries and orifices, which are partly determined by the conductances and suction capacity of the pumping system, are generally below 0.2 mm.

Chiu and Beattie [90,127] and Yuen et al. [51] have summarized methodologies used to interface TG to MS, including direct connection under vacuum and direct connection under reagent gas. Eppler et al. [71,81] have described different coupling techniques between TG and MS, in particular for the investigation of low and high boiling compounds released during thermal decomposition in air or other gas atmospheres.

Essentially, two principal coupling systems coping with the necessary pressure reduction are distinguished:

capillary systems, most of them combined with a valve and/or a pin hole diaphragm [61,71,82,97,118,129,137]

free jet (molecular beam) inlet systems [54,59,71,89,130].

Major modern coupling designs include the capillary, two-stage orifices and an orifice–skimmer combination, where the latter is the most advanced; not all couplings can readily be adapted to a specific TG apparatus without the need for a major redesign.

Wenz et al. [109,110] have recently optimized the capillary sampling system: sensitivity and transient response for higher molecular masses up to m/z 450 have been tested by a transfer experiment with a commercial UV-absorber Tinuvin 234. The interface, which meets the requirements of forensic science investigations, is free of memory effects; high boiling and high molecular weight compounds can be transferred. Another simple way of coupling, being versatile and inexpensive is by using a heated capillary with laminar flow conditions to extract the gas from the TG, and a (metallic, ceramic or vitreous) orifice system arranged at the outlet of the capillary to ensure a molecular flow into the ionization chamber of the mass spectrometer. This forms the basis of a commercially available TG-MS Netzsch instrument [65,87]. The dimensions of the inner diameter, restricting orifice and length should be such that viscous sample flow exists in order to avoid mass separation. This system, however, has the disadvantage of possible losses of components from the gas sample due to condensation, adsorption and chemical reactions, which can be more severe than in molecular beam sampling devices. Many compounds being analysed in practice condense at 100°C. Detection of high molecular mass molecules is obviously also desired.

More recently a skimmer has been arranged in the compression zone behind the orifice to achieve a parallel molecular beam into the electron impact ion source of the mass spectrometer. This new TG-MS coupling system [83,84] has increased sensitivity for low volatile materials, allowing condensable vapours with saturation pressure $p > 0.1$ mbar to be detected.

Apart from the direct vacuum couplings and the pressure reduction interface systems, in some TG-MS couplings the mass spectrometer inlet operates at high pressure (up to 1 mbar) thus avoiding complicated pressure reduction systems between thermobalance and mass spectrometer [96]. The TG-APCIMS system (Table 7) offers the great advantage in using the purge gas of the thermobalance as a reaction gas in the chemical ionization (CI) source; a drawback is the possible interference of the reaction gas with the evolved gases. High gas flow rates through the microbalance help prevent deposition of sample on the transfer tube walls and shorten the time lag between evolution and analysis; disadvantages are upward pressure and static charging. The use of CI has the advantage of avoiding all interface problems and of restricting the fragmentation of released volatile compounds. Therefore, this technique allows the identification of volatiles and the determination of their sequence of release even in complex decomposition reactions [118].

Limitations of the previously described techniques are also the inability to identify gas phase species that evolve from the sample but interact with the apparatus in some manner prior to entering the m.s. (condensation) and the inability to correlate exactly the measured weight loss with the m.s. ion signal, due to the variable time lag associated with transport of the evolved species to the m.s. This is overcome in the simultaneous thermogravimetry and modulated molecular beam mass spectrometry apparatus (STMMBA) [115].

In spite of all efforts, none of the aforementioned interfaces even though optimised, meets all the desirable features for an ideal coupling (Table 11). This is not surprising as optimal design of the interface ideally should take into account the sample characteristics.

5. Experimental

5.1. Sample requirements for polymers

Vacuum requirements for most mass spectrometers have originally promoted sample heating in vacuum (cfr. Table 7); however, controlled heating can be carried out equally well in an inert gas or oxidizing atmosphere. Sample requirements for TG-MS vary according to the amount of volatiles liberated and the sensitivity of the mass spectrometer for a given component. Moreover, as the temperature that corresponds to the maximum evolution of a fragment is particle-size dependent, there is a size requirement as well. When determining low level additives it is often quite necessary to weigh out as much as 100 mg; sample sizes of 3–6 mg are a usual acceptable compromise between efficient balance operation and overloading the mass spectrometer. For sample sizes <5 mg, problems associated with heat transfer and surface collisions are minimized; these samples are more amenable to maintaining a low system pressure and reducing bimolecular collisions. The pressure limit condition for the mass spectrometer implies that there is an upper limit for the product of the rate of heating, dT/dt, and the mass M of the compound to be decomposed: $dT/dt.\ M < C$, where C is dependent upon instrument and sample. This condition should especially be considered in case of kinetic studies and quantitative measurements [149].

For TG work it is generally recommended to use as little sample as possible within the limits of resolution of the microbalance. The homogeneity of a sample can sometimes limit how little sample can be used (e.g. in case of polymer blends). Powdered samples, of small particulate size, have the ideal form for TG studies. However, in polymer science samples are often also in the form of films, fibres, sheets, pellets, granules or blocks. The packing density should be as uniform as possible.

5.2. Operation mode

Table 12 describes a trade-off between minimizing pyrolysate condensation and maximizing sample temperature/weight measurement accuracy of several instrumental approaches of thermal analysis using mass spectrometry [4,69]. Having selected TG-MS instrumentation for polymer research, the next step required is to set the experimental conditions (Table 8) yielding the maximal information to the problem. Proper attention should be given to optimizing TG-MS conditions necessary for maximizing its discriminative power. In this respect it is good to remember the influence of experimental conditions on the shape and characteristics of TG curves, as recently stressed again by Hatakeyama et al. [150].

In compliance with the instrument and problem at hand the operation mode should be chosen:

integrated high vacuum in thermoanalyser and the mass spectrometer; or

atmospheric pressure in the thermoanalyser and high vacuum in the mass spectrometer.

A few of the most important variables that affect the composition of the resulting volatiles include the thermal degradation temperature, sample size and texture, the mode and characteristics of the TG step, environment and flow rate. The sample size may affect

Table 12
Qualifying features of techniques for thermal analysis using mass spectrometry [4]

Feature	EGA-MS [a]	TG-MS	TPPMS [d]
Temperature information	No	Accurate	Accurate
Weight information	No	Accurate	No
Condensation	No	Possible	No [e]
Pressure increases at degradation	Not prohibitive	Not prohibitive	Not prohibitive
Qualitative tool (fingerprinting)	Yes [c]	Yes	Yes
Mixture analysis	Prohibitive	Difficult [b]	Difficult
(Calibration for) quantification	Complicated [c]	Feasible	No
Monitoring of chemical changes	Sensitive	Yes	Yes
Reliable chemical kinetics parameters	With considerable caution [c]	With caution	Less useful
Oxidative degradation	No	Yes	No
Sequence analysis	No	No	Discriminates

[a] Direct insertion technique, solid probe design.
[b] Eased by TG-MS/MS.
[c] Powerful qualitative tool for analysis of additives in polymers [4] but can be used in quantitative manner [47].
[d] Ref. [10] describes the advantages of TPPMS over conventional TG; cfr. also Refs. [8,9,11,12].
[e] Requires intermediate buffer volume.

the nature of the reaction taking place during thermal degradation. Minor differences in temperature rise time, the final degradation temperature, and the duration of degradation can affect the volatile distribution and separation. The carrier gas can play a passive or active role and is an important variable in interlaboratory reproducibility. The influence of the various parameters on the evolved gas analysis has not been described in a systematic way.

Once the sample has been degraded the volatiles are swept by a flow of carrier gas into the mass spectrometer. It is here that the TG-MS experiment is most often compromised. The result is a substandard separation and reduction of available information content compared to that ideally contained in the volatiles. Especially loss of information from the higher molecular weight fragments may occur.

Depending on the pressure conditions of the thermogravimetric measurement a variable fraction of the atmosphere of the microbalance is introduced into the spectrometer (quantities $< \mathrm{ng\,s^{-1}}$). In the molecular regime (10^{-5}–10^{-3} mbar) the link between microbalance and spectrometer usually consists of a diaphragm (300 μm).

The first stage in the examination of a polymer sample of unknown thermal behaviour would be to perform a TG experiment, while recording sequential mass scans during any weight loss stages. This gives the development profile for the full gas stream. The gaseous products thereby identified may then be monitored continuously in the multiple ion-monitoring mode in which only a limited number of preselected ions are measured as a function of time. This scan mode has an inherently higher sample rate and reveals more detail of the course of the decomposition process. For the majority of applications, however, practically all masses are monitored up to a certain value. This results in voluminous data sets. A major difficulty in simultaneous TG-MS is data analysis of the acquired mass spectral information being a scan of 'fingerprints' of the evolved molecules.

Mass spectrometric thermal analysis cannot be done effectively without a computer. Software deals with the organization of the mass spectrometric measurement, the fast processing of the mass spectrometric peaks, the quick acquisition of time-averaged weight and temperature determination [51,151]. Software greatly determines the usefulness of the information generated [152]. TG-MS involves two distinct axes of information with significantly different time frames. For each sampled point along the thermogravimetric axis an entire mass spectrum must be acquired. The rate of data collection along the mass spectrometric axis far exceeds the sampling rate along the thermogravimetric axis. Utility of a full range mass spectrometry analysis requires that the rate of spectral generation be sufficient so as not to lose information along the thermogravimetric axis. The same applies to other hyphenated techniques, such as GC-MS [153].

TG-MS data are presented as temperature profiles of W, dW/dT, ΣI and I, where W is the sample weight, dW/dT the first derivative of the weight loss, ΣI the total ionization or sum of all of the ion intensities, and I the intensity at each m/z ratio; at total ionization ΣI must correspond with the shape of the DTG curve. Based upon the plots of ion intensity vs. temperature for all masses and known mass-spectral fragmentation patterns, in principle the evolved volatiles can be identified. Determination of the relative magnitude of the volatile products requires additional knowledge of mass discrimination in the mass spectrometer, the probability of ionization for each product and different flow rates through the pressure reduction system. Absolute abundance of the product is best estimated from the weight loss, requiring discrimination of weight-loss regimes for different volatile products.

5.3. Calibration and interlaboratory reproducibility

The major hurdle to be overcome before a technique gains acceptance within the analytical community and in practice is the achievement of interlaboratory validation. For this purpose, the specification and control of thermodegradative, interfacial and mass spectroscopic variables are necessary. Using reliable TG-MS equipment, standardization of the experimental parameters determines success of interlaboratory reproducibility. Failure to develop uniform reliable operational TG-MS parameters will hamper efforts at formulating and implementing quality control standards, using TG-MS equipment; such standardization is especially required in an industrial setting.

The key to proper use of TGA is to recognize that the decomposition temperatures measured are procedural and dependent on both sample and instrument-related parameters (Table 8) [154]. Considerable experimental control must be exercised at all stages of the technique to ensure adequate reproducibility on a comparative basis. For (intralaboratory) standardization purposes it is absolutely required to respect and report a number of measurement variables (cf. Table 8). ICTA recommendations should be followed [155] and should accompany the TG record. During the course of experiments the optimum conditions should be standardized and maintained within a given series of samples. For any particular TG-MS apparatus tests with model substances showing complete recovery of eluted components, and no significant delay in TG operations are required. Once the reproducibility of (quantitative) TG-MS analyses has been determined the stability of the system should also be monitored. In this respect much has still to be done. In fact, it is quite obvious from the missing details in the compilation of Table 7 that nowadays very often not even the essentials defining the TG-MS instrument combination are properly described!

Where (quantitative) data have to be extracted from a mass spectrum calibration is necessary in order to correlate the ion currents measured with the partial pressures or concentrations sought. Courtault [156] has critically considered calibration of TG, MS and the TG-MS coupling.

In cases where the MS data are calibrated in terms of the actual mass of component involved, an EGA system results. Such a calibration results from a correlation of the integrated peak area of a selected mass peak with the corresponding TG mass loss for a sample of known composition.

There is sufficient scope for good standard reference materials to optimize TG-MS experiments. The use of such representative materials would greatly enhance qualitative interlaboratory reproducibility. Only taking into account all critical sample-related parameters (such as standardized sample size, heat conductivity, etc., cfr. Table 8) one may hope for quantitative reproducibility. Accurate temperature calibration using the NIST-ICTA temperature standards [157] is common practice for DSC and DTA. Calibration of thermobalances is more cumbersome. However, these standards can be used for simultaneous instrumentation [58,158]. This is particularly important for TG kinetic studies and for accurate monitoring of percent volatility against temperature.

NBS traceable standard gas mixtures [114] or perfluorokerosene [144] are nowadays being used for mass calibration. Pavlath et al. [159] reported TG-MS calibration with model compounds, such as $NaHCO_3$ for water, in order to enable the quantitation of the signal. The TG(-MS) apparatus is often calibrated with calcium oxalate monohydrate; the dramatic illustration of the differences observed by Morelli [4] in comparing the thermal decomposition of calcium oxalate under vacuum with that obtained at atmospheric pressure with a N_2 purge is convincing evidence for the need of standardizing experimental conditions for interlaboratory reproducibility. The analytical community is strongly urged to take rapid action to guarantee the much needed *quantitative* reproducibility in view of validation of industrial problem-solving procedures.

Dependency of the mass change characteristics of a material on the experimental conditions employed, as illustrated by the marked differences in results obtained in polymer degradation using various thermal techniques (e.g. TG-MS vs. Py-MS) and by discrepancies between (TG-MS) data from various laboratories (cfr. e.g. Ref. [77] for PVC), does not really encourage interlaboratory comparison. While the former results may be rationalized, the latter are more worrying. Standardization will at least partly overcome these problems.

In the last decades efforts of the analytical TG-MS community have mainly been directed towards solving interfacial problems. While not all instrumental details are completely solved at this time, reliable TG-MS coupling systems have now evolved. Obviously, the appearance of TG-MS spectrograms should not depend on the particular construction of the interface. This would make interlaboratory and long-term comparisons of materials by TG-MS an uncertain exercise, restricting its utility at best to short-term intralaboratory comparisons, provided that the operator has calibrated his instrument and has adopted an optimized standard procedure for setting the experimental variables. TG-MS shares this drawback with Py-GC, where the appearance of the pyrogram depends on the composition, construction and condition of the GC column [160]. It is distressing to note that since the attention paid to short-term reproducibility by Smalldon et al. [61] no serious attempt has been made to report on the long-term intra- and/or interlaboratory reproducibility of the TG-MS coupling.

6. Requirements and potentials of TG-MS for the study of complex polymeric materials

The methods for analyzing change in a degrading polymeric material may be classified in several ways. Analytical methods may be divided into those which measure properties in the bulk phase of the degrading polymer substrate and those which measure the properties of volatile fragments. Methods may also be separated by whether they measure properties related to the changes in concentration of individual chemical compounds or functional groups.

