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SIMULTANEOUS THERMOGRAVIMETRIC AND MASS-SPECTROMETRIC ANALYSIS OF HIGH-TEMPERATURE POLYESTERS

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ABSTRACT

The routine application of simultaneous thermogravimetry–mass spectrometry (TG–MS) in the analysis of liquid crystalline polymers is discussed. Isothermal and dynamical analyses have been carried out in an inert atmosphere. The TG–MS interface was modified to overcome condensation and memory effects. A low cost, high performance quadrupole mass spectrometer in a TG–MS coupling allows identification of the volatile decomposition products (weight loss), providing both quantitative and qualitative information about the evolved gases, with temporal resolution between the two analytical procedures.

INTRODUCTION

Various high-temperature resistant polymers have recently been developed and are now industrially available either as engineering plastics (eventually reinforced) or as fibers [1]. An important requirement for these materials is their high temperature resistance (373–573 K), often in combination with an equally good resistance to aggressive chemicals and/or dynamic mechanical properties. Of primary importance is that the materials' properties remain stable during use. Obviously, the requirements vary with the application, and are different in detail for the (chemical) process industry, the electronic and electric sector, the automotive, aeronautical and aerospace segments.

During their life cycle the HPMs (high performance materials) are frequently subject to high temperatures. During synthesis and processing (compounding and/or injection moulding), these HPMs are often brought in the molten state. In use, they are exposed to high temperatures and oxidative media. High continuous use temperature is therefore desirable. A higher melting point of a polymeric material is generally reflected in a higher heat resistance.

In this respect, a new class of high-performance materials is constituted by liquid crystalline polymers (LCPs), which are currently gaining much attention. Some commercial materials are produced by Hoechst-Celanese (Vectra®), Amoco-Dartco (Xydar®), BASF (Ultrax®) and Rhône-Poulenc (Rhodester®). Thermotropic (or melt-processable) LCPs are materials with exceptional unidirectional mechanical performance (high stiffness and strength, heat distortion temperature and dimensional stability) and physico-chemical properties (UV and radiation resistance). They are inherently flame-retardant and chemically resistant towards a great variety of chemicals and corrosives. All these properties however, depend strongly on their chemical composition.

Considerable research effort is directed towards these polymers [2–7] and it is expected that the materials' intrinsic properties will soon lead to endproducts with even higher strength/stiffness, low article weight and exceptional dimensional stability. Up till now, this combination of properties could only be met by some thermoset materials. The exceptional properties of LCPs stem from their molecular structure and morphology.

Thermotropic LCPs are polymers with a rigid backbone, usually consisting of aromatic structural units in an extended-chain conformation [7]. By applying elongational flow (e.g. during injection moulding) the materials obtained have highly desirable properties owing to their peculiar, material intrinsic process-induced morphology. A high degree of molecular orientation (and anisotropy) in the process direction is usually achieved, which is maintained even in the solid state [8].

As thermotropic LCPs with their high melting points (up to about 725 K) are designed for continuous use at temperatures up to about 525 K, it is useful to gain insight into their thermal stability, in particular in view of polymer processing.

THERMOGRAVIMETRIC-MASS SPECTROMETRIC ANALYSIS (TG–MS)

Thermogravimetric (TG) analysis is used to provide quantitative information on weight losses due to decomposition and/or evaporation of low molecular material as a function of time and temperature. In combination with simultaneous mass spectrometric analysis (MS) the nature of the released volatiles may also be deduced, thus greatly facilitating the interpretation of the thermal degradation processes.

Although TG–MS combinations are not original [9–16], and have previously been applied to the analysis of polymers [10–12,17–19], considerable technological problems are encountered. For routine thermal investigation of high-melting polymers reliable coupling of the various system components is essential. Thermal degradation products of high-melting materials, such as LCPs, may foul the interface or recipient leading to memory effects and/or physical obstruction. The design of the TG–MS coupling, as described in this paper, for the study of the decomposition of some commercially available thermotropic LCPs overcomes many such inconveniences.

It is obvious that the coupling of predominantly atmospheric pressure techniques, such as TG or ICP, with a high vacuum technique, such as mass spectrometry, requires some ingenuity. Therefore, it is not surprising that methods for implementation of TG–MS coupling vary widely. There have been several solutions to overcome the atmospheric pressure–vacuum problem. These range from total vacuum systems [9,17,20] to the use of inlet purge gases [12], micrometering valves [13,18], capillaries [10,11], constant volume samplers (microvalve–trap total condensation method) [21,22], jet separators [18,23], and interfacing the thermogravimetric analyzer to a mass spectrometer designed for atmospheric pressure chemical ionization (APCI) [24]. 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 mass (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.

