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COMBINED THERMOGRAVIMETRY–HIGH-RESOLUTION GAS CHROMATOGRAPHY FOR POLYMER DEGRADATION STUDIES

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SUMMARY

An automated system is described for the simultaneous thermogravimetry–high-resolution gas chromatography, designed for studying the kinetics of polymer thermal degradation. The method has been applied to polystyrene.

INTRODUCTION

Polymers generally decompose on heating to give a mixture of volatile products, the composition of which may range from low-boiling small molecules to high-boiling chain fragments. Accurate measurements of both the weight loss and the rate of evolution of each volatile product are necessary for detailed studies of the kinetics and mechanism of the reactions during the thermal degradation of polymers. It is well known that these reactions depend strongly on the experimental parameters, such as sample size and geometry, heating rate, temperature distribution in the sample and rate at which volatile products are removed from the polymer during degradation. Combined thermogravimetry–high-resolution gas chromatography (TG–HRGC) is, in principle, the most suitable technique fulfilling the above requirements. However, a number of possible shortcomings, such as condensation and secondary decomposition of degradation products in the transfer system, must be taken into account in interfacing a thermobalance with a gas chromatograph. In addition, different techniques generally perform best under different conditions. When two such techniques are combined, the operating conditions must be carefully chosen to obtain the best compromise in the performance of both.

In this paper an automated combined TG–HRGC technique is described, which was designed and developed with the aim of optimizing the data from studies on the thermal degradation of polymers, and an example of its application is given.

INSTRUMENTATION AND SYSTEM DESIGN

The principle of the system is the periodic sampling of the volatile products evolved by the polymer during degradation in the thermobalance by means of a valve, which injects them into a gas chromatograph equipped with a capillary column. The rate of evolution of each degradation product is calculated from the area of the related

gas chromatographic peak and is referred to the degree to which the process has advanced, as measured by the weight loss at the moment of sampling. A schematic diagram of the TG-HRGC system is shown in Fig. 1.
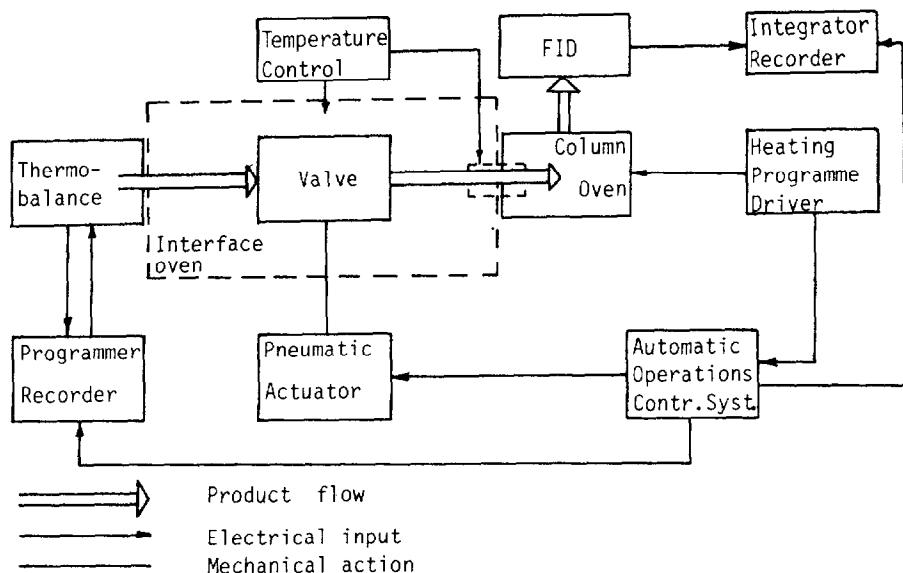

Fig. 1. Schematic diagram of the TG–HRGC system. FID = Flame-ionization detector; Contr. Syst. = control system.

Thermogravimetry

Thermogravimetry is carried out on a DuPont 951 thermobalance, driven by a DuPont 990 thermal analyser unit, which also records the weight loss of the polymer as a function of time in isothermal experiments or of temperature in dynamic experiments. The termobalance is designed so as to allow purging with an inert gas of the tube enveloping the weighing arm of the balance on which the sample holder hangs (quartz furnace tube, Fig. 2). The volatile degradation products are thus swept towards the end of the furnace tube. The flow of the purge gas is carefully controlled by a needle valve. The furnace of the thermobalance was rebuilt and its length extended in order to ensure uniform heating of the last portion of the furnace tube, normally emerging unprotected from the furnace. In this way, condensation on the wall of the furnace tube of high-boiling products, swept along by the purge gas, is avoided. The narrowing far end of the furnace tube is inserted directly into the interface oven housing the interface lines and the sampling valve, because the edge of the furnace is in contact with the wall of the oven (Fig. 2).

