Thermochimica Acta, 10 (1974) 259–268

SIMULTANEOUS THERMOGRAVIMETRY AND MASS SPECTROMETRY IN POLYMER CHARACTERIZATION

G. J. MOL

International Business Machines Corporation, General Products Division, San Jose, Calif. (U.S.A.)
(Received 1 July 1974)

ABSTRACT

The assembly and operation of a simple, directly coupled thermobalance and quadrupole mass spectrometer are described. Usefulness of the method and ease of operation are illustrated by the decomposition of TDI and MDI polyurethanes, ABS plastic and a capped and uncapped polyester.

INTRODUCTION

The weight change of a sample as a function of either time or temperature has been used widely to estimate relative polymer stability[1] and to evaluate the kinetics of degradation[2]. The literature on this technique, thermogravimetry (TG), is extensive[3]. In addition, many workers have found it useful to analyze the gaseous products of decomposition[4]. This requires additional instrumentation and frequently an appropriate coupling mechanism between the two machines. TG systems have been combined with gas chromatography (GC)[5], mass spectrometry (MS)[6], both GC and MS[7] and GC plus infrared[8]. However, most workers using these combined machines attest that numerous instrumental problems have been encountered at every stage of design and operation.

From an analysis of the method it is evident that the more direct the coupling and the simpler the system to which the TG is attached, the lower the level of difficulty in design and operation. Quadrupole mass spectrometry (QMS) is one such approach we have studied in our laboratories. The purpose of this paper is to describe a working system and illustrate the operation with several polymer samples.

INSTRUMENTATION

A Mettler Thermoanalyzer I was coupled to a UTI 100C precision mass analyzer by attaching a vacuum connector to the quartz furnace tube. The direct coupling to the furnace tube eliminates the problems inherent in trapping or collecting fractions for subsequent analysis, such as secondary reactions and/or contamination or products from more than one reaction. Other systems of this type[9,10] attach the quadrupole mass spectrometer (QMS) inside the cold trap chamber. Analysis of easily condensable gases is not possible with such an arrangement.

The coupling of the Mettler Thermoanalyzer I to the UTI 100C precision mass analyzer (F) is shown in Fig. 1. A Cajon "flexible glass-end tubing" made of 321 stainless steel fused to a Type 7740 Pyrex glass on one end served as the interface between the UTI 100C flange and the quartz furnace of the thermoanalyzer. A graded quartz-to-Pyrex seal was used for the furnace connection. Quartz tabs were made on the furnace to hold the nichrome heating element below the interconnecting tube. The 321 stainless steel was vacuum welded to a 2–3/4 in. "Con Flat" flange. The distance between the sample pan (R) (4 mm high and 3 mm diameter) and the quadrupole mounting flange is 20 cm. The interconnecting orifice has a 23-mm inner diameter which, along with its short length, results in a negligible dead time. The ability of the quadrupole mass filter to accept the filtering ions over a relatively large inlet-energy spread and at varying entrance angles makes it well suited for use in this application.

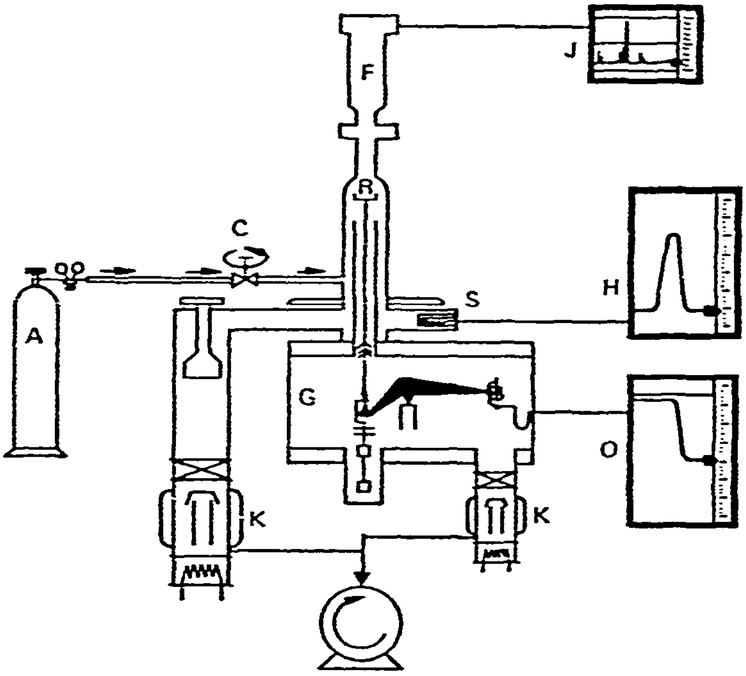

Fig. 1. Instrumentation.