TG/EI-MS is not well suited for studies of combustion and other thermooxidative processes. The use of CI overcomes some of the limitations of EI-MS. Prime et al. [25,26] and others [24] have recently described a TGA/APCI-MS tandem triple quadrupole mass spectrometer system for evolved gas analysis. This system, however, further restricts another limitation of conventional TG–MS namely the fact that usually only molecular weight information is available. In the absence of other sources of information, structural assignment on the basis of molecular weight is an arduous task. Thermogravimetric analysis coupled with sequential mass spectrometry (MS/MS) offers greatly improved structural identification of compounds evolved during thermodegradative processes without interruption of the TGA–mass spectrometer analytical procedure. Collision-induced dissociation techniques (MS/MS) can be used for direct analysis of mixtures without prior chromatographic separation. These advanced techniques permit identification of chemicals co-evolved during complex thermogravimetric processes. This is especially useful for the identification of individual compounds during polymer degradation. GC–MS or MS/MS identification of co-evolving compounds, combined with weight loss data obtained from TGA, furnishes a means of delineating complex thermolytic pathways.

In this paper we attempt to show that coupling TG with a technically less advanced mass spectrometer results in acceptable performance and high user friendliness. Furthermore it allows routine operation.

EXPERIMENTAL

Materials

Two neat thermotropic LCP resins were studied, namely Vectra® A950 (Hoechst-Celanese Corp.) and Xydar® SRT-500 (Amoco-Dartco). Both materials are aromatic copolyesters obtained by polycondensation.

Vectra® A950, which is a common injection-moulding grade polymer, is composed of 2,6-hydroxynaphthoic acid and *p*-hydroxybenzoic acid monomeric units. Xydar® SRT-500 is also an injection-moulding grade polymer, composed of *p*-hydroxybenzoic acid, p,p'-biphenol, terephthalic acid and isophthalic acid.

Apparatus

Isothermal and dynamical measurements were carried out by means of a coupled TG–MS system, consisting of a Perkin Elmer TGS-2 thermogravimetric analyzer coupled to a Balzers Quadrupole QMS 420 mass spectrometer (detection limit 200 a.m.u.) A Perkin-Elmer TGA-7 thermoanalyzer (not used in the present study) was also linked to the system, as indicated in Fig. 1. Dynamical measurements were carried out in an inert helium atmosphere with a (dry) flow rate of $2\ \mathrm{l\ h^{-1}}$ between 303 and 1173 K and with a heating rate, $\delta T/\delta t$, of $20\ \mathrm{K\ min^{-1}}$, heating taking place by induction. Sample sizes were selected in the 3–6 mg range as a compromise between efficient balance operation and overloading the mass spectrometer.

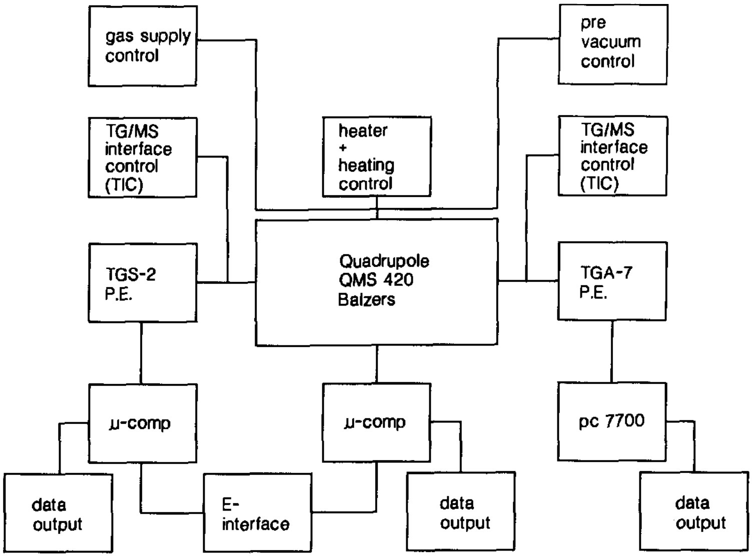

Fig. 1. Schematic view of the TG–MS coupling.

Prior to the isothermal measurements (also carried out in a dry helium atmosphere) the oven was heated at a rate of 200 K min^{-1}. Volatiles were immediately carried off in a He-gas flow via a heated ($T = 433$ K) fused-silica transfer line to the MS unit for on-line analysis.

Design of an improved TG–MS coupling

During TG-analysis of polymers the problem of handling large quantities of material released during sample decomposition has to be considered. In many cases (although not for LCPs), the components of interest are light molecular weight compounds, such as entrained solvents and plasticizers, present in low concentrations. These tend to evolve before the sample reaches its own anaerobic decomposition temperature.