Sampling valve and transfer lines

The purge gas from the thermobalance is sampled by means of a stainless-steel dual external loop valve which can operate up to 300°C (Valco Instruments, Houston, TX, U.S.A.) (Fig. 2). The valve has two positions and is operated by a pneumatic
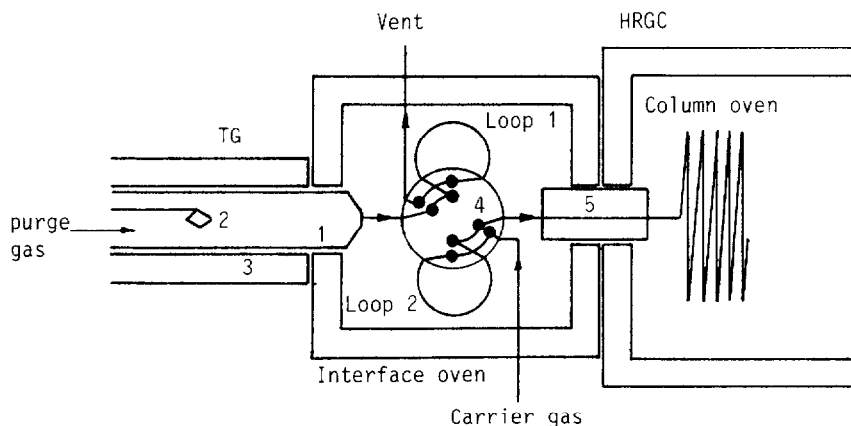
Fig. 2. Layout of sampling valve and transfer lines. 1 = TG furnace tube; 2 = TG sample pan; 3 = TG furnace; 4 = sampling valve; 5 = heated aluminium block.

actuator (Valco Instruments). In the position in Fig. 2, loop 1 is being loaded while the sample in loop 2 is being injected in the capillary column. The reverse occurs when the valve is switched to the other position.

In order to avoid condensation of high-boiling products, the valve and all transfer lines and connections are enclosed in a box of insulating material (asbestos-free Mono-lux 500; Cape Board) in which a heating strip is loosely arranged through void spaces. Uniformity of the temperature inside the oven is ensured by natural circulation of air. As there is no direct contact of the heating element with the apparatus, thermal degradation of the products at "hot spots" is avoided.

The gas sample is directly injected into the capillary column, which has its end section straightened for connection to the sampling valve. Across the walls of the interface oven and of the gas chromatograph, the temperature of the straightened end section of the column is regulated by an aluminum block, provided with a cartridge heater. A temperature control unit (Fig. 1) provides power for heating the interface oven and the aluminum block and keeps their temperatures at the same selected value by means of control thermocouples (Pt 100). A stainless-steel tube (1/16 in.O.D., 0.03 in.I.D.), connecting the furnace tube to the valve, supplies the carrier gas and is used for the outlet line. Zero dead-volume fittings are used for connecting the loops, the carrier gas line and the capillary column to the sampling valve. Thus, the effect of dead volumes on the GC separation is made negligible, as shown by the symmetry of peaks obtained when methane is introduced into the system, which does not retain it.

High-resolution gas chromatography

A Carlo Erba Fractovap 4160 gas chromatograph is used, equipped with a fused-silica capillary column, a flame-ionization detector and a Hewlett-Packard 3390A reporting integrator.

Automatic operations control system (AOCS)

This unit provides the control of automatic operations. Once the TG system is started by manually switching on the heating programme of the gas chromatograph,

the input to the AOCS switches on the integrator–recorder and the pneumatic actuator which makes the valve inject the content of the sampling loop, which was being loaded and marks the event on the TG recorder. At the end of the heating programme, the AOCS switches the integrator–recorder to the print function. The cycle starts again automatically after cooling, once the heating programme is reactivated.

OPERATING PARAMETERS

Interface oven temperature

The temperature of the interface oven, housing the valve and the transfer lines, must be carefully selected in order to obtain reliable results. The major problems are condensation and decomposition or polymerization of the products to be analysed. The following procedure was used for choosing the appropriate temperature. The polymer to be studied was thermally degraded in a separate experiment in a closed system. The products were collected in a cold trap and subsequently separated by HRGC at a 15°C/min heating rate. The temperature of the interface oven in the TG–HRGC system was set to the temperature at which the highest boiling product is released from the column. The entire TG–HRGC system was then tested by introducing a sample of the mixture of the degradation products in the sample pan of the thermobalance and letting it evaporate at a constant rate in the stream of purge gas. Repeated injections must give reproducible areas of GC peaks.