A clamping and pneumatic lifting mechanism supports the mass analyzer and facilitates sample changes by eliminating the need to break the furnace-to-mass analyzer seal. The pneumatic cylinder is a dual action type with rate controllers on each air line. The power supply for the mass analyzer is mounted on a stand attached to a tube inserted into the high-temperature furnace support tubing. The quadrupole electronic control console is mounted in the Mettler electronic cabinet.

Signals from the QMS multiplier after amplification are displayed on an oscilloscope or a pen recorder (J) at slow (2-min) scans. Two 60 l sec^{-1} diffusion pumps (K) evacuate the balance housing (G) and sample chamber. Total pressure is determined with an ionization gauge (S) and is continually recorded (H) during the analysis. Pressures as low as 2×10^{-6} torr have been achieved with this system. The TG signal is recorded (O). Purge gas is furnished from cylinder A through metering valve C.

PROCEDURE

A sample (1–2 mg) is loaded on pan R and a suitable vacuum is obtained (usually less then 1×10^{-5} torr) using the pumping system; the background is recorded at an ionization energy of 70 eV. This background is then used to correct all subsequent spectra. The thermal analyzer is heated at a programmed rate (2, 4, or 6°C min^{-1}) and the mass spectra are recorded continuously over a 2-min period. Thus, the same mass peak is monitored every 4, 8, or 12°C. After completion of the analysis, the data are converted to A gm^{-1} and plotted as a function of temperature. From the gas-release patterns, pressure and weight loss curves, the kinetics and decomposition mechanisms can be determined by any of the methods given in the literature[3]. In addition to the simple weight loss rates, the rate of appearance of certain mass peaks can be used in activation energy and reaction order calculations.

At the end of each run, the furnace is heated to 600 or 700°C and held there for 2 or more hours, and the mass probe is heated to 340°C to bake out the system.

RESULTS

ABS

A typical mass spectrum of the background at the beginning of the analysis is shown in Fig. 2. Figure 3 shows the mass spectrum at four progressively higher

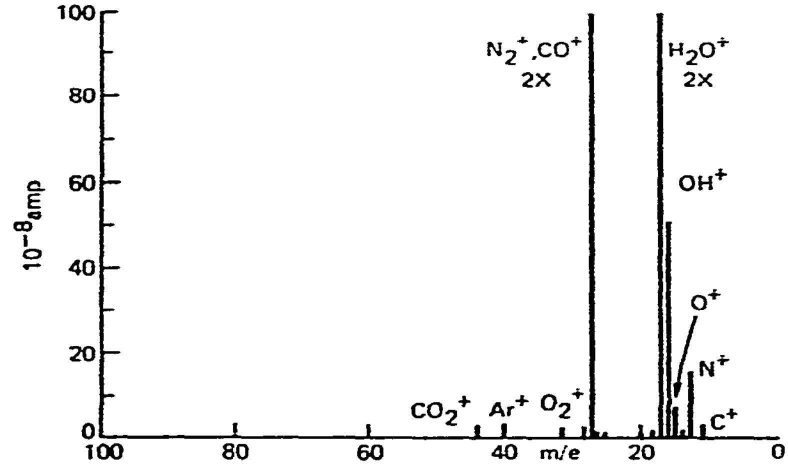

Fig. 2. Typical mass spectrum of the background at the beginning of analysis.