During the process, large volumes of materials are expelled as a mixture of decomposition products and particulates. Portions of this material invariably condense in the cooler sections of the flow system. The design of a TG–MS interface cell must 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 the sample are swept from the furnace by a stream of purge gas and condensation occurs easily given the low temperatures of the wall of the furnace tube, leading to fouling of the cell, inlet system and ionization chamber of the mass spectrometer. In order to meet a number of desirable criteria, namely: (a) rapid response time; (b) absence of 'memory' effects; (c) conditioned gas transport; (d) flexible TG–MS coupling; (e) easy (de)coupling of the two instruments; (f) rapidly interchangeable inlet capillary; and (g) short cleansing times of furnace, both the furnace tube and TG–MS interface were (re)designed for use in combination with the Balzers mass spectrometer, all within the specifications of both analyzers. As to 'memory' effects, these may either be caused by traces of a previous sample or originate from long residence times of (high molecular weight) components released during decomposition. The following design features solve the problem.

Furnace tube with decreased fouling and memory effects

Condensation in the thermobalance appeared to be the main source of fouling and of the aforementioned 'memory' effect. The problem is reduced by modifying the furnace by insertion of an interchangeable inner mantle of glass into the measuring compartment, which forms a flexible seal with the anticonvection shield. The temperature at the inside of the double-walled furnace then drops less rapidly and thus avoids condensation in this part of the system. During the experiments the TGA cell contents are efficiently purged using a typical gas flow rate of 33 ml min^{-1}, which minimizes the residence time of the effluent gases in the furnace tube without impairing

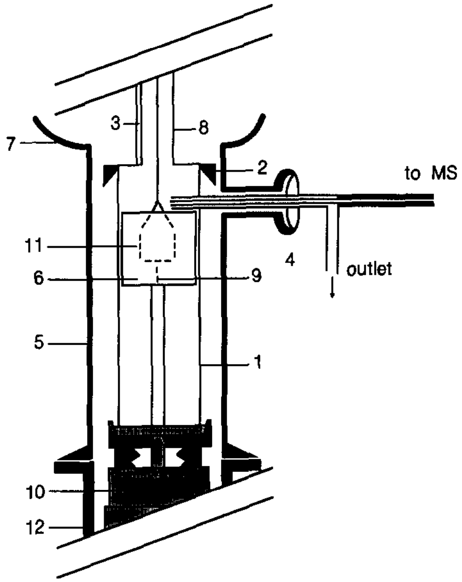

Fig. 2. Modified thermobalance furnace. 1, Inner mantle; 2, anti-convection shield; 3, oxygen inlet; 4, outlet (metal/glass coupling) to MS; 5, furnace-tube; 6, furnace; 7, ball-joint; 8, antistatic tube; 9, thermocouple; 10, positioning device; 11, sample pan; 12, socket. Items 1, 2, 3, 4, 5, 10 and 12 were (re)designed.

the balance stability by turbulence. By reducing the residence time of the evolved gases by bringing the volume of the furnace back from 160 to ca. 6 cm^3 the second ('memory') effect strongly decreases (Fig. 2). The inner cell body is a separate assembly which quickly snaps in and out of the heated chamber and may be easily exchanged between TG experiments so that condensation products are removed and the 'memory' effect is decreased. Materials which condense on the walls of the furnace do not contribute to the mass spectrum.

We have also altered the antistatic and anticonvection tube of the instrument. In our system helium, diluted oxygen or air is admitted through a glass capillary connected with the antistatic tube ending on top of the sample (Fig. 2). The modifications of the standard balance have the following advantages: (a) the frequency of cleaning the measuring compartment is drastically decreased; (b) the risk of breakage of the furnace is greatly diminished; (c) calibrations are needed less frequently; and (d) the use of He instead of N_2 leads to less critical positioning of the sample pan and to absence of interference with MS-spectral features of the sample because of the low molar mass (m/z 4 a.m.u.).

Transfer system

Having modified the furnace, condensation will then mainly arise in the inlet system of the mass spectrometer. The inlet system, which is a flexible refractory capillary tube (fused silica 0.3 mm i.d. in a steel sleeve with metallic/quartz probe and gas leak), attaches directly to the furnace tube of the TGA via a ball-and-socket glass/metal connection, is able to withstand high temperatures (up to about 873 K), and acts as an interface between the thermobalance (operating at near atmospheric pressure) and the ionization chamber of the mass spectrometer. To avoid fouling of the QMS, the vacuum is built up in two steps. The partial pressure in the recipient is 10^{-7} mbar. The amount of TGA effluent allowed into the pre-vacuum is controlled by the capillary restriction (the pressure drop is directly proportional to the flow across the capillary) and the amount of effluent allowed into the ion source is controlled by a gas inlet valve. Thus the mass spectrometer and the thermobalance do not influence each other. Evolved gases are transferred in an inert atmosphere from the thermobalance to the mass spectrometer in ca. 300 μs. The length of the coupling between TG and MS is less critical compared to previously described systems and the analytically desired lighter components are carried through this zone without condensation. The device enhances the capacity of the apparatus and leads to higher reliability of the results. Precision of the TG measurements is 0.1 wt.% with a reproducibility of better than 1%.