Sampling volume

Several variables must be considered in order to arrive at an appropriate volume for the sample loop, namely, amount of polymer degraded, rate of volatilisation and flow-rates of the purge and carrier gases. To take full advantage of HRGC, the efficiency of the GC separation is the parameter that must guide the choice of the variables involved. For example, high sensitivity of the TG–HRGC system to degradation products evolved at a low rate would require a large sample loop. However, high efficiency of GC separation requires a small sample loop to minimize the injection time. In routine analysis the maximum volume of the sample loop to be used was established by comparing the efficiency of the GC separation, as measured by the separation number, TZ, obtained by manual injection of a C_{10}–C_{11}–C_{12} mixture, with that obtained for the same mixture, introduced in the thermobalance, when loops of different size are used in the TG–HRGC system. The data in Table I show that, when helium is used

TABLE I

TZ VALUES FOR MANUAL INJECTION AND IN THE TG–HRGC SYSTEM

Column: SE-54. Temperatures: TG system, 25°C; column, 95°C; flame-ionization detector, 300°C; injector (manual), 250°C; interface oven (TG–HRGC), 250°C, carrier gas, helium, 2 ml/min (50 cm/sec); purge gas, nitrogen, 40 ml/min.

Injection	Injection time (sec)	Products	
		C_{10}–C_{11}	C_{11}–C_{12}
Manual, 0.5 µl, split 250:1	–	20.76	23.74
TG–HRGC loop, 30 µl	0.9	10.37	17.25
TG–HRGC loop, 10 µl	0.3	20.38	22.54

as the carrier gas, an efficiency close to that obtained by manual injection is produced by a 10-μl sample loop (ca. 0.3 sec injection time). Larger loops could be used with higher flow-rates of the carrier gas, but this is not advisable, as the efficiency of the separation would decrease.

Once the volume of the sample loop has been selected, the minimum rate of evolution of degradation products from the polymer for which the kinetics of the process can be studied with the TG–HRGC system depends on the nature of the polymer, the size of the sample introduced into the thermobalance and the flow-rate of the purge gas. In order to remove the degradation products from the sample as soon as they are formed and to avoid secondary decomposition, the thickness of the sample must be low. In general, to obtain reliable results with the DuPont 951 thermobalance, the sample should not exceed 30–50 mg. By lowering the flow-rate of the purge gas, the concentration of volatile degradation products increases, and so does the amount of such products stored in the sample loop. However, rates below 30 ml/min should not be used in order to avoid secondary decomposition. When the kinetic study involves high rates of volatilization of the polymer, the opposite problem arises, namely overloading of the column. In this instance, smaller samples of polymer, smaller loops and higher flow-rates of purge gas must be adopted.

CALIBRATION

Calibration is carried out with pure compounds, identical with or similar to those obtained from the thermal degradation of the polymer, which were previously identified by separate degradation, collection of products and analysis by gas chromatography–mass spectrometry. Preparative GC could supply the individual pure products.

A short glass capillary (1 cm), filled with the pure compound, is introduced into the sample pan of the thermobalance and allowed to evaporate at constant temperature under the purge gas stream in the TG–HRGC system. As the evaporating surface is constant during evaporation, the rate of weight loss is constant long enough for evaluating with high accuracy the proportionality factor between the area of the gas chromatographic peak and the rate of evolution, as calculated by the weight loss and the time elapsed. The constancy of the factor over a range of evolution rates can be tested by changing the temperature or the dimensions of the capillary. The reproducibility of the calibration was found to be better than 1 %. The calibration obviously holds only for a given set of operating parameters.

APPLICATION TO POLYSTYRENE DEGRADATION

Polystyrene is degraded on heating to a mixture of toluene, styrene, a-methylstyrene and dimeric, trimeric and tetrameric fragments[1-3]. The operating parameters for TG–HRGC, selected on the basis of the above procedure are as follows: polystyrene, 4 mg; TG temperature, 350°C; purge gas, nitrogen, 40 ml/min; interface oven, transfer line temperature, 275°C; sample loop, 10 μl; capillary column, 20 m × 0.3 mm I.D., SE-54 (0.2-μm coating thickness); detector temperature, 340°C; carrier gas, helium, 2 ml/min; column oven, 80°C isothermal for 2 min, 15°C/min to 280°C, isothermal for 4 min, 20°C/min to 310°C, cool to 60°C; standby, 2 min at 80°C.