Mass spectral methods of polymer analysis are twofold, namely, those which involve

> degradation of the material prior to analysis of the volatile fragments (e.g. TG-MS, TG-GC-MS, Py-MS, Py-GC-MS, laser Py-MS, SIMS, Py-FI-MS, Py-FD-MS); and
> vaporization/ionization of intact nonvolatile, higher molecular weight molecules into the mass spectrometer (e.g. MALD).

Potentially, a wealth of information may be derived [22,161], concerning:

1. molecular weight distribution and average molecular weight
2. fingerprint pattern for polymer identification
3. compositional analysis (sequence of monomeric units, length distribution and homogeneity)
4. branching, cross-linking, or other side-chain substitutions
5. copolymer structures or variations in the polymeric system; blends and compounds
6. identification of degradation products; outgassing phenomena
7. additives or impurities present.

In practice no single mass spectrometric (nor indeed any spectroscopic) technique can provide an answer to all these topics. Depending upon the ancillary separation method, such as GC, HPLC, TG and/or chemical modification steps, either off-line or in tandem, a problem is addressed. In case of (tandem) TG-MS, mainly items 2, 5, 6 and 7 may be investigated (whereas item 1 is the domain of the specialised technique of GPC and 3 and 4 of NMR, etc.). As for gathering information on such phenomena as cross-linking (topic 4), which is often introduced upon heating, TG-MS is not the method of choice in the absence of weight changes. Quite obviously, the extent to which MS will be applicable to the solution of a given problem will depend on the method of ionization employed, as illustrated above.

It should be realized that in combination with TG no mass spectrometric measurements are performed directly on the polymer; only evolved gases are detected and identified. Factors influencing component loss from polymeric matrices are volatility, rate of diffusion, solubility in the polymeric matrix, flow rate, temperature, ΔT, sample thickness, etc. Therefore, information about the polymeric matrix is obtained in an indirect way, and concerns especially the thermal stability, degradation mechanism and kinetics, performance behaviour, reactivity, and analysis of volatile additives, residuals, monomer occlusions and trace impurities. Proven performance and complexity of tasks (Table 13) in the characterization of (commercial) plastics, fibres, paints and other polymeric materials have made TG-MS a desirable analytical tool, in competition with methods such as Py-GC [160]. The technique is especially useful for samples which cannot easily be studied by spectroscopic means, such as carbon black-filled elastomers.

Single-stage TG-MS instrumentation is in principle not designed to identify, although it has this capability in simple cases (evolution of low m.w. gases, such as CO_2, CO, formaldehyde, etc.). Consequently, in its simplest form, the technique is more suited to degradation studies than to characterization of higher m.w. species (volatile oligomers, etc.). Total identification, as now more and more requested, requires more powerful means, such as TG-MS/MS, TG-MS/GC-MS, TG-GC-MS or TG-CT/GC-MS (Tables 13 and 14), in which only the first combination operates on-line in a simultaneous mode (μs time frame of the separation step between TG and the tandem mass spectrometer). Obviously, when no thermal information is required other techniques, such as HS-GC-MS,

Table 13
Complexity of tasks of TG-MS in polymer chemistry [a]

Challenge	Requirements	Competitive techniques
Qualitative analysis	Routine performance	EGA-MS
Detection of volatiles (residual solvents, degradation products) [b]	Speed	
Fingerprint identification	Standard references	Comparative techniques
Time-temperature resolution of polymer	Concurrent coupling	Hyphenated TG-techniques
Intercomparison of materials properties; product performance behaviour	Standardization; short-term reproducibility	
Thermal stability	Correlation with temperature	TG-FTIR
Characterization of reaction processes	Temperature control	TG-FTIR
Dynamics of liberation of volatiles	Temperature control	TG-FTIR
Identification of evolved gases	Consecutive coupling	Py-GC-MS, HS-GC-MS, TG-MS/MS
Thermal degradation mechanism	Knowledge of initial and final state; analysis of volatiles and residues	Solid state characterization [d]
Quantitative analysis	Calibration; linear and quantitative coupling	Total condensation methods
Outgassing of polymers [c]	Sensitivity; atmospheric conditions	HS-GC-MS, Py-GC-MS
Determination of additives [c]	Stability, sensitivity	Direct probe methods; extraction procedures
Compositional analysis	Complex aggregate analysis	NMR
Complex (gaseous) mixture analysis	Separation and identification	TG-MS/MS, HS-GC-MS
Industrial problem solving capability	Simulation of manufacturing and/or use conditions; pragmatism	No esoteric equipment
Quality criteria	Long-term interlaboratory reproducibility	Validated techniques
Kinetics	Kinetic parameters; degradation mechanism; interlaboratory reproducibility	TVA, STA-MS

[a] In order of increasing complexity.
[b] High temperature, relatively high concentration, low m.w. compounds.
[c] Low temperature, relatively low concentration, high m.w. compounds (low volatility).
[d] Characterization of aggregate changes in the bulk of the material (MW, MWD, CCD, etc.).

Table 14
Some selected principles of hyphenated thermal techniques

SD	SDD	SSD
TG-MS TG-FTIR, TG-DSC-FTIR DTA-MS TG-(DTA-DTG)-MS TEA-DT-MS Py-GC, TG-GC Py-MS, TPPMS DPMS TPF-MS	TG-FTIR-MS	TG-GC TG-CT-GC TG-GC-FTIR HR TG-MS Py-GC-FTIR
SI	**SDI**	**SSI**
(Py-MS)	(TG-FTIR-MS)	(TG-MS/GC-MS) (TG-GC-MS) (Py-GC-MS) Py-MS/MS TG-MS/MS

S = separation (thermally, chromatographically).
D = detection (spectroscopically, chromatographically), verification (retention times, etc.).
I = identification (fragmentation patterns)

IR, NMR, etc. may be called in for identification purposes.

For TG-MS analysis of unknown polymeric materials the following considerations apply [151]:

1. All ions in the range where volatiles may arise have to be monitored since a priori the characteristic products are unknown;
2. Minor and major products are to be monitored simultaneously when insight is to be gained in the degradation mechanism. Since it is necessary to measure the highest value of the main components together with the smaller values of an important minor component intensities of the measured ions may differ by more than 4 magnitudes;
3. The time available for the mass spectroscopic measurements is limited. Practically, in dynamic experiments the intensities of the monitored ions have to be measured at least every 0.1 s of time interval. Usually heating rates of 10–20 K $\min^{-1}$ are applied which means a time limit of 2 s for the acquisition and storage of the monitored quantities. Present scan speeds (10 scans/s) are well within this limit.

It is to be considered that the carrier gas strongly dilutes the products to be measured. Thus the concentration of the minor products may be below 1 ppm; high gas flow rate and low sample mass are needed for elimination of diffusion control and secondary reactions. However, due attention should be paid to the fact that low mass samples of polymers may not be representative.

Table 15 lists the inherent advantages of the TG-MS technique [97,102]. Restrictions on atmospheric conditions imposed by the vacuum requirements of the mass spectrometer can place a limitation on mass spectrometric analysis. With TG-MS, however, the atmosphere can be varied according to the needs of the experiment through the selection of appropriate purge gases. For all practical purposes, the sample environment remains constant for the duration of the experiment; this minimizes the effect of varying atmospheric conditions caused by fuel consumption, which can be a factor in batch-type thermal degradation studies.

The time between product evolution and introduction into the mass spectrometer ion source is short. In the early developments, with degradations or pyrolyses conducted in a static system, especially when a solid was involved, the time for a volatile product to

Table 15
Advantages of TG-MS coupling

High detection sensitivity
Detailed fingerprinting (characterisation technique)
Ability to control degradation atmospheres
Relatively short dead-time
Short analysis time in conjunction with computerized data handling facilities
Simultaneous molecular analysis
Discriminates between various TG weight change processes
Provides basic information on mechanisms of thermal degradation
Provides information about the order of product evolution
Evolved gas evolution can be regulated by varying experimental parameters
Allows evaluation of kinetic parameters
Complements other thermal methods (such as DSC and TMA)
Facility for revealing subtle differences in polymer composition
Identifies trapped solvents, unreacted reagents, trace impurities and volatiles released during curing or degradation
No sample contamination
Applicable to a wide variety of solids
Small and large masses
Minimal sample preparation

reach the ion source could be in the order of minutes or longer; nowadays this is achieved in some 50 ms.

The limitations of the TG-MS method [102] are summarized in Table 16. Restrictions to quantitative MS analysis arise from sublimation, mass discrimination, pressure, stability, drift, variations in flow, etc. The mass spectrum of the polymeric substrate cannot be obtained, only its thermal degradation products can be. Other limitations are that the samples must remain in the hot zone until degradation temperatures are achieved and that TG-MS suffers from problems with vapour fractionation and condensation. Post-degradation products, such as H_2 and CH_4, may pertain to degradation of the intermediate char rather than to the original sample.

TG-MS is applicable to a wide variety of solids (organics, inorganics, polymers) and allows revelation of subtle differences in structure (e.g. in the compositional character of polymers). Although evaluation of kinetic parameters of thermal degradation has improved as compared to TG experiments predictions concerning long-term thermal stability are still dangerous ground in view of extrapolation in time and temperature (lack of sufficient reproducibility), diffusion, etc.

Table 16
Limitations of TG-MS coupling

Limited identification of evolved gases and residuals
Complicated, concurrent thermal degradation processes difficult to sort out
Difficulty of quantitative analysis
Due attention for sample inhomogeneities at small sample size
Standardization of experimental TG-MS parameters still to be achieved
Dependency on gas flow rate, sample size and heating rate
Insufficient interlaboratory reproducibility
Problems with vapour fractionation and condensation difficult to overcome
Cost of interface (depending on application)
Less cost effective than Py-GC

7. Comparison of TG-MS to related techniques

Failure of the analytical community to develop uniform TG-MS parameters has led to unsatisfactory reproducibility. Where the appearance of TG-MS spectrograms depends on the construction of the interface, the utility of the technique is restricted to short-term intralaboratory comparison just as in case of PyGC [160].

TG-MS is ideally suited to reveal differences in pressure behaviour during thermal decomposition of materials. This has been illustrated by Mol [129] in TG-MS analysis of toluene diisocyanate (TDI) and methylene bis-4-phenol isocyanate (MDI)-based polyurethanes, where the observed greater increase in pressure for the TDI polyurethane than for the MDI derivative indicates a higher loss of low molecular weight fragments. This is not possible to deduct from the TG curves alone. Such indications are of great importance when evaluating kinetics or considering mechanically similar materials for heat sensitive applications.

From Table 3 it is evident that spectroscopic methods ideally follow degradation reactions, that is, by measuring directly changes in the functional groups as they take place in the degrading polymer. Fig. 1 indicates that the growth rate of TG-FTIR now exceeds that of TG-MS. This situation differs from the previously described comparison in 1991 [94].

Although the suggestion for using FTIR in EGA was first made by Low [162] in 1967, and while experimental results obtained from coupling of TG and FTIR spectroscopy were reported in 1981 [163], dedicated TG-FTIR instruments were not commercially available until 1987 [164–166]. Up to that time most work on the identification of evolved gases from TG had been in the TG-MS combination and reports on polymer studies using hyphenated TG-FTIR were relatively scarce [44,167]. The commercial availability of FTIR systems capable of highly sensitive detection and completely automated sampling and data manipulation, have brought TG-FTIR polymer analysis with all the advantages of classic IR spectroscopic interpretation. TG-FTIR has become a very popular, versatile, cost-effective and informative instrument for modern polymer analysts concerned with structure-/mixture compositions, and degradation/reaction mechanism studies. While Fig. 1 confirms the role of IR as a leader in general polymer and materials characterization, it is equally true, however, that for unambiguous identification more powerful methods are required (Table 14).

Advantages of FTIR detection are: functional group identification and specific compound analysis on the basis of vibrational spectra; simultaneous spectral information on many species; continuous scanning of effluent from direct thermal processing; quantitative analysis (±10%) using proper calibration from well-known absorption coefficient information for IR-absorbing compounds [168]; reference spectral libraries for over 250 000 species. The technique is especially useful for smaller molecules where the high specificity of strong IR absorption bands makes up for the relatively low sensitivity of IR detection. It is rather difficult to use IR to analyze mixtures of compounds with similar functional groups or mixtures of weak IR absorbers in the presence of strong absorbers. FTIR cannot detect gases without IR absorbance (e.g. O_2, N_2) and does not readily distinguish hydrocarbons above C_3H_8. TG-FTIR configurations do have some advantage over TG-MS in the handling of high-boiling oligomers and heavy tar products which can be analyzed as fine aerosols in a gas stream [166,169], and in distinguishing structural isomers [94]. The power of an on-the-spot TG-FTIR technique, in which the IR beam is focused directly into the TG system, was illustrated by the detection of a high molecular-mass component, namely octabromodiphenylether (m.w. 801 Da [40]); similar species have never been detected in TG-MS experiments.

TG-FTIR allows quantitative analysis to be performed (calibration necessary) even when more than one component of interest pyrolyzes during a single weight loss [170]. TG-FTIR in polymer degradation is described in Refs. [40,171–174] and is reviewed by Mittleman et al. [154].

On the other hand, MS requires special high vacuum capabilities and more stringent operating conditions but exhibits detection levels which are several orders of magnitude more sensitive than FTIR (pg and sub-μg ranges, respectively). In some conditions, MS results can be misleading because of secondary products resulting from ion fragmentation [64]. Like IR, mass spectrometry has the capability of analyzing simultaneously and independently a number of volatile components from a weight loss step. Yet, MS identifies each individual compound and not a class of compounds of the same functional group characteristics. Both MS and FTIR need the support of a full spectrum vapour phase library.

As the strengths of MS and FTIR complement each other [94], for complex degradation studies the linking of TG to both an MS and FTIR spectrometer (either in parallel or in tandem) will enable more complete evaluations to be accomplished. The distinction in the use of the two techniques is not very strict, both drawing an equal share on polymer applications [94,154,173,174]. As to the ability to identify evolved gaseous species the specificity decreases from unambiguous to not highly specific in the order TG-MS/MS > TG-FTIR-MS > TG-MS > TG-FTIR (cfr. Table 14). Despite the utility of these techniques, a distinct disadvantage is that very low concentration components may be masked by higher concentration interferants; in such cases, devices based on thermal desorption (absorbent packing, static headspace sampling, cryogenic trapping) may prove useful.

Discontinuous TG-GC, TG-GC-MS and TG-Tenax-TD-GC-MS [175] are obviously inherently slower than TG-MS. The possibilities are improving though by using a fast column and an accurate fast sampling valve. However, only the fragments that are non-reactive, thermally stable, and volatile can be analyzed by GC, whereas MS has none of these limitations.

McClennen et al. [169] have shown the enhanced capability of the doubly hyphenated thermogravimetry-based analytical techniques TG-IR-MS and TG-GC-MS for detection of minor products. Quite obviously, neither TG-GC-MS [33,72,91,169,176–180] nor TG-GC-FTIR [169,181] provide continuous monitoring of evolved gases. A major disadvantage in routine analysis by these techniques is the throughput of samples; the analysis time is determined by the longest retained compound. The hybrid instrumental combination TG-MS/GC-MS (with interchangeable TG-MS and TG-GC-MS operations) has been described and used for the study of coal [178] and ethylacrylate/ethylhexylacrylate and ethylene/maleic anhydride copolymers [182].