Mass spectrometer

The mass spectrometer used in this study is a low-cost quadrupole instrument with the following main features: analyzer: axial ion source (90 eV energy), 6 mm rod filter, multiplier detection, $m/z < 200$ a.m.u.; electron impact ionization.

The MS operating parameters were set to collect mass fragments produced in the positive mode of ionization. The mass spectrometer was usually set to scan the full mass range up to 200 a.m.u.; a new scan was started each 200 ms. In the dynamic mode the first scan of the mass spectrometer was coordinated with the start of the temperature program and a mass scan for each 25 K rise in program temperature was collected. Monitoring the abundance of a limited number of preselected ions with time is also possible, thus producing several scans per minute.

In the isothermal mode the first scan of the mass spectrometer was also started with the temperature program ($\delta T/\delta t = 200$ K min^{-1} up to 733 K). The operation of the TG–MS combination was checked against calcium oxalate monohydrate.

Data evaluation

The standard Balzers software (Quadstar®) was utilized for rapid control of the instrumental settings, real time data collection and post-acquisition processing. All spectral information was displayed on the screen during the run and mass-specific thermograms were plotted as chemo-selective records as the gases were evolving. Histogram spectra of the breakdown products were collected over the whole mass range available (200 a.m.u.). The major components evolving over the temperature cycle were monitored in the more accurate selected multiple ion mode (intensity vs. time).

RESULTS AND DISCUSSION

Application of the combined TG–MS system to the study of the thermal stability of LCPs

Thermal degradation mechanisms of conventional aliphatic and (fully) aromatic polyesters have been investigated for a great variety of materials [27]. The main characteristics of the various mechanisms appear to be well understood. Much effort has gone into the kinetics of these processes and identification of the secondary and tertiary degradation products. To this purpose generally slow or flash pyrolysis has been used in combination with gas chromatography–mass spectrometry (Py–GC–MS) or simply MS.

Important primary fragmentation processes of polyesters are usually inter- or intra-molecular ester exchanges and β-CH hydrogen transfer. The former process accounts for randomization of the polymer sequence and/or (cyclic) oligomers and is the main factor in fully aromatic polyesters. The process starts above about 773 K.

The second process leads to formation of ketene already at relatively low temperatures (for simple polyesters from about 473 to 673 K). After primary degradation, additional thermal decay is possible in which the primary products are fragmented. Some mechanistic possibilities include hydrolysis and decarboxylation. For fully aromatic polyesters decarboxylation is the main secondary or tertiary degradation process and results ultimately in CO and CO_2 as the main fragmentation products. Consequently, our simultaneous TG–MS measurements, carried out according to the aforementioned procedure were focused on the compounds and masses listed in Table 1. Although during pyrolysis of condensation polymers, such as LCPs, many other compounds evolve, the products listed are usually found in higher concentrations. Amongst these, H_2O, CO, CO_2 and phenol predominate. Carbon monoxide and dioxide, generally [28–33] indicated as being the main, albeit non-specific, products of thermal degradation of aromatic polyesters, are formed by rupture of ester-group radicals, namely CO_2 from $-\phi-COO^{\bullet}$ and CO from $-\phi-CO^{\bullet}$. Phenol (m/z 94 a.m.u.) is easily formed as a decomposition product of 4-hydroxybenzoic acid. Xanthon is a characteristic pyrolysis product for polymers containing 4-hydroxybenzoic acid, and naphthalene and 2-hydroxynaphthalene characterize the 2-hydroxy-6-naph-

TABLE 1
Characteristics of compounds used in TG–MS measurements

Material	M_w	Component	Characteristic features (a.m.u.)
Vectra® A950	18	Water	18, 17, 1, 16
	28	Carbon monoxide	28, 12, 16
	44	Carbon dioxide	44, 28, 16, 12
	60	Acetic acid	43, 45, 60, 15, 18
	78	Benzene	78
	94	Phenol	94, 39, 66
	102	Acetic acid anhydride	43, 15, 42, 45, 60
	128	Naphthalene	128, 32, 51
	144	Hydroxynaphthalene	144, 115
	196	Xanthon (dibenzopyron)	196
Xydar® SRT-500	18	Water	18, 17, 1, 16
	28	Carbon monoxide	28, 12, 16
	44	Carbon dioxide	44, 28, 16, 12
	60	Acetic acid	43, 45, 60, 15, 18
	78	Benzene	78
	94	Phenol	94, 39, 66
	102	Acetic acid anhydride	43, 15, 42, 45, 60
	166	Terephthalic acid	149, 166

thoic acid moiety. The presence of benzene in the evolved gases is characteristic of terephthalic acid moieties. Acetic acid and its anhydride are important indications for residual solvent molecules and terminating groups in the condensation polymers.