The testing procedure showed that the degradation products collected in a sep-
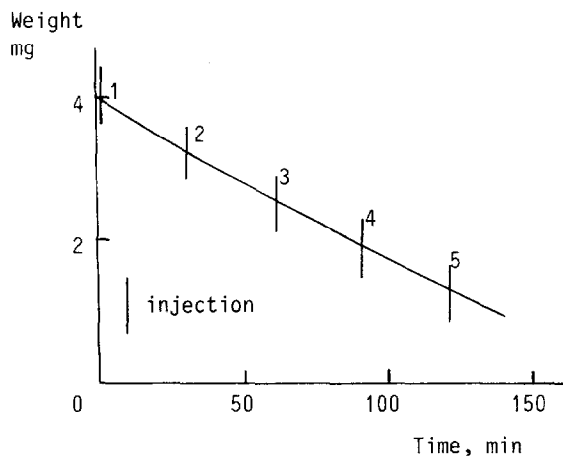
Fig. 3. Isothermal weight loss curve of polystyrene at 350°C. For experimental results of injections 1, 2, etc, refer to Table II.
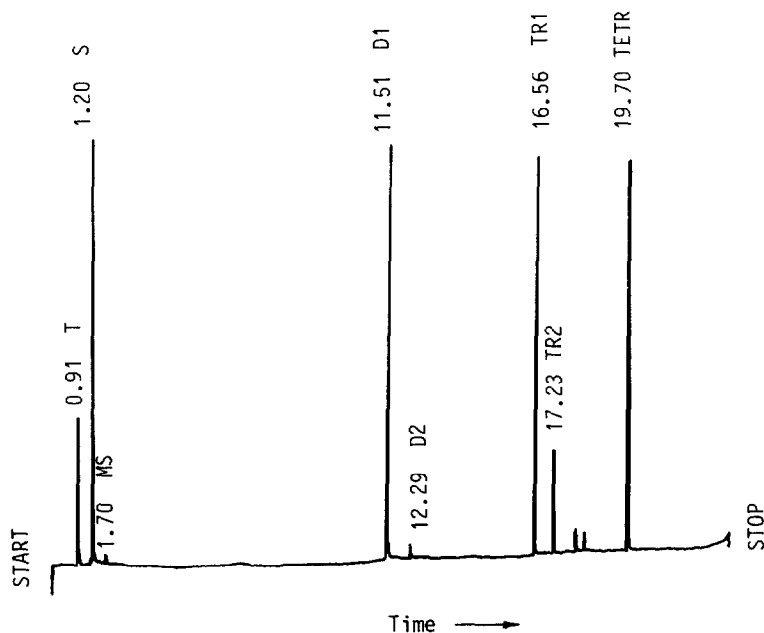

Fig. 4. Gas chromatogram of degradation products of polystyrene, degraded at 350°C in the TG–HRGC system. T=Toluene; S=styrene; MS=α-methylstyrene; D1 and D2=dimeric fragments; TR1 and TR2=trimeric fragments; TETR=tetrametric fragments.

arate degradation experiment were quantitatively transferred from the thermobalance to the HRGC system. The calibration was carried out with toluene, α-methylstyrene, styrene and the mixture of dimeric fragments, isolated by preparative GC of the degradation products. As the same proportionality factor, on a weight-basis, was found for

TABLE II

RATES OF WEIGHT LOSS AND OF EVOLUTION OF DEGRADATION PRODUCTS FOR POLY-
STYRENE AT 350°C.

Abbreviations as in Fig. 4.

Injection No.	Time (min)	Rate (mg/min × 10³)							
		Weight loss	T	S	MS	D1+D2	TR1	TR2	TETR
1	1	25.3	0.24	11.14	<0.04	2.06	12.70	0.60	0.42
2	31	26.6	0.12	8.82	<0.04	1.72	11.56	0.30	1.08
3	68	22.4	<0.04	8.56	<0.04	1.40	11.64	0.28	1.16
4	93	18.6	<0.04	6.10	<0.04	1.22	9.02	0.24	1.16
5	124	14.6	<0.04	3.66	<0.04	0.42	7.48	0.18	0.90

α-methylstyrene, styrene and the dimeric fragments, the same proportionality factor
was used to evaluate the rate of evolution of trimeric and tetrameric fragments.

Figs. 3 and 4 show, respectively, the thermogravimetric curve and a typical gas
chromatogram obtained from TG–HRGC of polystyrene. Table II gives the rate of
total weight loss and the rate of evolution of the degradation products.

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Fig. 1. Schematic diagram of the TG–HRGC system. FID = Flame-ionization detector; Contr. Syst. = control
system.