Rapid growth is expected for techniques of materials characterization by separation of gaseous components and their subsequent detection and identification (Table 14), with extensions into such systems as STA-FTIR [64,183] and STA-FTIR-MS [64].

8. Applications of TG-MS in polymer science

There is a clearly defined industrial need for reliable and fast methods to study the stabilisation and characterization of polymeric materials, to obtain knowledge on their properties and behaviour, the effects of modifying structure, additives and processes to engineer the most suitable material for any given application. Also, there is an increasing (environmental) need to study the effects of ageing, the thermal stability, the degradation processes and the products of decomposition under a wide range of conditions. During synthesis and polymer processing (compounding and/or injection moulding) polymers are often brought in the molten state whereas during their life cycle polymers are subjected to thermal and thermooxidative processes and to light (UV resistance). More often than not the polymeric material is a blend or compound and charged with a variety of additives and fillers (e.g. flame retardants). Consequently, in such complex systems one may expect chemical interactions (e.g. between some of the components of the additive package) and physical phenomena (migration, blooming, crystallization, sublimation, etc.) to occur. It is obvious that TG-MS is a very suitable tool for elucidating phenomena involving a mass change accompanying the aforementioned processes.

A TG-MS system generates large volumes of information on the composition of the evolved gases, their relative amounts, and temperature-release profiles. By combining the evolved gas information with the thermal analytical data, a fairly complete characterization of the decomposition path for a wide variety of materials can be obtained.

TG-MS has been used in a wide variety of qualitative and quantitative problem-solving cases:

a. Thermal stability and degradation studies

testing of thermal and thermo-oxidative degradation of polymers
testing the close-response relationships of additives (stabilizers)
identification of degradation products
elucidation of thermal degradation mechanisms (random chain scission, end chain scission, chain-stripping and crosslinking)
intercomparison of materials properties
characterization of insoluble polymers.

b. Structural characterization and chemical analysis

identity, equivalency and structure of polymeric materials
fingerprint identification (classification of competitor products)

compositional analysis for identification of components in blends of additives, etc.

c. Reactivity and curing

shortcomings in the synthesis route
characterization of cure processes

d. Product development

optimization of production processes of polymeric materials
quality and batch-to-batch control
determination of end-use conditions
performance behaviour
product recycling

e. Analysis of evolved gases during synthesis, processing and recyling

outgassing phenomena
trace solvent, monomer inclusions or impurity analysis
analysis of additives or processing agents
determination of the effect of stabilizers
corrosion
toxicology of combustion
environmental impact of polymer degradation
health protection studies
workplace safety studies

f. Kinetics

chemical reaction kinetics
life-time predictions

g. Quantitative analysis

determination of the composition of copolymers, blends and polymer mixtures.

Polymeric studies represent by far the largest application area of the recognised thermal techniques [184]; Table 17 refers to the pertinent TG-MS studies. As may be seen the majority of the work described involving polymeric materials seeks to elucidate the mechanism of complex multistaged degradation reactions and basic combustion phenomena, or to characterize the (micro)structure. Reports on product development and formulation, reactivity and curing, as well as quantitative studies are less numerous. This is not surprising and in agreement with Table 13, which shows increasingly demanding applications for TG-MS, starting from simple fingerprint identification, solvent retention studies, detection of degradation products, to the characterization of advanced polymers for high temperature, crosslinking or inter- and intramolecular reactions resulting in little weight change, early stages of degradation ($\leq 5\%$ weight loss) often corresponding to significant losses in mechanical properties (outgassing, concern for environment) and complex mixture analysis in industrial problem solving with high quality standards. It is easily understood that TG-MS is the method of choice in matters requiring determination of the dynamics of liberation of evolved gases (correlation with temperature); on the other hand, HS-GC-MS and Py-GC-MS are preferred (amongst others) for merely determining which compounds evolve (identifying power).

Table 18 lists the broad variety of polymeric materials sampled by TG-MS in various forms (powder, granulate, film, fiber, etc.); similarly, Table 1 of Ref. [4] indicates examples of polymeric systems studied using TPPMS techniques. Thermogravimetry and coupled TG-MS for chemical analysis of polymers

Table 17
TG-MS studies of polymeric materials

Topic	References
Thermal stability/degradation mechanism	[77,78,91–93,102,107–109,119,123,129,134,142,144,147,156,185–198,202,279]
Structural characterization, identification	[31,61,90,124,129,136,187,191,200,201,203–205,280,281]
Reactivity, curing	[31,58,86,124,125,201,206–208,216,282]
Product development/formulation	[24,64,67,119,125,188,205,206,210]
Analysis of volatiles, additives	[51,57,62,83,97,107,120,127,141,147,189,192,201,209,215,217,279]
Reaction kinetics (activation energies)	[30,102,103,117,128,137,142,187,188,190,193,205,206,220]
Quantitation	[31,90,136,156,205]

Table 18
Classes of polymers studies by thermogravimetry – mass spectrometry [a]

acetylene-terminated-bisphenol-A [102,281]
acetylene-terminated sulfones [102]
acrylics [61,109,126,128,137,190,204]
acrylonitrile [61] *
amides [220], acrylamide [97], aromatic amides [95], nylon 4,6 *, star nylons *
aramides [206]
aryl ether ether ketone [186]
benzimidazoles [134]
benzoxazoles [185]
biopolymers [194,195]
butadiene [136] *
carbonates [192] *
carbosilane [125]
cellulose [159]; cellulose acetate [124] *
coal (bituminous vitrinite) [121,283] *
cyclic aromatic hydrocarbons [284]
epoxies [207] *
esters [94,108,129] *
ethers [107,144,200]
ethylenes [272] *
ethylene oxide [197,272] *
flame retardants (DAMP, DMMP, TCEP, TCPP) [279] *
fluorocarbons [142,192,193]
fluoroolefins [127,142,193]
gums [96]
imides [31,102,188], aryl-alicyclic imides [78]
isoprenes [210]
liquid crystalline polymers [108]
LLDPE [119] *
methylene sulfide [97,131]
methylmethacrylates [123,131], t-butylmethacrylate [109,119,123]
methylphenyl silicone elastomers [189]
organometallics [191,198]
oximes [203]
oxymethylene [128,131] *
phenolics [135,201,207] *
o-phthalate alkyds [61]
propylene *
saccharides [141,263]
silanes [64] *
siloxanes [198,285] *
styrenes [128,131,136,152,169,220] *
urethanes [120,129,137,217] *
vinylacetate [90] *
vinylalcohol [156] *
vinylchlorides [65,67,77,92,117,120,128,131,137,156,216,220,269,273] *
vinylpyridine [208]
wool [57,273]

Copolymers/blends/composites/mechanical mixtures
acetal-tetrafluorethylene [31]
acrylamide-co-acrylic acid, acrylamide-co-sodium acrylate [196]
acrylate copolymer [123]
acrylic acid-alumina [30]

Table 18
(Continued)

acrylonitrile-butadiene-styrene [129] *, acrylonitrile-styrene [137], acrylonitrile-vinyl [61]
adipic acid-uranyl nitrate hexahydrate [280]
amic dialkylamide/imide [205]
bismaleimide composites [215]
chlorosulfonated polyethylene elastomer [24,286]
divinylbenzene-styrene [202]
elastomer blends (NBR/SBR/BR) [93,126] *
ethylacrylate-ethylhexylacrylate [182]
ethylene-co-vinylalcohol [150]
ethylene-hexene [272]
ethylene-maleic anhydride [182]
ethylene-propylene rubbers [190], ethylene-propylene-1,4-hexadiene (EPDM) [126] *
ethylene-vinylacetate [51,90,272] *
hexafluoropropene-tetrafluoroethylene [192,193]
maleic hydrazide methyl vinyl ether [97]
melamine-formaldehyde composites *
methylmethacrylate-styrene [91], – tetrafluorethylene [90], – vinylchloride [131] *
phenol-formaldehyde [63,86,190,273], phenol resins [216] *
phenol-formaldehyde/hexamethylene tetramine [58,282]
phenolic resole resin (Methylon 75108) [124]
polypropylene/melamine [83]
PVC/PE/PP/PS/PA6 [117] *
recycling material *
SMA *, SMI *
styrene-butadiene [51,136] *, – isoprene [169], – phenylene oxide [192]
styrene-isoprene-styrene (Kraton SIS triblock polymer) [124] *
toner resin [209]

[a] Polymers (non-biological) marked with * are unpublished work from the authors' laboratory.

have previously been reviewed [44,102]. The limitations of particular TG-MS couplings must be borne in mind when considering a given application. The accuracy of simultaneous TG-MS measurements is much higher than the homogeneity of the industrial products and this technique will therefore detect impurities.

8.1. Thermal stability/degradation mechanism

Thermal stability is a most critical property of any polymeric material; temperature-dependent changes set a limit for heat exposure and determine durability. As almost all thermal degradation reactions of polymers occur at temperatures at which the resultant products are in the gaseous state, evolved gas analysis has become an indispensable tool in polymer analysis.

The advantage of TG-MS quantitative measurement of individual evolved gaseous species is considerable when compared to TG which measures only total volatiles. In the latter case the measured property reflects aggregate changes in the bulk of the material (Table 3). Obviously, TG-MS concentrates on sample degradation mechanisms initiated by thermal means rather than those brought about by mechanical action (friction) and electromagnetic radiation, which restricts the field of application. The complexity of the problem increases when oxygen is present (thermo-oxidative degradation) but evolution of CO_2 and H_2O is not really usable for mechanistic considerations; instead, they are somehow related to stability. Quite clearly, both the chemistry and physics leading to evolved gas species are detected by TG-MS (Table 1).

Polymer degradation and thermal behavioural studies have been reported for fluorinated polymers for transparent canopy materials applications [185], PEEK [186,187], PVC [77], polyimide films [188], polymeric composites (such as ethylene–propene rubber) and elastomers [189], synthetic and carbon fiber reinforced phenol–formaldehyde copolymers [190], organometallic polymers [191], polylactone [192], PTFE and HFP-TFE copolymers [142,193], cellulose acetate [93], biopolymers (such as carbohydrates and cellulose) [147,194,195], aliphatic-aromatic polybenzimidazoles [134], polyurethanes and polyesters [108,129], copolymers of acrylamide and acrylic acid [196], etc. Time-resolved analysis of the decomposition of poly (*tert*-Bu methacrylate) UV stabilized by Tinuvin 234 was reported as a forensic science application [109,110]. Jones et al. [197] determined the stability of poly(ethylene oxide) and PEO-based solid electrolytes. The oxidation/volatilization behaviour of a polyether was described by Lever et al. [107]. Usually the work aims at the identification of the degradation products [147,191] and understanding of scission reactions [186], at the elucidation of complex degradations [196], at intercomparison of material properties [109,142,193] or is a suitability test for certain applications [185,188].

Especially for routine thermal investigations of high-melting polymers reliable coupling of the various TG-MS system components is essential. Thermal degradation products of high-melting materials, such as LCPs, may easily foul the interface or recipient, leading to memory effects and/or physical obstruction. Dufour et al. [108] have studied the aromatic copolyesters Vectra® A950 and Xydar® SRT-500 by means of isothermal and dynamical measurements in a coupled TG-MS system. These materials are not greatly accessible to the classical analytical spectroscopical methods owing to their complex composition, insolubility and high chemical and thermal stability. Dynamic TG-MS measurements show that the degradation process of Vectra® A950 takes place mainly as one step; $(\delta G/\delta T)_{\max}$ is reached at 816 K, as opposed to 837 K in case of Xydar® SRT-500. Results of various dynamic TG and DTG experiments show that in spite of rather similar $(\delta G/\delta T)_{\max}$ values thermal decomposition of Xydar® SRT-500 begins at much higher temperatures (Table 19). This complies with the stronger interactions between the Xydar® polymer chains.

Isothermal TG-MS measurements at temperatures well exceeding the DSC melting points (i.e. above injection moulding and/or compounding temperatures) were made to gain insight into the processing stability of these LCP materials. In view of the high thermal stability of the polymers an isothermal run time longer than the normal average residence time of the polymer melt in the cylinder of an injection moulding machine was used. Vectra® A950 is exceptionally stable even at 613 K (isotherm), a temperature exceeding that of normal injection moulding conditions, which confirms the excellent stability of the polymer. The measured products of degradation depend on the manner in which the degradation is carried out. Vectra® A950 can be kept for about 20 min at up to 70 K above its melting point before significant decomposition is detected. After initial pyrolysis and continuous CO/CO_2 evolution as well, Xydar® SRT-500 is highly thermally stable, but a limit is reached at about 713 K (60 K above m.p.) when C–C bond degradation sets in. Xydar® SRT-500 should not be processed above this temperature. Investigations of the thermal degradation of commercially available LCP samples prove the use and applicability of a combined TG-MS method for on-line control of the polymer thermal degradation process. A combination of these techniques on the same samples greatly improved the qualitative interpretation of TG curves.

Like LCPs, organometallic polymers are difficult to characterize with other methods than TG-MS as they are also only sparingly soluble. Carraher et al. [144]

Table 19
Results of dynamic TG and DTG measurements

Material	Temperature (K) at which a % weight loss occurs					T(K) at $(\delta G/\delta T)_{\max}$.	Ash content at 1173 K (%)
	$a = 0.1$	$a = 1$	$a = 5$	$a = 10$	$a = 20$		
Vectra® A950	666.9	743.3	790.5	802.0	813.5	816	38.7
Xydar® SRT500	732.2	787.9	813.5	823.9	834.3	837	37.2

have examined the heat stability of titanium polyethers (UV stabilizers for exterior coatings) by continuous monitoring of the evolved chemical products; also polysiloxanes were studied by means of TG-MS [198]. In both cases the site of least stability can potentially be identified.

Decompositions studied by TG-MS systems are usually continuous processes. Discontinuous processes, for example, explosions, are seldom examined by thermobalance systems, although a TG-MS study of a pyrotechnic system has recently been reported by Charlsley et al. [39].

Also *T*-jump/FT-IR spectroscopy provides insight into chemical and physical processes where a high heating rate exists, as during ignition, combustion or explosion, as illustrated on organo-azide polymers by Brill et al. [199].

8.2. Structural characterization

Knowledge of the constituents in a commercial polymeric material may be needed for the following applications:

1. verification of composition in production materials;
2. analysis of competitive or otherwise unknown materials;
3. investigation of manufacturing problems that may arise from raw material errors;
4. studies of industrial product quality or cost.