Dynamic measurements

Figure 3 shows the TG and DTG curves of Vectra® A950 as a function of time during dynamic heating (20 K min^{-1}, 303–1173 K). The DTG curve of Vectra® A950 in an inert atmosphere shows a small shoulder at 763 K. Below about 743 K the polymer is stable, whereas above this temperature decomposition is rapid. Maximum weight loss $(\delta G/\delta T)_{\text{max}}$ is observed at 816 K (Table 2). Weight losses occur up to about 1123 K and then slow down considerably, finally resulting in 40% ash.

The $\delta G/\delta T$ curve shows that the degradation process takes place mainly as one step; primary degradation products are phenol (m/z 28, 44, 94 a.m.u.) (Fig. 4) and CO, CO_2. At $(\delta G/\delta T)_{\text{max}}$ some acetic acid (and almost no acetic acid anhydride) is observed (Fig. 5) together with a very small amount of benzene (m/z 78 a.m.u.). Several other species, such as H_2O (m/z 18, 17 a.m.u.), xanthon (m/z 196 a.m.u.) and naphthalene (m/z 128 a.m.u.) are observed as secondary pyrolysis products (after passing $(\delta G/\delta T)_{\text{max}}$). Xanthon and (very little) naphthalene confirm that 4-hy-

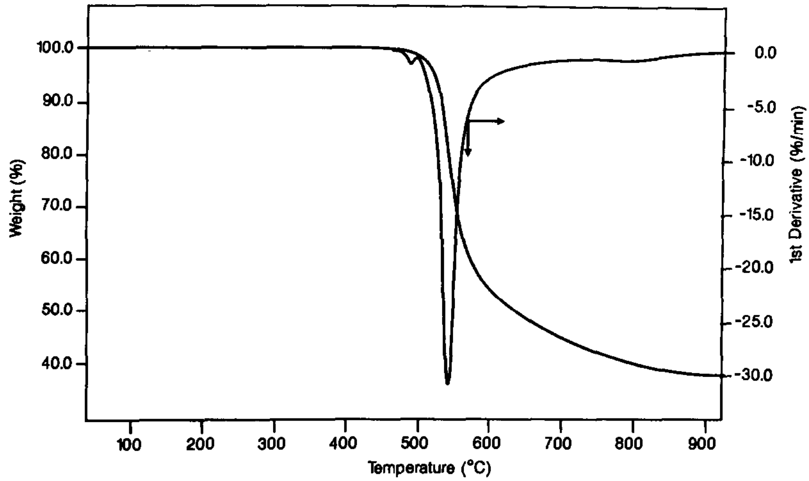

Fig. 3. Dynamic TG and DTG curves of Vectra® A950.

TABLE 2
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	743.4	790.5	802.0	813.5	816	38.7
Xydar® SRT-500	732.2	787.9	813.5	823.9	834.3	837	37.2

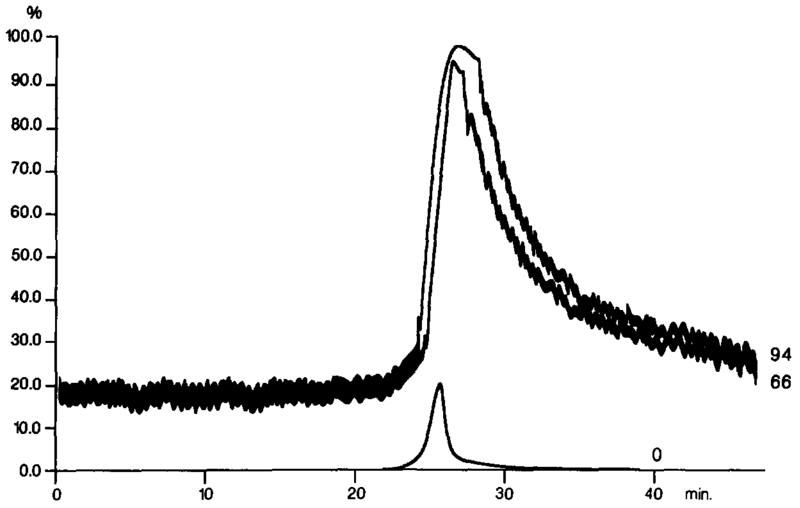

Fig. 4. Dynamic mass spectrogram of Vectra® A950 for phenol ($\delta G/\delta t$ on an arbitrary scale).