TG-MS also provides information on the identity, equivalency and structure of polymers, such as large cyclic polyethers [200], phenolic resins [201], triblock polymers [124], organic sizings [187], high temperature polymers [202], organometallic polymers [191], titanium polyoximes [203], etc. The characterization of oxidative and nonoxidative degradation reactions of highly crosslinked divinyl benzene–styrene copolymers has been described [202] and closely related polymeric materials have been compared [61]. The characterization of such materials is of interest in widely different fields, such as industrial troubleshooting and forensic science [61,109]. In crime investigations, a significant limiting factor is frequently the quantity of the material available for analysis. In this respect, TG-MS has provided more detailed information than TG on a set of 27 commercial acrylic fibres, even on samples two orders of magnitude smaller (10 μg) [61].

The thermal characteristics of atactic and syndiotactic poly(acrylic acid) differ significantly with regard to the thermal stability, that is, the temperatures at which maximum H_2O evolution (due to anhydride formation) and CO_2 evolution (due to anhydride decomposition) occur in TG-MS experiments [204]. These differences may be a direct consequence of tacticity or possibly an indirect effect due to enhanced hydrogen bonding in the syndiotactic polymer. Also the TG-APCIMS system used by Dyszel [136] has proved to be sensitive to conformational changes in the polymer system, as demonstrated by the observed differences between the mass intensity ratio behaviour of *cis* and *cis-trans* polybutadiene.

One of the most useful applications of coupled TG-MS is compositional analysis of unknown complex materials. Chiu and Beattie [90] have made use of a sampling tube interface for quantitative analysis to determine the composition of a coating (43% PMMA and 56% PTFE) with excellent correspondence between TG and MS results. Quantitative results were also reported for ethylene/vinylacetate copolymers [90], a polyacetal resin [31], poly(amic dialkylamides) [205] and styrene–butadiene rubbers [136], all using TG-MS.

Polymer blends represent a large class of valuable materials which are difficult to evaluate by conventional TG and which, therefore, represent a considerable opportunity for HR TG [106]. Polymer fibres, frequently blended together with natural fibres to make fabrics, thread, or yarn, constitute another area which may benefit from HR TG-MS. The technique should also perform better than TG-MS in generating 'fingerprints' that facilitate comparison of competitive products or checking batch-to-batch in formulation.

8.3. Reactivity/curing

Thermosetting polymers and their composites are being used increasingly in high temperature applications. The temperature range of many of these applications has increased to the point that improved thermosets are required to meet the design specifications. These improvements are usually accomplished through alteration of the curing cycle, and/or the use of coupling agents, control of morphology during processing, reinforcement, etc. Important facts to be determined are the types and quantities of volatile gases given off during a cure reaction. TG-MS is then a most powerful and pragmatic tool for characterizing the effect of these various changes on the performance of thermosets.

Several reports emphasize the use of TG-MS in problems connected to chemical reactivity and the characterization of cure processes (e.g. solvent loss, deblocking of protecting groups and evolution of condensation reaction products). Examples are the thermal crosslinking reaction of aramids [206], curing of a polyimide prepreg [31], the analysis of a phenolic resin prepolymer and its curing and thermal degradation products [201], the chemistry of an epoxy-phenolic magnetic disk coating [207] and polymer–Cu interactions in the preparation of ultrafine copper particles in poly(2-vinylpyridine) [208]. Curing of glass-reinforced phenol–formaldehyde resin was described by Henderson [86].

8.4. *Product development/formulation*

The industrial problem-solving capability of TG-MS (Table 13) is highly valued. Holzapfel [209] has used TG-MS to define moulding conditions (T, t) for polymeric material in order to minimize degradation during processing of both the polymer and the added cross-linking agent triallylisocyanurate (TAIC) in a toner for high performance laser printers. Panke [123] has verified the effect of oxygen concentration on the processing temperature for injection moulding of PMMA. Determination of use conditions is an important excuse for having recourse to TG-MS, as in case of rigid-rod polymide films for micro-electronic applications [188]. Indeed, outgassings and degradation properties of engineering plastic products are important quality criteria for the E&E industry defining maximum use temperature and life time [209].

Both the ability to recycle and toxicological problems have been motivations for investigating the thermal degradation of PVC and post-chlorinated PVC by means of TG-MS [77]. It was shown that the process is more complex than just dehydrochlorination. A TG-DTG-DTA-MS study of PVC phone cable coatings containing di-(2-ethylhexyl)phtalate (DDP) as a plasticizer has given insight in combustion toxicology [67].

The suitability of TG-MS for optimization and batch-to-batch control of rubber recipes have been described by Möhler et al. [62]. TG-MS has also been used to characterize polymer derivatives as fuel oil additives with respect to the propensity to volatilise or oxidise under end-use conditions.

Keen et al. [210] have studied the controlled release of the volatile antioxidant butylated hydroxytoluene (BHT) from cross-linked alginate matrix particles. TG-MS results demonstrate that controlled release can be successfully achieved (i.e. BHT is retained beyond its normal evolution temperature); polyisoprene rubber is more resistant to oxidation when protected by the controlled release antioxidant which acts as a thermal stabiliser of the capsule matrix.

TG-MS data were also used to determine the maximum in the rate of the imidization process in poly(amic dialkylamides) [205]. Also, the synthesis of thermally crosslinkable rigid-rod aramids was accompanied by TG-MS exploration; all cured polymers were stable up to 420°C [206].

In the field of product development the thermal conversion of poly(carbosilane) precursors into ceramics [125] is worth mentioning; Redfern et al. [64] report on an STA-MS study of a polysilane ceramic precursor. Tsuneto et al. [119] have analysed evolved gases in a process for removing binder polymer (polybutylmethacrylate and LLDPE) from ceramics obtained by injection moulding.

8.5. *Analysis of volatiles, additives*

Knowledge of compounding ingredients is needed for a number of applications [211]:

The verification of ingredients in compounded stocks;
Reconstruction of formulations in unknown materials;
The investigation of manufacturing problems;
The identification of odorants or irritants that evolve from polymeric materials during processing or use;
Studies of product quality.

The identification of these ingredients in a compounded polymer is a difficult analytical task which is made complex by a number of factors:

1. wide variety of additive types, varying greatly in molecular weight, volatility and polarity;
2. lability of many additives;
3. compounding of complex mixture of additives;
4. low organic additive concentrations (< 1–5%).

As a result of their limited volatility, identification of organic additives in polymers by using TG-MS is considerably more difficult than that of residual volatiles. Actually, TG-MS is an ideal technique for identifying residual volatiles in polymers. The detection of residual volatiles (and of other impurities) can often yield clues as to manufacturing processes.

During processing of polymeric materials, especially at elevated temperatures, outgassing of initially present low molar mass products, possibly accompanied by degradation products, may occur, causing deterioration of the properties of the material. Outgassing phenomena may also be related to mould contamination and reprocessability, suitability for finishing processes (e.g. glueing, welding, lacquering and plating), to product lifetime, admissable temperatures for use, contact and environmental contamination in product applications, or may concern toxicological and aesthetic aspects [212,213]. For manufactured plastics flammability and toxicology are of great concern: using a programmable oven Moncur et al. [13] have reported a TA-MS survey (without gravimetric measurements) of aerospace materials for potentially toxic substances. The study of outgassing phenomena has also been found to be very useful for identification of components that are responsible for environmental stress cracking (ESC) of plastic products. Through outgassing experiments using TG-MS and related techniques, harmful components causing ESC can be detected and identified [41]. Also problems such as surface crazing, bubble formation, and chemical degradation of the polymer can sometimes be caused by residuals.

Data concerning evolved gases are important in the evaluation of the performance of polymers in their interaction with electric contacts and semiconductor elements and may determine the best material of choice for a given application. In the TG-MS study of the thermo-analytical behaviour of toners (polystyrene–acrylate, polyester or epoxide) it has been important to study the outgassing behaviour in relation to the detection of corrosive or toxicologically suspect substances [209]. The thermal degradation of the vulcanization accelerator TMTD (tetramethylthiuramdisulfide) in rubber has been studied with TG-DSC-MS [62]. TG-MS couplings are increasingly used by the rubber industry especially since aromatic plasticizers are toxicologically suspect.

In many cases, such as in the determination of highly volatile materials (e.g. moisture in nylons or in polysaccharides [141]), or of residual solvents or plasticizers (as in polyvinylbutyral) [214], use of TG-MS is requested. Specifically, there are reports on the entrapment of curing volatiles in bismaleimide laminates [215] and elastomers [189], on the detection of a curing agent (dicumylperoxide) in EPDM rubbers and of bromine flame retardants in electronic waste [83], of plasticizers such as bambuterol hydrochloride [57] or triphenyl phosphate and diethylterephthalate in cellulose acetate [147], on solvent extraction and formaldehyde loss in phenolic resins [201,216], and on the evolution of toxic compounds from PVC and polyurethane foams [120]. PU foam containing the flame retardant tetrakis (2-chloroethyl)ethylenediphosphate decomposes in an oxidative atmosphere at standard pressure in one rapid reaction whereby several highly toxic species are formed; the TG-MS detection limit of this flame retardant was determined [217]. The most striking fact is the very early generation of vinylchloride from the flame retardant, while HCN is produced at much higher temperatures.

Comparison of the thermal stability of various polyurethanes illustrates the use of TG-MS in the evaluation of similar materials for heat sensitive applications. The presence of impurities and additives such as PVC as a fire retardant in polyurethanes has also been detected by means of TG-MS analysis [129].

In other applications the pattern of evolution of styrene, butadiene and acrylonitrile as a function of temperature has provided a unique way for classifying different types of ABS. The loss of the antioxidant BHT was also detected by MS preceeding ethylene-vinyl acetate copolymer degradation [51]; BHT was identified at a concentration level of 20 ppm.

Kaisersberger et al. [83] have reported detection of nitrosamine precursory compounds during rubber vulcanisation (originating from vulcanisation agents) and the determination of toxic or environmentally damaging exhaust gases during technical burning processes (polycyclic aromatic compounds, PCB, etc.).

Degradation of both impure polymethylene sulfide (containing residual monomer or solvents) and samples of high purity have allowed to propose thermal and oxidative degradation mechanisms, to identify the primary and secondary degradation products, to determine the effect of various (phenolic) stabilizers in competitive type analyses and to establish conditions for efficient solvent removal and the thermal conditions required for the evolution of specific products. An example is the determination of the temperature required for the selective generation of water and ammonia from polyacrylamide [97].

Additive effects on the thermal stability of fuel oils have also been assessed with TG-MS [107]; the effect of impurities on thermolysis of a variety of polymers has been reported [192].

The power of TG-MS is illustrated by the identification of fifteen volatile products in polyimide resins [102], amongst which unwanted solvents, indicating shortcomings in the synthesis route.

The sensitivity needed for identification of additives is, in general, greater than that needed for identification of volatile pyrolyzates. In comparing different means of introducing a polymer into a mass spectrometer for additives analysis, Lattimer et al. [211] consider that in vacuo direct probe introduction is usually preferable to external heating (continuous flow or molecular leak) devices. The main reasons are:

(a) the vacuum allows components to desorb at lower temperatures,

(b) there is less chance for components to decompose or condense on the walls in transit to the ionization region.

Consequently, higher molecular weight (less volatile) additives can generally be detected more readily with the introduction of direct probe.

Bloom identification, an important practical problem in rubber analysis, can best be accomplished by *direct* analysis using desorption ionization methods (FD, FI, FAB).

Although the combination of TG and MS allows assessment of effects of additives on the thermostability of polymers, both at processing temperature and in conditions of use, this does not mean to say that this method could be a substitute for others defining the ultimate lifetime for commercial utilization of polymeric materials [218]. Similarly, in spite of the reported use of TG-MS in additive identification in (competitor) products, (quantitative) analysis of additive packages is usually carried out with procedures not routinely including TG-MS [219]. In view of their low concentrations, analysis of additives using TG-MS equipment is best carried out with a condensation trap [31,37] in which there is no dilution of the evolved samples.

As already noted in Section 4.3, sublimation is a less desirable phenomenon in TG-MS experimentation.

8.6. Kinetics of polymer degradation

For applications in pyrolysis or thermal degradation of polymers the combination of TG and MS is a basis to combine the kinetics of the weight loss of the heated samples with the identification of the developed gaseous products. As pointed out by Korobeinichev [68], for the purpose of a kinetic study it is required to remove either all the product as it is formed or a negligible amount. One method for the determination of kinetic parameters from TG measurements is given by Knümann et al. [220]. The procedure for determining the apparent activation energy E is as follows. Thermograms at different heating rates are recorded and the temperatures corresponding to a constant degree of conversion are extracted. From this plots of log $\mathrm{d}T/\mathrm{d}t$ vs. T^{-1} at different degrees of conversion are constructed. The slopes of these plots give E. Some more information about the process of decomposition can be gathered from the mass spectrometric data. For any species i in the mass spectra recorded during decomposition thermogram-like curves can be obtained indicating the fraction of the solid sample that is converted into the fragment i. The apparent activation energy for the appearance of the species may thus be obtained. Although the mass spectral detail of TG-MS provides a wealth of kinetic information, it was pointed out by Jones et al. [102] that the methods for extracting apparent activation energies may be too simple to permit meaningful data to be obtained for complex degradation schemes.

It has been demonstrated that conversion dependence of the activation energy is always accompanied by a heating rate influence on the kinetic parameter. This is one of the most important conclusions resulting from the kinetic analysis of the thermal degradation processes of polymers.

For the purpose of kinetic studies it is difficult to ensure that the TG-MS coupling system is linear and quantitative [47]. This appears to have been achieved though by the two interfacing methods developed by Emmerich and Kaisersberger [65]: both interfaces were claimed to be quantitative and capable of providing a gas throughput of unvaried composition. This is because the proportion of gases sampled is at such a pressure that viscous, laminar flow is ensured prior to entry into the MS analyzer. Also the TG-DTA-MS coupling of Barnes et al. [145] via a jet separator is suitable for kinetic studies; Székely et al. [105] state without proof that their two modes of connection are suitable for kinetic purposes. Dollimore et al. [47] have reported theoretical considerations for kinetic studies considering the role of MS/sample interfacing methods, gas flow, pressure, etc.

In the application of TG-MS in kinetic studies of polymers we notice the determination of the activation energy of the thermal crosslinking reaction of aramids [206], the lifetime estimates for PEEK and poly(diallylphthalate) molded products [104], the kinetics of degradation of PVC, polystyrene and polyamides [220], the kinetics of (oxidative) thermal degradation of PMMA, polyurethanes and ACN/styrene copolymer [137], the determination of the degradation rates, rate constants of degradation and activation energy of degradation for ethylene–propene rubber and phenyl–formaldehyde copolymers [190], the calculation of activation energies for the evolution of various degradation products of a variety of fluorocarbon (co)polymers [142,193], etc. Székely et al. [103] have discussed the kinetics of simultaneous polycondensation–thermal decomposition reactions; the kinetics of anhydride formation in a poly(acrylic acid)–alumina composite was studied by Greenberg et al. [30] using the cold trap TG-MS technique. Under inert conditions nylon-6,6 was reported to undergo only one degradation step, as opposed to two under oxidizing atmosphere. Polystyrene decomposes recovering the monomers [220].

For designing recycling procedures the behaviour of decomposition of polymers with regard to decomposition products and the kinetics of decomposition must be known. Knümann et al. [117] have investigated the kinetics of pyrolysis of PVC and mixtures of PVC with PE, PP, PS and PA6 by means of TG-MS. According to Knümann et al. [220] PVC degrades by eliminating HCl in a first step; decomposition proceeds in a second step under destruction of the polymer chain. The high value of the apparent activation energy hints at a decomposition mechanism different from simple depolymerization.

By means of TG–MS it is possible:

to determine the mass velocity of destruction and the thermal characteristics of composite polymer materials under conditions of rapid heating during temperature measurements directly on the sample;

to obtain under these same conditions data on the composition and the dynamics of liberation of individual volatile products, and also to determine the kinetic parameters of their formation;

to determine the dependence of the effect of the heating rate on the dynamics of the liberation of individual volatile products and on the kinetic parameters of their formation;

to investigate the process of destruction and depolymerization according to the observed characteristic peaks if the spectrum of the volatile products contains nonsuperposed peaks of a monomer.

Kinetic data can be used to predict dominant thermal loss processes at various temperatures; from a mechanistic point of view the rate determining step in the processes may be indicated (in the case of a sulfone resin cleavage of a S–C bond, followed by loss of SO_2 and phenol) [102].

A word of caution, though, has to be expressed. Friedman [16] and Garn [221] have already raised the question of the meaning of thermogravimetric kinetic parameters, taking into account the heterogeneous character of solid–gas processes and changes of both the reaction mechanism and rate determining step with conversion and temperature. Any kinetic description should take into account the fact that evolved gases detected by TG–MS originate from chemical and physical processes. In complex cases (e.g. component—chemical decomposition–diffusion–desorption–transportation) the calculated 'apparent' rate constants and activation energies are dependent upon the heating rate ($\Delta T/\Delta t$). In others, for example, involving sublimation, mass transport by the gas flow may be a crucial parameter, while $\Delta T/\Delta t$ still plays a role. Also, dense packing can inhibit the diffusion of evolved gases through the sample and significantly alter the observed decomposition kinetics. Further complications may arise as during degradation and weight loss processes the diffusion rate of evolved gases changes.

Unfortunately, a great portion of the thermoanalytical publications dealing with reaction kinetics has presented contradictory or meaningless results, which have induced a great deal of pessimism about the applicability of reaction kinetics for the evaluation of thermoanalytical curves [222]. Considering that thermogravimetry only indicates weight changes, it is evident that not all possible kinds of polymer degradation processes can be observed. This creates problems even in attempts at estimating the thermal stability of polymers. At least molecular weight changes have to be analyzed concomitantly.

Even if no changes in mechanism occur kinetics supposes not only estimation of the kinetic parameters, but also knowledge of the degradation mechanism. These are in fact the requirements of any kinetic investigation and analysis of the degradation mechanism assumes knowledge of the initial state and of the final state of the chemical reaction. In thermogravimetry at best the initial state is well known, and without further analysis of both the solid residue and the evolved gaseous products, no statements concerning the probable degradation mechanism are possible. Under such conditions the elementary requirements of kinetic interpretation are neglected [223]. Kinetic interpretation of thermogravimetry of polymers must verify first if the observed weight loss is related to the conversion or if it depends on the volatility of reaction products already occurring at lower temperatures. Only in the first case are thermal stability determinations and kinetic evaluations justifiable. But even anticipating the degradation mechanism of the polymer, unequivocal kinetic parameters are not accessible in the nonisothermal conditions of thermogravimetry because of the chain character of the process. For the kinetic interpretation, supplementary investigations concerning the nature of the reaction products, both gaseous volatiles and solid residues, are necessary. Once these are known reflections upon the reaction mechanism are allowed. Kinetics can be determined with more confidence by means of TVA (thermal volatilization analysis) [6]. Similarly, MTA (mass spectrometric thermal analysis), as first described by Langer and Gohlke [15] and applied to polymers by Friedman [16] and Shulman et al. [17,18], has been used for overcoming some of the problems of TG regarding kinetics. In this respect the benefits of TG-MS were recognized in an early stage [103,137]. Chemical reaction kinetics can also readily be made with the STMMBA configuration.

Statements concerning the real degradation mechanism are possible only after detailed analysis of the reaction products, both volatile and residual solids. Without exact knowledge of the degradation mechanism, any chemical kinetic analysis by thermogravimetry is fiction [102,223].

In life-time predictions based on TG studies it is assumed that temperature is the only accelerating factor from service conditions to test conditions, with the activation energy representing the temperature dependence of the degradation process. Not all practical requirements for thermal stability are monitored by TG: such assessments do not take into account physical transitions, nor do they monitor property losses which do not involve weight loss. Flynn et al. [224] have developed a method to predict the lifetime of polymers which was based on the evaluation of several mass-loss curves obtained at different heating rates. A number of polymers has successfully been studied with this method although caution has been expressed [41,218]. Stability assessment is beset with difficulties and thermal methods serve only as a qualitative answer to this problem. Kinetic studies of thermal stability by means of TG may yield comparative data of utility in specific situations [225]. These studies, however, should be made under the least complicated conditions, namely, isothermal conditions. Even under these conditions degradation behaviour as monitored by TG may not give results directly relatable to the degradation mechanism. The shortcomings associated with the use of TG-MS for stability assessment are not much different from those of other thermal methods (cfr. Ref. [226] and Table 5 of Ref. [218]). It should be stressed here that weight loss alone (with or without identification of the evolved components) is no criterion for stability.

8.7. Quantitation

Quantitation of sample components by conventional TG may be made only if a stoichiometric relationship exists between the gaseous decomposition products and the original material.

If molecular flow conditions exist in the TG-MS apparatus, the basic assumption is made that the MS ion current is proportional to the concentration of the volatile leaving the sample which is, in turn, a measure of the rate of release of that species from the sample. Ion currrents (I) are then proportional to the rate of release of any volatile product. It is also assumed that the total area under the MS profile is proportional to the original sample mass. Consequently, $\mathrm{d}W/\mathrm{d}T$ and total ionization current correspond closely. The proportionality constant is different for each product and will depend upon many factors, such as selection of representative ion, mass-spectral fragmentation pattern of the product, total ionization cross-section and mass-spectral discrimination. Discrimination of the relative magnitude of the volatile products evolved in TG-MS therefore generally requires knowledge of mass discrimination in the m.s. and the probability of ionization of each product [102].

As already noted, mass spectrometers need calibration to establish the exact relation between the ion current measured and the concentration of the gas sample supplied. Courtault [156] has described quantitative aspects of TG-MS coupling, still a difficult matter. It is of interest to note that the STMMBA technique allows a quantitative interpretation of the m.s. data without the need to determine ionization cross-sections, ion cracking factors, the transmission of the quadrupole mass filter, or the sensitivity of the ion detector for each species evolving from the sample [115].

Using the total condensation method with constant volume sampling quantitative analysis of a PMMA–PTFE coating has been described; the same authors report quantitative results also for ethylene/vinylacetate copolymers [90]. Tan et al. [205] have determined the imide content of poly(amic dialkylamides), Dyszel [136] the styrene content in styrene-butadiene rubbers, and Chiu et al. [31] the composition of a polyacetal resin.

The complexity of quantitative measurements of thermal analysis using mass spectrometry has recently been pointed out by Morelli [4]. The development of a Hi-Res TG-MS [107] is possibly beneficial to the ability to obtain more accurate, quantitative results. Unless results are made quantitative it is arduous to draw any definite conclusions about mechanisms of decomposition.

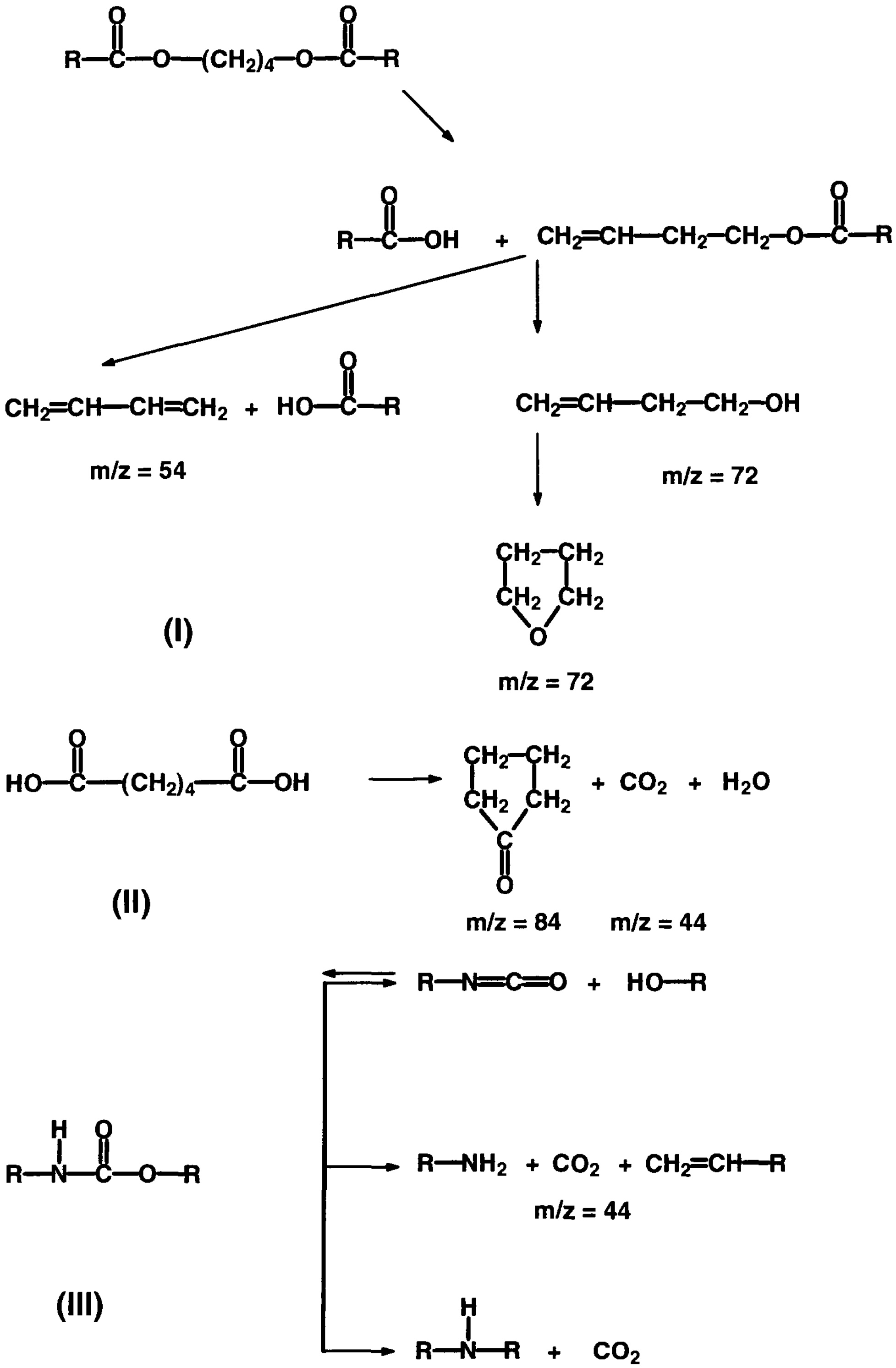
9. Illustrative examples

The following case studies illustrate some practical polymer-related problems tackled by TG-MS.

9.1. Thermal degradation of a polyester urethane

Adequate characterization of industrially applied polyurethanes is necessary because of the composition-dependent variation in properties. Thermal degradation of polyurethanes has been carried out by Py-GC-MS, TVA and Py-EGA-FTIR with the purpose of the identification of polymer type, and comparison of samples and evolution profiles (Ref. [227] and references contained therein). In our case, the degradation of a complex, urethane-based, thermoplastic elastomer, as observed by viscosity measurements following high temperature production and processing, was studied and the nature of the volatile products (mainly CO_2, 1,3-butadiene, THF and cyclopentanone) identified by TG-MS and GC-MS (cfr. Ref. [213] for related material). While CO_2, THF and HCN were observed by TG-MS a much richer evolved gas composition with $m/z = 44, 54, 70, 72, 84, 90, 200$ (all components identified) was detected with TG-CT-GC-MS. The main degradation mechanisms were identified as thermal degradation of ester bonds of adipic acid and urethane moieties (Scheme 1). Thermo-oxidative effects are less important.

This very complex polymer material was chosen deliberately in an attempt to illustrate the limitations of the TG-MS technique. As expected, not all the gases were readily identified. Several of the weight loss transitions are caused by complex decomposition processes resulting in multiple materials being evolved. Similar problems are encountered in the characterization of composite materials and copolymers [196]. Particularly if some of the components are present in minor amounts, the separation becomes an integral part of the analysis. Recourse to GC-MS is an



Scheme 1. I. Degradation reactions involving ester groups; II. Degradation reaction with formation of cyclopentanone; III. Main degradation routes of urethane moieties.

obvious choice in case of complex mixtures in the TG atmosphere for which simple MS identification of the component organic substances is not possible [182,209]. This approach has also been used in the study of flame and smoke retardants and additives in complex polymer systems [228].

9.2. *Styrene maleic anhydride (SMA) copolymer*

The thermostability of SMA was studied under dynamic measurement conditions (Fig. 2). The first derivative of the TGA measurement of SMA shows maxima at 150°C and 410°C.

Simultaneous mass spectrometric analysis of the volatiles demonstrates that SMA degrades at high temperature (T_{max}.: 410°C). At the lower temperature, the mass spectrum shows only loss of styrene (m/z = 103, 104 a.m.u.) which was present as a rest monomer. Styrene evolution preceded by CO_2 evolution (m/z = 12, 44 a.m.u.) combined with lactone formation are the most important processes during thermal degradation at higher temperatures.

9.3. *Dimelaminephosphate*

TG-MS experiments have been carried out on the flame retardant dimelaminephosphate. The DTG curve (Fig. 3) shows five peaks at 133°C, 187°C, 287°C, 392°C and 587°C with an onset temperature of 87°C. TG-MS data (Fig. 4) show that up to 357°C only H_2O is detected; above this temperature a range of pyrolysis products is observed, namely, NH_3 (m/z = 15,16,17 a.m.u.), CO_2 (m/z = 12,44 a.m.u.), H_2O (m/z = 17,18 a.m.u.) and HCN (m/z = 26,27 a.m.u.). It is concluded that the salt is stable up to 357°C. Water detected is from different origin and mobility (adsorbed, enclosed and/or physically bound). The results agree with those of Costa et al. [228a] based on chemical methods (Table 20).