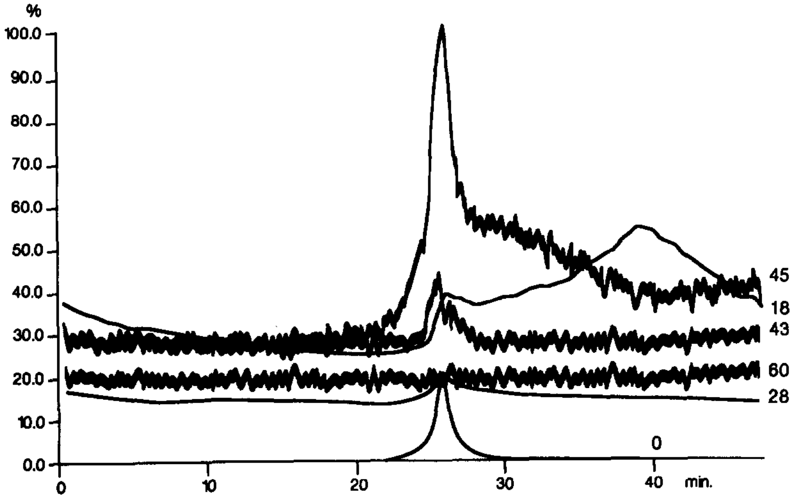

Fig. 5. Dynamic mass spectrogram of Vectra® A950 for acetic acid (anhydride) ($\delta G/\delta t$ on an arbitrary scale).

droxybenzoic acid and 2,6-hydroxynaphthoic acid monomeric units are present in the polymer chain. It is noticeable, however, that no hydroxynaphthalene was detected.

Xydar® SRT-500 behaves similarly but without a shoulder in the DTG curve (Fig. 6). The $(\delta G/\delta T)_{\max}$ value is reached at 837 K with 37% ash after pyrolysis at 1173 K. Mass spectrograms for CO/CO_2 and phenol are given

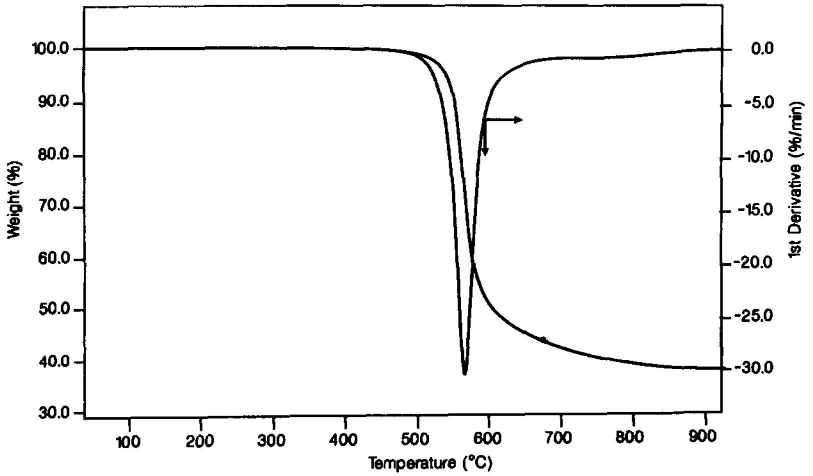

Fig. 6. Dynamic TG and DTG curves of Xydar® SRT-500.

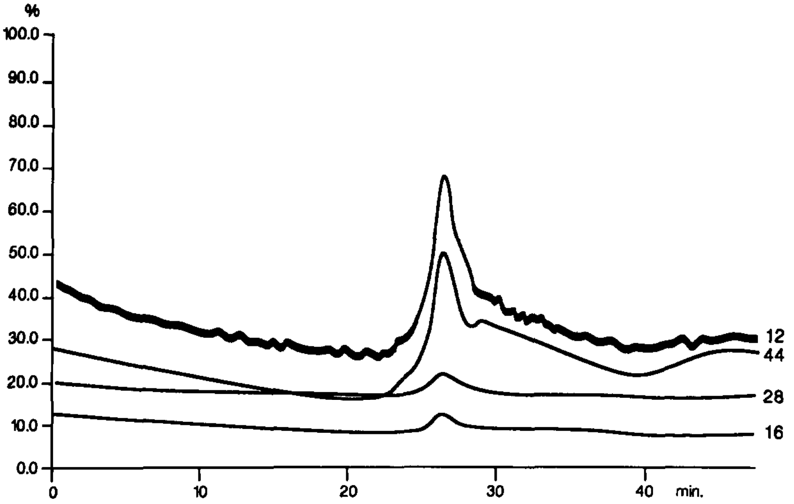

Fig. 7. Dynamic mass spectrogram of Xydar® SRT-500 for CO/CO$_2$ ($\delta G/\delta t$ on an arbitrary scale).

in Figs. 7 and 8. From the results of the various dynamic TG and DTG experiments (Table 2) it can be seen that in spite of rather similar $(\delta G/\delta T)_{\max}$ values, thermal decomposition of Xydar® SRT-500 begins at much higher temperatures. This accords with the more rigid linear backbone structure of this material; the naphthoyl units in Vectra® A950 disturb the linearity of this polymer. Therefore, stronger interactions between the Xydar®