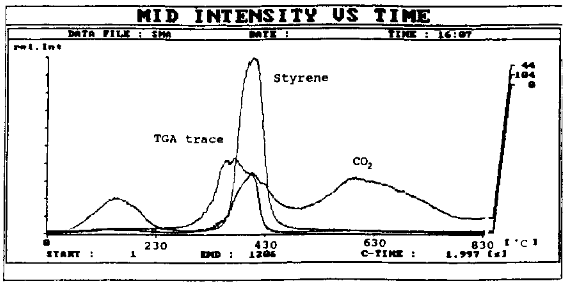


Fig. 2. Dynamic DTG (o) and mass spectrogram of SMA for styrene (m/z = 104 a.m.u.) and CO_2 (m/z = 44 a.m.u.) in inert atmosphere at dT/dt = 20°C min^{-1}.

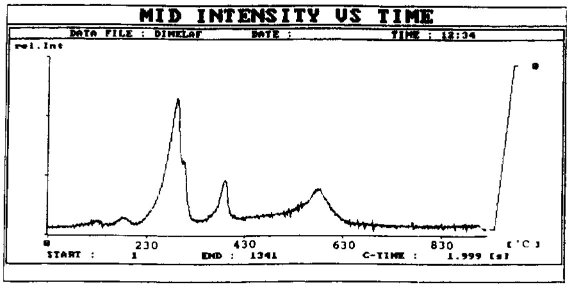


Fig. 3. DTG curve of dimelaminephosphate during dynamic heating (20°C min^{-1} from 30–900°C).

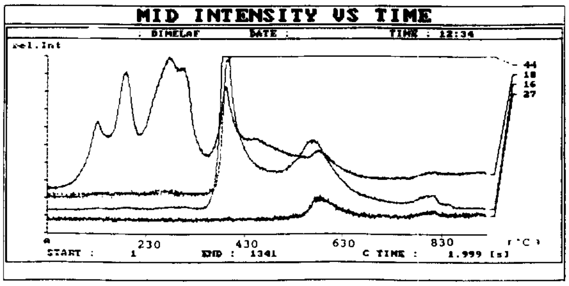


Fig. 4. TG-MS curve of dimelaminephosphate (CO_2: m/z = 44 a.m.u.; H_2O: m/z = 18 a.m.u.; NH_3: m/z = 16 a.m.u.; HCN: m/z = 27 a.m.u.) in inert atmosphere at dT/dt = 20°C min^{-1}.

9.4. *EPDM*

The different material properties of EPDM (Keltan® type) are largely determined by the third monomer and the presence of additives, fillers, plasticizers, carbon black, etc.

Fig. 5 shows a TGA/DTG curve of EPDM A, a product without filler and plasticizer. The dynamic mass spectrogram (Fig. 6) shows that during the maximum weight loss phenomenon ENB (m/z = 66,91,105 a.m.u.), aliphatics (m/z = 43,56,69 a.m.u.) and olefines (ethene:

Table 20
Thermal decomposition of dimelaminephosphate

Temp. [a]	Evolved gas [a]	Temperature range [b]	Evolved gas [b]
133°C	H_2O		
187	H_2O		
287	H_2O	230–350°C	H_2O
392	H_2O, NH_3, CO_2	350–440	H_2O, NH_3
587	H_2O, HCN	440–650	unidentified
		650–940	degradation products

[a] TG-MS experiments.
[b] Ref. [228a].

$m/z = 26{,}27$ a.m.u.; propene: $m/z = 40, 41, 42$ a.m.u.) are detected. Figs. 7 and 8 show the dynamic DTG and MS curves in inert atmosphere of EPDM B, a compound charged with oil, filler and carbon black, and indicate loss of oil (max. at 336°C), thermal stability of the polymer up to about 420°C (maximum decomposition at 485°C), and decarboxylation of the filler at 730°C (CO_2: $m/z = 12{,}44$ a.m.u.); finally, above 900°C in O_2 atmosphere carbon black is detected. It is instructive to compare the release of ENB in EPDM A and EPDM B compounds (Fig. 9), which gives information about bonding of the third (ENB) monomer. While in EPDM A ENB is released in one thermal event, in EPDM B the compound ENB evolves at much lower temperature and in two separate events. Qualitative results obtained from EGD-MS coupled with quantitative analysis obtained from TGA/DTG may serve as a basis for kinetic analysis.

9.5. EPDM-SBR blends

A comprehensive range of EPDM grades is offered in the market with a choice of vulcanisation speeds, type and amount of the third monomer (DCPD, ENB), etc. Physical properties depend on the ethylene/propylene ratio, molecular weight, polymer and/or blend structure. Fig. 10 shows little difference between the TGA/DTG curves of a 30/70 wt.-%

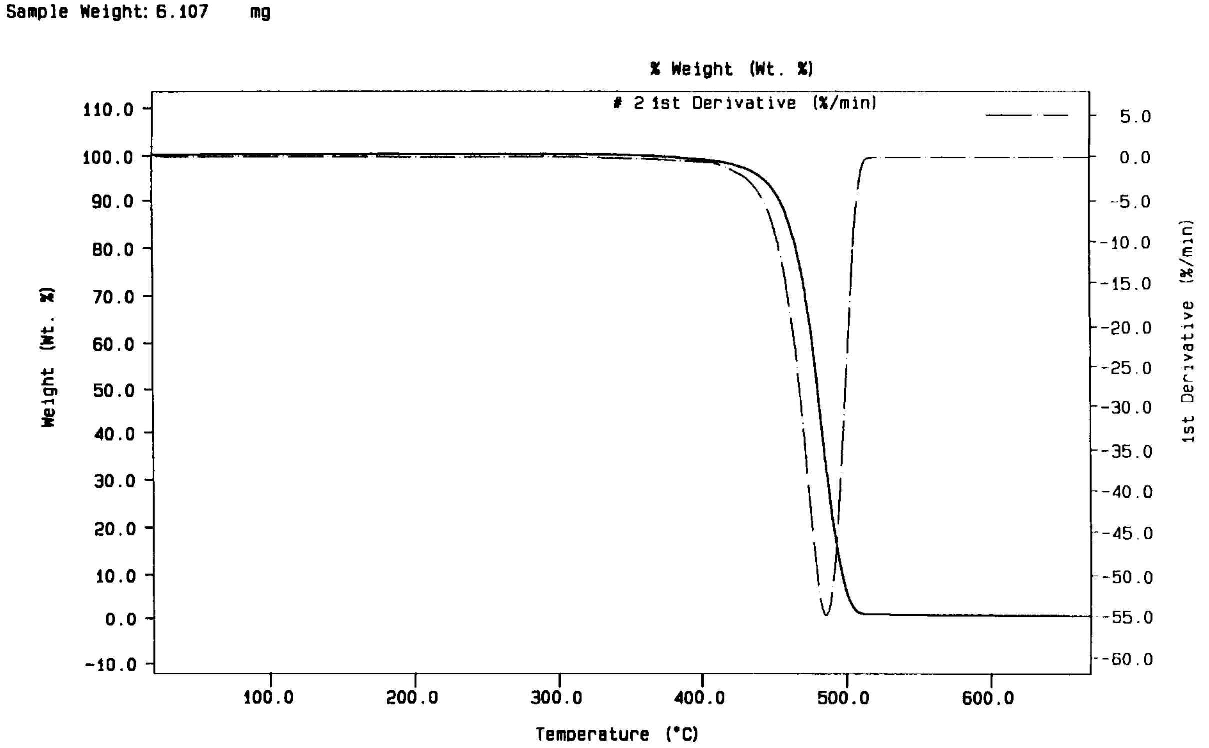


Fig. 5. Dynamic TGA and DTG curve of EPDM A in inert atmosphere at $dT/dt = 20°C\,min^{-1}$.

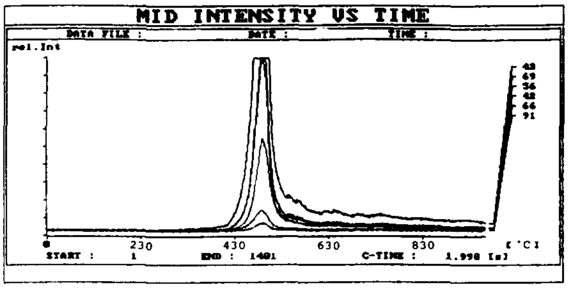


Fig. 6. Dynamic mass spectrogram of EPDM A (ENB: m/z = 66, 91 a.m.u.; propene: m/z = 42 a.m.u.; aliphatics: m/z = 43, 56, 69 a.m.u.) in inert atmosphere at $dT/dt = 20°C\,min^{-1}$.

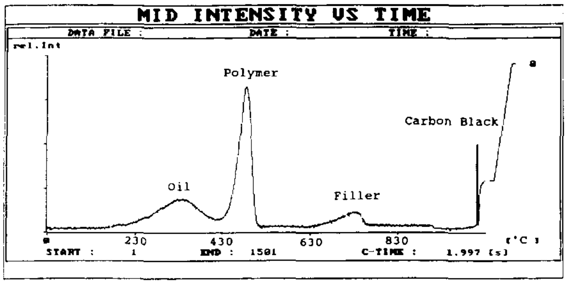


Fig. 7. Dynamic DTG curve of EPDM B compound in inert atmosphere at $dT/dt = 20°C\,min^{-1}$ up to 900°C; in O_2 above 900°C.

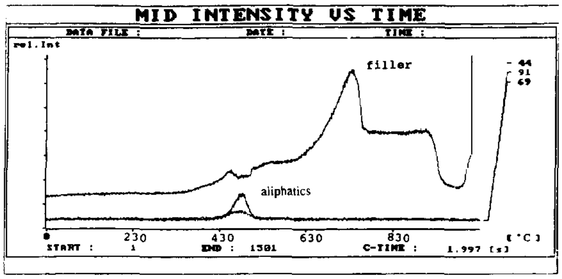


Fig. 8. Dynamic mass spectrogram of EPDM B compound in inert atmosphere at $20°C\,min^{-1}$ (CO_2: m/z = 44 a.m.u.; ENB: m/z = 91 a.m.u.; aliphatics: m/z = 69 a.m.u.).

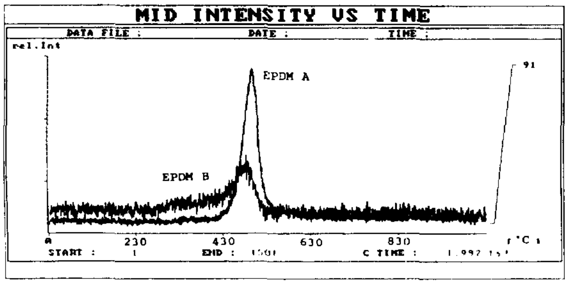


Fig. 9. Release of ENB in EPDM A and EPDM B compound in inert atmosphere at $20°C\,min^{-1}$.

EPDM B (containing 9 wt.-% ENB)/SBR 1502 and a 30/70 wt.-% EPDM C (containing 4.5 wt.-% DCPD)/SBR 1502 blend. On the other hand, in the dynamic MS spectra (Fig. 11) pronounced differences are observed in the release of propylene (m/z = 41, 42 a.m.u.), alkanes (m/z = 69 a.m.u.) and ENB/DCPD (m/z = 91 a.m.u.) between 380°C and 530°C. Interpretation of the conventional TGA/DTG curve (Fig. 10) is therefore rather misleading. A more accurate investigation (Fig. 12) confirms significant differences between the two blends, with ethylene release for EPDM B/SBR 1502 between 380–440°C, 450–480°C and 480–525°C and between 360–430°C and 430–530°C for EPDM C/SBR 1502.

10. Future prospects of TG-MS in polymer characterization

TG-MS is a very early example of a hyphenated technique. It is one of many evolved gas analysis techniques, actually even one of a subset of thermal analysis-evolved gas analysis techniques [44,45,47]. In this area, competitive analytical systems correlating thermal and chemical behaviour are TG-IR, TG-GC, TG-GC-IR, TG-GC-MS, Flash Py-GC and others. Therefore, it is difficult to predict what will happen to each of these related techniques in the next decade.

Amongst the evolved gas analysis methods TG-MS has conquered a respectable market share, in spite of the ever-increasing variety of competitor methods. On the basis of Fig. 1 a slow growth may reasonably be foreseen. The bright prospects are confirmed by the fact that the market leader of TG instruments has announced the development of commercial TG-MS instrumentation.

Having surveyed the applications of TG-MS to polymer analysis covering more than three decades, we are now in a position to make some general comments and recommendations on conducting TG-MS studies in this area. Combinations of thermal analytical instrumentation with MS provide a powerful means of analyzing and characterizing polymeric

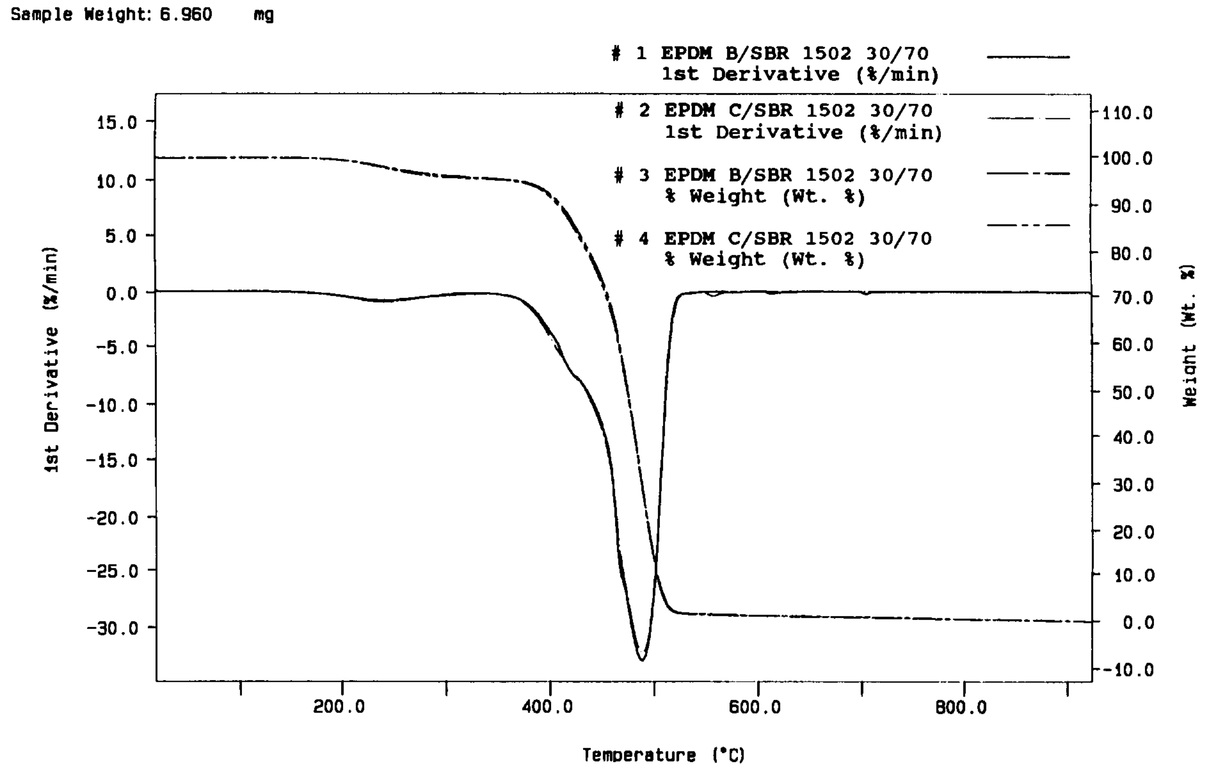


Fig. 10. Dynamic TGA/DTG curve of a 30/70 wt.-% EPDM B/SBR 1502 (-) and an EPDM C/SBR 1502 (-.-) blend at $dT/dt = 20°C\,min^{-1}$ between 30°C and 900°C in inert atmosphere.