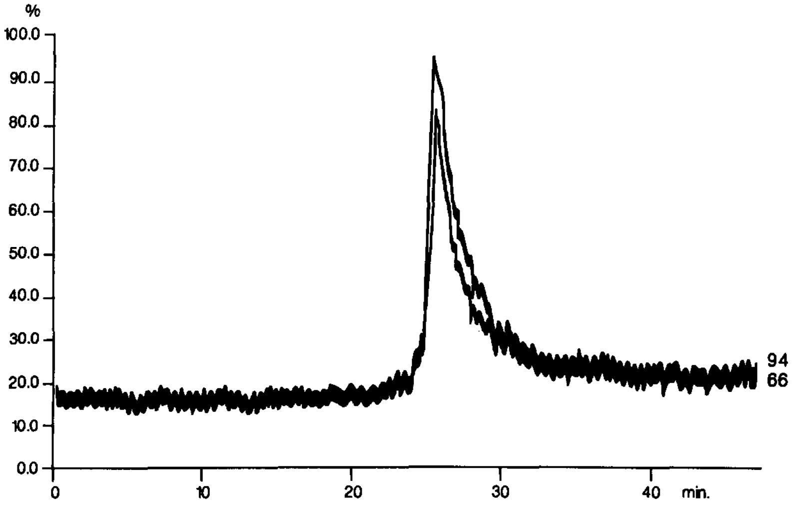

Fig. 8. Dynamic mass spectrogram of Xydar® SRT-500 for phenol ($\delta G/\delta t$ on an arbitrary scale).

polymer chains occur. Similar results have been reported by Crossland et al. [34] for closely related LCPs using pyrolysis–GC–MS (Py–GC–MS).

Isothermal measurements

TG–MS measurements of Vectra® A950 were carried out in isothermal conditions (1 h at 613 K, or 60 K above m.p.). In DTG measurements (Table 3), the experimental parameters (isotherm temperature, sampling time) were chosen so as to gain insight into the processing stability of these materials. In all cases isotherms were chosen at temperatures which exceed the DSC melting point by 10–70 K (i.e. above injection moulding and/or compounding temperature). 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. In normal practice, and with proper adjustment of the shot volume in relation to the cylinder volume, a residence time of 5 to 10 min is used. However, for safety reasons it is advisable to take into account the possibility of longer residence times due to unexpected processing problems.

After an initial degradation at the onset (10 min) of the 613 K isotherm no further weight loss occurs. Vectra® A950 is exceptionally stable even at this high temperature, which exceeds that of normal injection moulding conditions. Pyrolysis products are H_2O (m/z 18, 17 a.m.u.), CO and CO_2 (m/z 44, 28, 16, 12 a.m.u.) and some acetic acid (anhydride) during the first step of the process. Contrary to the dynamic measurements, in isothermal conditions phenol (m/z 94, 66 a.m.u.), naphthalene (m/z 128 a.m.u.) and xanthon (m/z 196 a.m.u.) are not found. This confirms the excellent stability of the polymer. The dependency of the measured products of degradation upon the manner in which the degradation is carried out has been observed previously [34]. In the case of Xydar® SRT-500 (isothermal treatment 1 h at 713 K, or 60 K above m.p.) a slightly different degradation pattern is obtained (Fig. 9). The $\delta G/\delta T$ vs t curve shows that the pyrolysis process is dualistic at the outset. During pyrolysis large quantities of H_2O evolve (m/z 18, 17, 16 a.m.u.) as crystal water or absorbed moisture. Only a small amount of benzene (m/z 78 a.m.u.) evolves; no phthalic acids are found. CO/CO_2 is formed in the second step of the degradation process. In contrast to Vectra® A950 evolution of these products continues even after $(\delta G/\delta T)_{\max}$.

The percentage weight losses are very small at the high isothermal temperatures (Tables 3 and 4) and denote very great stability of both materials. Vectra® A950 can be kept for about 20 min. at up to 70 K above its melting point before significant decomposition is detected. This is important in practice as during compounding of such a material with glass and/or other fillers higher temperatures may easily occur locally (e.g. owing

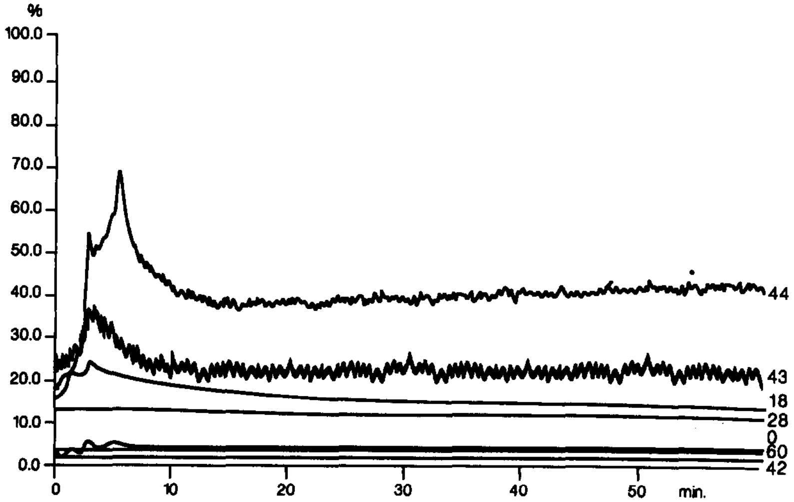

Fig. 9. Isothermal TG–MS curves of Xydar® SRT-500 at 713 K ($\delta G/\delta t$ on an arbitrary scale).

TABLE 3
Results of isothermal DTG measurements of Vectra® A950

Isothermal temperature (K)	Weight loss (ΔG) after t min (%)			
	$t = 10$	$t = 20$	$t = 30$	$t = 60$
563	< 0.1	0.2	0.5	0.8
583	< 0.1	0.3	0.6	0.9
603	< 0.1	0.5	0.7	0.9
623	0.8	1.0	1.2	1.4

to hot spots on the screw elements, internal friction as a result of the presence of the filler, etc.).

Xydar® SRT-500 is also, after initial pyrolysis and continuous CO/CO_2 evolution, (very) highly thermally stable, but a limit seems to be reached at about 713 K when C–C bond degradation begins. In fact, in the temperature range 713–733 K decomposition of the material is considerable, certainly if

TABLE 4
Results of isothermal DTG measurements of Xydar® SRT-500

Isothermal temperature (K)	Weight loss (ΔG) after t min (%)			
	$t = 10$	$t = 20$	$t = 30$	$t = 60$
663	< 0.1	0.3	0.4	0.6
673	0.1	0.4	0.5	n.d.
693	0.3	0.6	0.8	n.d.
713	0.4	0.8	1.1	n.d.
733	1.8	3.8	5.1	13.0

compared to Vectra® A950 in analogous conditions. Therefore, Xydar® SRT-500 should not be processed above about 713–723 K.

Comparison with related techniques

Using Py–GC–MS experiments v.d. Peyl and Cremers [35] have described other (minor) decomposition products of Xydar® and Vectra®. Up to m/z 200 a.m.u. these are for the 4-hydroxybenzoic acid unit: 4-hydroxybenzaldehyde (m/z 122 a.m.u.), hydroxynaphthalene (m/z 144 a.m.u.), dibenzofuran (m/z 168 a.m.u.), phenoxybenzene (m/z 170 a.m.u.), hydroxydibenzofuran (m/z 184 a.m.u.), hydroxyphenoxybenzene (m/z 186 a.m.u.), xanthon and phenylbenzoate (m/z 198 a.m.u.); for 2-hydroxy-6-naphthoic acid of Vectra®: naphthalene (m/z 128 a.m.u.) and hydroxynaphthalene (m/z 146 a.m.u.); for the terephthalic acid unit in Xydar®: benzene (m/z 78 a.m.u.); and for p,p′-biphenol: phenylphenol (m/z 170 a.m.u.) and 4,4′-dihydroxybiphenyl (m/z 186 a.m.u.). Accordingly, Py–GC–MS yields additional information due to different degradation conditions [34]; the method allows no quantitative analysis (see Table 5). According to Py–MS experi-

TABLE 5
Thermochemical methods

Method [a]	Thermal effects		Evolved gas analysis			Ref.
	With mass change	Without [b] mass change	Quant. [c]	Semiqual. [e]	Qual. [f]	
TG	+	–	–	–	–	36
TG–DTA	+	+	–	–	–	36, 37
TG–DSC	+	+	–	–	–	38
TG–MS	+	–	+ [d]	+	–	12, 14, 16–24
TG–MS/MS	+	–	+	+	+	25, 26
TG–GC–MS	+	–	+ [d]	+	+	39
TG–(FT)IR [g]	+	–	–	+	–	40, 41
Py–MS [h]	–	–	–	+	–	42–46
Py–GC–MS	–	–	–	+	+	45–47
PEGA [i]	+ [j]	–	+ [k]	–	+	48

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

ments [35] oligomeric structural units may also evolve eventually as a result of the reaction of different pyrolysis fragments.

Table 5 summarizes the main features of various thermochemical techniques. In the case of pyrolysis techniques, quantitative information is usually gathered by rather involved classical processes of hydrolysis in an autoclave at high temperature and pressure, followed by LC analysis of the monomer. In our case, LCPs are not greatly accessible to the classical analytical spectroscopical methods owing to their complex composition, insolubility and high chemical and thermal stability.

CONCLUSIONS

Investigations of the thermal decomposition 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, provided condensation and memory effects are suppressed, especially in the furnace tube and interface. Combination of these techniques on the same samples greatly improves the qualitative interpretation of TGA curves. To ensure routine application of TG–MS a rapidly interchangeable coupling device has been constructed allowing a high through-put. The instrumental combination (and its prospective commercial version) exhibits the following features: dynamic analysis, rapid response time, temporal correspondence between TG and MS data, ability to operate in a variety of atmospheres (oxidizing, inert), routine analysis by easy (de)coupling and short cleansing times. Product identification is based on evolved decomposition products on the basis of the molecular ion peak.

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