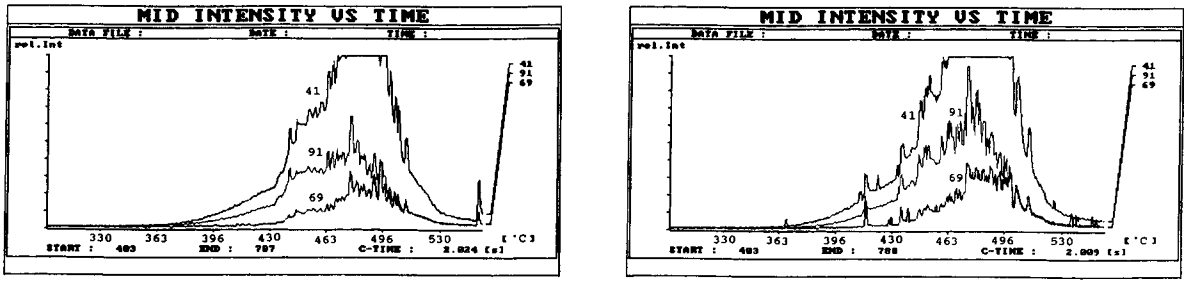


Fig. 11. Dynamic mass spectrogram in inert atmosphere at $20°C\,min^{-1}$ of a 30/70 wt.% EPDM B/SBR 1502 blend (left) and a 30/70 wt.% EPDM C/SBR 1502 blend (right); propylene: m/z = 41 a.m.u.; alkanes: m/z = 69 a.m.u.; ENB/DCPD = 91 a.m.u..

material, providing both qualitative data and giving quantitative applications. For polymeric materials it is important to have validated information in synthesis and processing so that the final formulated products meet their in-field performance requirements. TG-MS is not the solution to all problems in the study of polymer degradation and other techniques are required in order to completely identify the complete reaction scheme; however, in many instances this technique is a very valuable first experiment in order to delineate the reaction mechanism and to identify the major products. In some cases (e.g. outgassing problems) TG-MS is an obvious choice along with HS-GC-MS (though not providing any thermal information).

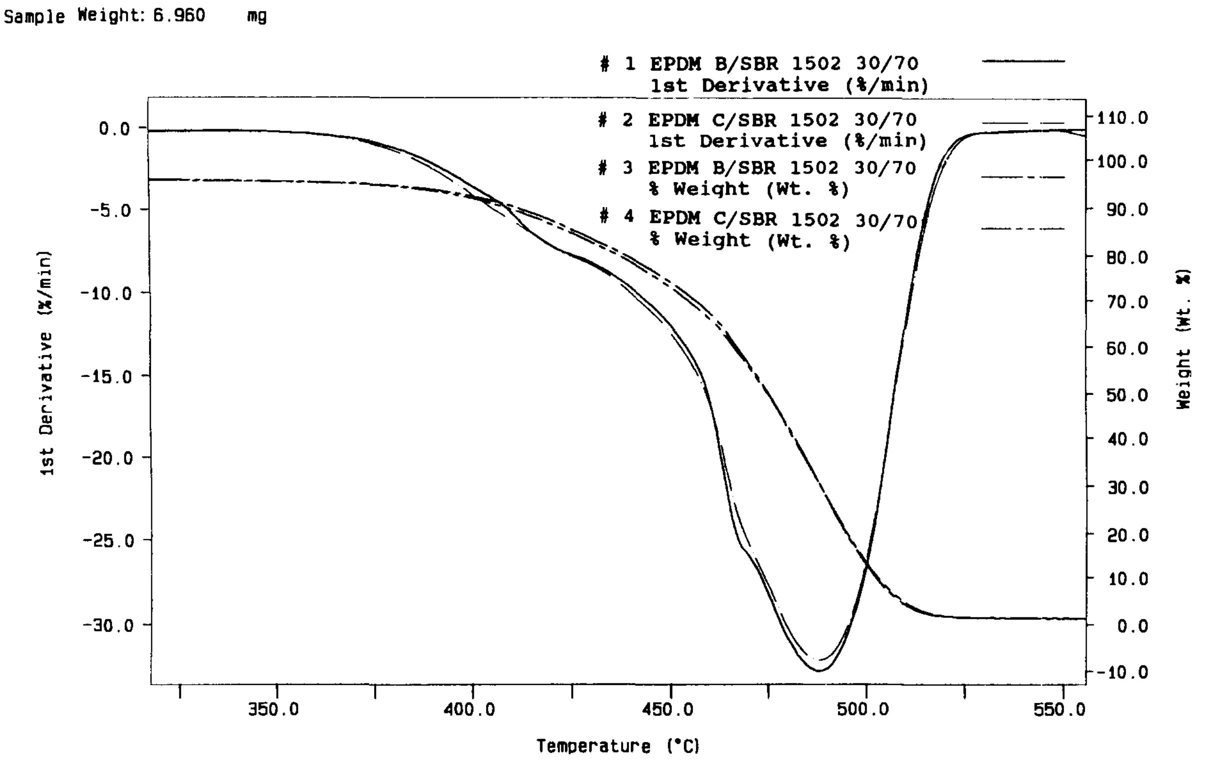


Fig. 12. Detail of the dynamic TGA/DTG curve of a 30/70 wt.% EPDM B/SBR 1502 (-) and an EPDM C/SBR 1502 (-.-) blend at $dT/dt = 20°C\,min^{-1}$ between 320°C and 555°C in inert atmosphere.

Awareness by the users of the experimental requirements and the availability of reference materials to optimize and standardize experimental set-ups to the level of precision and accuracy demanded by modern instrumentation make it likely that TG-MS will keep a key position in problem solving for polymer analysts. Clearly though, routine application of TG-MS requires skilled and dedicated operators. TG-MS instrumentation has not yet reached the black box stage of some other analytical methods.

Historically, the design and operating capability of TG-MS instrumentation have varied tremendously (Table 7). Instrumental problems have now greatly been overcome and reliable TG-MS equipment has evolved from the early research on the control of variables affecting the experiment. From the data presented in this paper it is evident that certain configurations of TG-MS couplings are more suited than others for polymer research. HR TG-MS may eventually be expected to improve the results that can be obtained from TG-MS experiments.

The problem-solving capability of TG-MS in polymer research is beyond doubt (cfr. Tables 13, 17, 18). The present trend towards ever-increasing product quality standards determines a challenge to TG-MS as more complex questions are being asked requiring identification instead of verification, for which the single-stage method is essentially ill-equipped. In fact, the interest of the material scientist has shifted from higher degradation temperatures (often meaning total decomposition with abundant evolution of simple molecules, such as CO_2, H_2O) towards lower temperatures (with evolution of a more complex mixture of components at much lower concentration at the onset of the reaction) more characteristic of stability under processing and continuous use conditions. In these cases, the need for quantification of components at very low concentrations demands high sensitivity, accuracy, and reproducibility of the analytical technique; simultaneously, the identification capability of the method requires strengthening.

The mandate today is not faster collection of mass spectral data over broader m/z ranges (with more stringent requirements on the interface quality), but rather more economical and rapid *identification* of co-evolved species. In this respect several approaches for improvement are possible. We mention three possible options:

1. TG-MS with empowered software able to unravel the superposition of fingerprint mass spectra of co-evolved species; this option requires ionization leading to sufficient fragmentation and powerful computing facilities. Work is in progress to achieve this goal.
2. Discontinuous TG-MS, that is, TG-CT-GC-MS or TG-GC-MS, both with an empowered (chromatographic) separation step. This option is already practiced but suffers from a compromise on speed; multiple hyphenated techniques are also inherently more difficult to operate.The system described by Whiting et al. [178], with readily interchangeable TG-MS and TG-GC-MS configurations, is nevertheless an attractive option. A TG-IR-Tenax-GC-MS system with the possibility of directing some of the gas flow from the TG into the MS is now reaching market introduction [154].
3. Tandem TG-MS/MS, that is, empowering by means of a second mass spectroscopic separation step. This solution, which is not new [93,124] and has the ability to distinguish between groups of samples having similar thermogravimetric behaviour, is becoming economically more attractive as a result of the recent availability of benchtop MS/MS apparatus. In general, GC-MS is preferable to MS/MS when a large number of unknown components in a mixture are to be identified. Analysis of targeted compounds in a mixture, however, can be performed extremely rapidly by MS/MS because of the essentially simultaneous access to mixture components.

In spite of the widespread use of single-stage MS in chemical analysis (Table 10), and in polymer analysis in particular [22], there has been little use of MS/MS. For this analytical tool three specific areas can be considered:

Table 21
Mass spectrometric analyzers [a]

Mass Discriminator [b]	Measured Quantity	Kinetic Energy
B	momentum/charge (mv/z)	keV
E	kinetic energy/charge (mv^2/z)	keV
Q	mass/charge (m/z)	eV
TOF	velocity (v)	keV
IT	mass/charge (m/z)	eV
FT-ICR	mass/charge (m/z)	eV

[a] Ref. [287].
[b] B = magnetic sector, E = electric sector, Q = quadrupole mass filter, TOF = time-of-flight mass spectrometer, IT = ion trap, ICR = ion cyclotron-resonance.

1. identification of organic additives in compounded polymers [229];
2. identification of volatile pyrolyzates in polymer pyrolysis studies (e.g. TG-MS/MS, Refs. [93,124]; (direct) Py-MS/MS, Refs. [25,230,231]);
3. characterization of individual oligomers in low molecular weight polymers [232].

In all these areas, the principal advantage in using (sequential or parallel) MS/MS is that more information is available from mixtures than can be obtained by direct analysis using conventional (single-stage) mass analysis. At present, there is a preponderance of multiquadrupole instruments in the MS/MS market. However, the recently developed diversity of MS/MS is such that it is difficult to analyze adequately all aspects of its application to TG-MS within the scope of this review. Table 21 lists the mass discriminator types and Table 10 the ionization modes. The 'soft' ionization technique of chemical ionization is often preferred in MS/MS [233]. The requirements for TG-MS/MS coupling for routine polymer analysis are given in Table 22. For maximum sensitivity in mixture analysis, fragmentation of the molecular ion ideally should produce only one abundant, characteristic daughter ion (chemical ionization). For qualitative analysis, as in structure elucidation, however, multiple fragment ions are desirable (electron impact) [234]. From Table 23 it can be seen that the most attractive geometries for tandem TG-MS/MS instruments are BE and BTOF (for two-sector devices), EBE and BEB (for three-sector magnetic/electric analyzers), EBEB (for tandem double-focusing MS/MS instruments),

Table 22
Requirements for TG-MS/MS coupling for routine polymer analysis

No transport problem
No fouling and absence of memory effects
Short cleansing times
Practicality; simple operation and interpretation
No mutual interferences and effects on specifications
Reproducibility of the ionization method
Ion flux: reasonable magnitude and persistance of the ion signal generated
Adequate mass range and mass resolution of parent ion and daughter ions
Controlled effect of changing concentration profiles across an evolved gas peak on the quality of the MS/MS data
Mixture analysis; identification of all evolved compounds
Universal; detection of all evolved substances
Standard set of conditions for generation, compilation and search of MS/MS spectra
Constant sensitivity and response factor
Long-term stability
Lab-to-lab reproducibility of MS/MS data
Availability of a mass spectra data base for the preferred ionization method and mass analyzer; automated library search software
No artifacts
Low cost/performance ratio; commercial instrumentation

QQQ (for multiple quadrupole devices), QTOF, QEB and BEQQ (for hybrid combinations) and ITMS. Amongst these, BTOF is envisaged as being applicable in GC-MS/MS [235], but is not commercially available. EBE-type MS/MS has been in use in GC-MS/MS combination [236] with 10 times higher detection limits as compared to GC-MS. BEB is considered to be superior to other three-sector analyzer geometries [237]; EBEB is high cost; QQQ (or TSQ) is the only MS/MS analyzer already coupled to TG [93,124]; and QTOF and QEB are at the low and high cost /complexity/performance end of the hybrid instruments, respectively. The most serious limitation of sector MS/MS instruments (except for the tandem double-focusing system) is the lack of simultaneous unit mass resolution of parent and daughter ions. Not surprisingly, as QMS are a mainstay of GC-MS, LC-MS and TG-MS (cfr. Table 7) as a result of their properties (rapid scanning, relatively small size, simplicity of operation and relatively low cost), multi-quadrupole systems are attractive for MS/MS. Of all the MS/MS instruments, the TSQ is designed for the broadest analytical market. As for interfacing with thermal analytical devices, quadrupole instruments are easier to couple than are sector instruments. The high voltage present at the ion source of the latter, combined with the precise positioning required of the source, makes interfacing sector instruments to standard thermal analysis devices difficult [4]. This restricts choice.

Most commercial MS/MS systems, which combine high sensitivity, high speed, high selectivity and capability to detect a wide variety of different compounds, are neither small nor inexpensive. Potentially advantageous for the coupling of MS/MS to TG is the observation that existing single-sector mass spectrometers could be modified for time-resolved detection, thus inexpensively extending the capabilities for MS/MS to laboratories already equipped with magnetic sector TG-MS [238]; however, these systems are rare (Table 7).

The anticipated direction of development is that of simple, less expensive MS/MS instruments, dedicated to a simple type of application or analysis. The ion-trap detector, being in fact a three-dimensional quadrupole, is an obvious candidate for TG-MS/MS coupling, in analogy to applications in GC-ITMS [239]. Table 24 compares the main characteristics of ion trap and beam instruments. ITMS enjoys distinct advantages over most beam-type mass spectrometers in experimental flexibility. Ion traps are well suited to tandem MS^n ($n \geq 2$) experiments in a single analyzer instrument [240,241] and allow structure characterization studies (targeted compound identification in mixture analysis). McLuckey et al. [241] have defined the conditions that must be met for an MS^n experiment

Table 23
MS/MS instrumental developments for analytical purposes [234,235,287,288]

Geometry	Selected properties [a,b]		References
	Advantages	Disadvantages	
I. Multiple-sector combinations [c]			
EB	High resolution	No mass selection of parent ion	[289]
BE	Mass-selection of parent ion; library; automated search system; preferable to EB	Poor m.r. of daughter ion peak; limited mixture analysis; spectral artifacts; complex scanning	[287,290]
BB	Improved daughter ion resolution	Operational problems; limited demand	[291]
BTOF	Rapid data acquisition; simple operation; low cost	Poor parent ion resolution; not commercially available	[238]
ETOF	As BTOF; easier control and monitoring	As BTOF; poorer parent ion resolution	[292]
TOFTOF	High accessible energy range; desktop (development)	Limited parent and daughter ion resolution	[293–295]
EBE	High m.r. of parent ion; high sensitivity; compact; commercial	Low product ion m.r.	[236]
BEE	High m.r. of parent ion		[296]
BEB	High m.r.; flexible; commercial		[237]
EBEB	Rapid scanning capability; unlimited m.r.; powerful; commercial	Very sophisticated data system; high cost	[297]
II. Multiple-quadrupole devices			
QQQ	Improved daughter-ion resolution (compared to BE); unit m.r. in both stages; operational simplicity; search system; no spectral artifacts; commercial (preponderant in MS/MS market)	Limited flexibility; unsatisfactory parent ion transmission; limited mass range (2000 Da/z); limited EI MS/MS library; cost	[298,299]
III. Sector-quadrupole hybrid combinations [d]			
BQ	High precursor-ion transmission; unit m.r. daughter-ion analysis	Moderate resolution; not commercially available	[287,300,301]
EQ	Unit m.r. for fragment ions; small; low cost	Not commercially available	[302]
EBQ	High-resolution precursor ion analysis	Id.	[301]
BEQ	Id.; unit m.r. daughter-ion analysis; versatile	Id.	[301]
BEQQ	Predominant sector/quadrupole geometry; highly versatile; commercial	Very sophisticated data system; cost	[229,303–305]
EBQQ	Predominant sector/quadrupole geometry; commercial	Id.; lower parent ion resolution (compared to BEQQ)	[306,307]
IV. Quadrupole/sector hybrid combinations [d]			
QB	Improved secondary-ion resolution (compared to Q)	Little follow-up; not commercially available	[308]
QTOF	Rapid data acquisition; relatively high sensitivity; low cost; simple operation; relatively small	Low daughter-ion resolution; limited access to variety of experiments	[309,310]
QETOF	As QTOF; improved daughter-ion resolution		[235]
QEB	High resolution for daughter and parent ions; high performance; distinguishes isobaric fragments; most flexible hybrid geometry	Very sophisticated data system; high cost; not commercially available	[301,311]
QBE	High-resolution daughter-ion analysis; unit m.r. precursor-ion analysis	Not commercially available	[301]
QQB	Low resolution precursor ion analysis; higher resolution daughter-ion analysis	Id.	[301]

Table 23
(Continued)

V. Ion-trapping techniques			
FT-ICR	Ultrahigh m.r. and accuracy below 2000 Da/z; mass range > 10.000 Da/z	Limited reliability in routine operation; superconducting magnet; pressure problem	[312,313]
Q-FTICR	Increases dynamic range of FT-ICR		[314]
IT	Automatic approach to MS/MS; very high sensitivity; variable time domain (msec-min); small; simple; low cost; commercial	Limited m.r.	[240,315,316]
Q-IT	Sensitive; eV range	Loss of high energy collision capability; reduced m.r. of parent ion	[317]
BE-IT	Increased mass range	keV range	[318]

[a] m.r. = mass resolution.
[b] For cost estimates cfr. Refs. [111,288].
[c] TOF is considered as a 'sector' technique.
[d] Hybrid instruments combine high (resp. low) kinetic energy of the ions for the first stage and low (resp. high) kinetic energy in the second stage.

Table 24
Comparison of ion trap and beam instruments [246]

Property	Ion trap [a]	Beam instrument [b]
Sequential analysis	In time	In space
Losses associated with transporting ions	No	Yes
MS-MS efficiency	Up to 100%	< 10%
Number of MS-MS stages limited by number of analyzers	No	Yes
MS^n ability	$n \leqslant 12$	$n \leqslant 5$
Detection limits (mole)	Ultralow (10^{-18})	$< 10^{-15}$
Sensitivity	Highest	Lower
Mass resolution	$> 10^6$	High
Mass accuracy	Relatively low	Higher
Analyte quantities	pg	ng
Mass range (Da/z)	> 70.000	Low - very high
Operating pressure (mbar)	10^{-4}	$< 10^{-5}$
Mixture analysis capabilities	Excellent	Variable
Speed	High (1000 a.m.u./0.1 s)	Variable
Time frame of experiments	Five orders of magnitude	Less
Control on time of experiment	Yes	Limited
Size	Small	Larger
Cost	Inexpensive	Variable

[a] ITMS.
[b] E, B, Q, TOF.

to be feasible in a quadrupole ion trap. As a high performance mass spectrometer, the ion trap has already been interfaced to a variety of separation techniques (GC [239,242], SFC [243], LC [244], ICP-MS [245] and HS [246]) and external high pressure ionization sources (API, ASGDI, ES, TSP, LD, plasma) [246]. Its high MS/MS efficiencies make it an attractive and ultrasensitive detector for organic and inorganic analyses [235,247–250]. The relative high charge densities found in the ion trap complicate the achievement of high mass accuracy, high abundance sensitivity, and wide dynamic range; there is a need for optimization of the collisional activation. A prerequisite for the TG-MS/MS with ITMS is a practicality which should not be limited to the analysis of targeted compounds having standards which allow pre-optimization of conditions [239]. A matter of concern is the relatively high operating pressure of the ion trap which eventually determines a transport problem and absence of molecular flow with possible consequences for quantification. As opposed to ITMS, combination of TG with a Fourier-transform ion cyclotron resonance spectrometer is not an obvious choice.

Quite obviously then, the diversity of MS/MS instrumentation offers considerable opportunities for improved TG-MS hyphenation. The best geometry for a particular application depends on a number of factors, including mass resolution in the first and second stages, mass range, sensitivity, available collision energy, the type of information required, data acquisition rate, etc. Table 22 can act as a checklist. Although any specific prediction on the future of TG-MS is, at best, an educated guess, it is felt that the developments in 'tandem-in-time' quadrupole ion trap mass spectrometry/mass spectrometry are likely to have an impact.

In the process of fingerprint identification of polymers, which relies on a comparison of mass spectra of evolved gases of unknown and reference samples, identification of peaks is not necessary. However, reproducibility should improve up to the extent that comparisons with library data are possible. In this respect single-stage TG-MS is lagging behind Py-GC and Py-MS. The problem of the interpretation of MS/MS spectra and sharing of MS/MS data among different laboratories should not be underestimated and requires utmost rigour in experimental operating conditions and instrumental parameters, the availability of suitable libraries of mass spectral data and automated library search systems for spectral comparison [235]. The compilation of a general MS/MS library independent of instrument conditions constitutes a considerable challenge and is essential for the successful implementation of TG-MS/MS. Without such libraries, GC-MS, albeit slower, is better equipped for the analysis of unknown mixtures because sustained by the existence of large specific reference libraries. On the other hand, less volatile compounds can more easily be determined by MS/MS than by GC/MS; the gain in analysis time is another asset for TG-MS/MS. As to fouling, in TG-GC-MS low volatile components are filtered by GC whereas in TG-MS/MS such compounds may condense in the electrostatic lens system.

Finally, it is to the noted that according to Johnson et al. [251], with proper attention to the instrumental parameters, TQMS and ITMS can yield essentially the same mass spectra for the compounds and conditions studied.

It may be envisaged that the need will arise to correlate not only thermal behaviour with the underlying chemistry (outgassing, thermostability, degradation) but to also consider physical phenomena (change in colour, blooming, cracking, foaming, migration) simultaneously. TG-MS is an excellent starting point for endoscopic, audiometric and magnetometric extensions.

11. Conclusions

For thermal analysis using mass spectrometry the experimentalist disposes of powerful tools (cfr. e.g. Table 12 and Ref. [4]), amongst which is TG-MS. This system allows a wide choice of TG instruments, interface systems, mass analyzers, ionization modes, etc., to suit specific requirements. Simultaneous TG-MS has a proven record of being a powerful thermo-analytical tool for industrial problem-solving.

Historically, the technique has experienced a long series of improvements in coupling techniques, has received considerable impetus from better computing facilities, has not yet taken full advantage of recent incremental TG resolution and faces a bright future on the wave of current (tandem) mass spectrometry developments.

While research in the fundamentals of instrumentation for TG-MS is still an active area, the use of non-standard or do-it-yourself instrumentation hinders the transfer of that technology into other laboratories and into routine application. Establishing acceptance of the technique remains a challenge. Acceptability of a specific TG-MS configuration amongst alternatives depends on several major factors including cost (capital investment and maintenance) and complexity of the required instrumentation, ease of operation, speed of analysis, reliability of the data gathered, the information content of the data and the quality of the interpretation.

Interpretation of TG data is facilitated on the basis of mass spectrometry information; TG data ease quantification of m.s. results. The study of polymeric materials by a combination of thermal analysis and mass spectrometry provides the chemist with a wealth of information. The m.s. data contain the much needed chemistry of a polymer as it is heated through various thermal transitions. In the case of TG-MS molecular weight information is collected concerning the evolved gases which are responsible for the detected weight losses. The chemical information obtained allows separation of concurrent or overlapping reactions. Complete identification of evolved species by mass fragmentation patterns is not always possible when multiple components are present. With careful calibration, however, semiquantitative compositional analysis may be made; determination of the reaction kinetics is more problematic. For complex decomposition processes it is advantageous to separate the components before analysis in the mass spectrometer.

Polymer characterization has been conducted with a range of unique and commercially available TG-MS instrumentation. A major objective of this work is to appreciate the level of sophistication, both in instrumental TG-MS capabilities and the practical use that is made of them for polymer systems. Meaningful information is provided on the polymer microstructure, reactivity, product development, purity, thermal stability of polymers, degradation mechanism and kinetic studies. TG-MS studies of polymer degradation provide details about the degradation pathway that cannot be obtained by sealed tube reactions or pyrolysis gas chromatography.

Problems of the past, which have hampered broad application of TG-MS, are instrumental in the transfer of a representative part of the real sample atmosphere to the ion source of the mass spectrometer, without delay in time. These problems have been solved and reliable high sensitivity instruments are now available. However, the polymer chemist pushes for further speed, scientific and technological progress. For degradation studies very low m/z values (<200) are quite appropriate, but for identification studies higher m/z values are desirable. A limit of about 500 a.m.u. (benchtop range) is likely to be set by interface design requirements. Thermogravimetry-tandem mass spectrometry (TG-MS/MS) is considered to be particularly effective for the differentiation of isobaric ions, which may co-evolve in complex thermal decomposition processes. The advantage of MS/MS is that complex mixtures can be analyzed more readily and with neither chromatographic separation prior to mass spectral analysis nor significant sample preparation. Identities of various evolved products can be established with much more confidence than by using direct single-stage TG-MS analysis.

Future advancements in TG-MS may be expected both from software development to ease the evolved gas identification process and from hardware design especially as a result of the rapid progress in m.s. equipment.

12. Nomenclature

12.1. Techniques

AP(C)I	atmospheric pressure (chemical) ionization
ASGDI	atmospheric sampling glow discharge ionization
B	magnetic sector
CAD	collisionally activated decomposition
CE	capillary electrophoresis
CI	chemical ionization
CID	collision-induced dissociation
CT	cold trap
DCI	desorption/chemical ionization
DPMS	direct pyrolysis-mass spectrometry
DSC	differential scanning calorimetry
DT	differential trapping
DTA	differential thermal analysis
DTG	differential thermogravimetry
E	electric sector
EGA	evolved gas analysis
EGD	evolved gas detection
EI	electron ionization
ESP, ESI	electrospray, electrospray ionization
FAB	fast atom bombardment
FD	field desorption
FI	field ionization
FT-ICR	Fourier transform ion cyclotron-resonance

(FT)IR	(Fourier transform) infrared spectroscopy
GC	gas chromatography
GD	glow discharge
HNI	heated nebulizer ionization
HPLC	high performance liquid chromatography
HR	high resolution
HSCG	head-space gas chromatography
IC	ion chromatography
ICP	inductively coupled plasma
ISP	ionspray
ITD	ion trap detector
IT(MS)	ion trap (mass spectrometry)
LC	liquid chromatography
LDI	laser desorption/ionization
LPTD	linear programmed thermal desorption
L-SIMS	liquid secondary ion mass spectrometry
LV	low voltage
MALD(I)	matrix assisted laser desorption (ionization)
MDTA	mass spectrometric differential thermal analysis
MIP	microwave induced plasma
MMB	modulated molecular beam
MS	mass spectrometry
MS^n	multiple stages of tandem mass spectrometry
MTA	mass spectrometric thermal analysis
NI	nebulization ionization
PD	plasma desorption
PEGA	packaged evolved gas analysis
PPA	programmed probe analysis
Py	pyrolysis
Q	quadrupole mass filter
QMS	quadrupole mass spectrometer
SFC	supercritical fluid chromatography
SID	surface-induced dissociation
SIMS	secondary ion mass spectrometry
STA	simultaneous thermal analysis (TGA-DSC)
STMMBA	simultaneous thermogravimetry and modulated molecular beam m.s. apparatus
TA	thermal analysis
TEA	thermal evolution analysis
TD	thermal desorption
TG(A)	thermogravimetry, thermogravimetric analysis
TI	thermal ionization
TLC	thin layer chromatography
TMA	thermomechanical analysis
TOF	time-of-flight
TPF	temperature-programmed fractionation
TPPMS	temperature-programmed pyrolysis mass spectrometry
TSP	thermospray
TSQ	triple-stage quadrupole mass spectrometer
TVA	thermal volatilization analysis

12.2. Chemical

ACN	acrylonitrile
BHT	butylated hydroxytoluene
BR	butyl rubber
CPVC	chlorinated poly(vinylchloride)
DAMP	diethyl-N,N-bis(hydroxyethyl)aminomethyl-phosphonate
DCPD	dicyclopentadiene (C_{10})
DDP	di-(2-ethylhexyl)phtalate
DMMP	dimethylmethylphosphonate
ENB	ethylene-norbornene (C_9)
EPDM	ethylene-propylene terpolymer
EVA	ethylene vinyl acetate
HFP	hexafluorpropene
LCP	liquid crystalline polymer
LLDPE	linear low density polyethylene
MDI	methylene bis-4-phenol isocyanate
NBR	natural butylrubber
PA6	polyamide-6
PE	polyethylene
PEEK	polyetheretherketone
PEO	polyethylene oxide
PMMA	polymethylmethacrylate
PP	polypropylene
PS	polystyrene

PTFE	polytetrafluorethylene
PVC	poly(vinylchloride)
PU	polyurethane
SAN	poly(styrene-acrylonitrile)
SBR	synthetic butylrubber
SMA, SMI	(imidized) styrene maleic anhydride copolymer
TAIC	triallylisocyanurate
TCEP	tris(chloroethyl)phosphate
TCPP	tris(ß-chlorisopropyl)phosphate
TDI	toluene diisocyanate
Tenax	absorbent charcoal
THF	tetrahydrofuran
TPE	thermoplastic elastomer

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