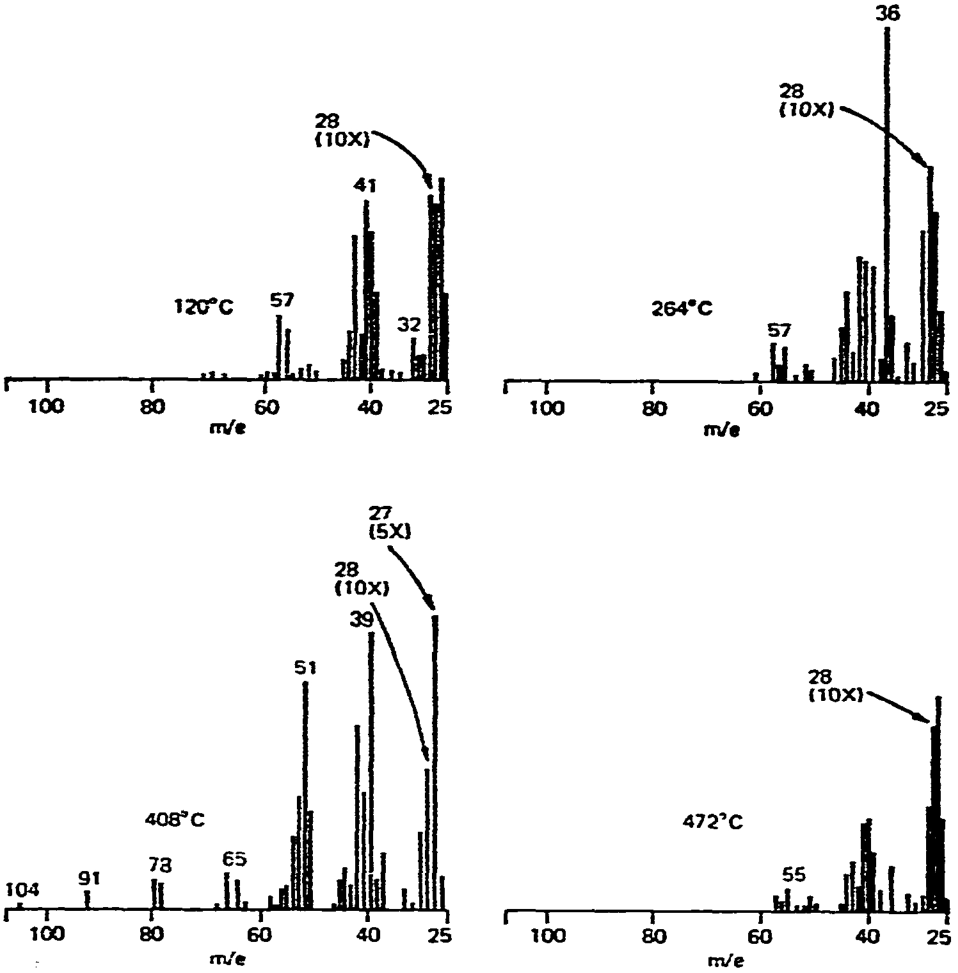

Fig. 3. Mass spectrum of Abson 89129 during heating cycle (no background corrections).

temperatures during the heating cycle. The spectrum taken at 120 °C indicates residual fractions of low-molecular-weight hydrocarbons. These are the alkene mass peaks at (*m/e* 41, 55, 69) and the alkane mass peaks at (*m/e* 43, 57, 71). At 284 °C the dehydrohalogenation of polyvinyl chloride (PVC) (employed as a fire retardant) proceeds at a rapid rate. The mass spectrum at this temperature shows the chlorine mass peaks at *m/e* 35 and 37 and the hydrogen chloride mass peaks at *m/e* 36 and 38. The isotope ratio ^{37}Cl to ^{35}C is at the natural abundance level of one-third. By 400 °C mass peaks characteristic of styrene (*m/e* 51, 78, 91, 104 and 105), acetylene (*m/e* 29 and 51) acrylonitrile (HCN fragment at *m/e* 27 and the monomer at *m/e* 53) and butadiene (*m/e* 54) become evident. The acetylene in that spectrum is from the decomposition of polyacetylene which was formed by the loss of HCl and HCN from PVC and polyacrylonitrile, respectively. At 468°C the decomposition is almost complete. The residual fractions of the mass peaks shown at 400 °C are still evident.

The thermogram of the ABS is shown in Fig. 4. Notice the correspondence between the pressure and the derivative of the thermogravimetric curve. Thus, the pressure of the gases is in direct proportion to the amount of the sample which has decomposed into a gas.

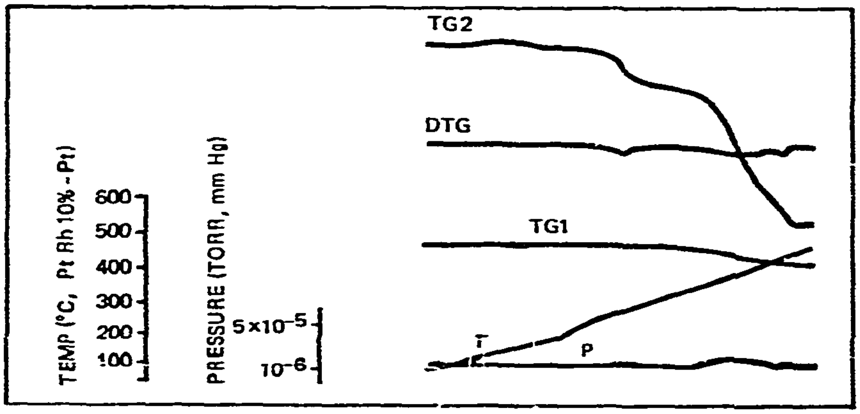

Fig. 4. Thermogram of ABS.

The pattern of evolution of the decomposition products from the ABS is shown in Fig. 5. The PVC, used as a fire retardant in this case, is represented by HCl evolution. The polyacrylonitrile degradation is represented by the evolution of HCN. Styrene is representative of the polystyrene degradation. The decomposition of polybutadiene gives rise to the evolution of butadiene.

This pattern of evolution of styrene, butadiene and acrylonitrile as a function of temperature provides a unique way for classifying different types of ABS. The

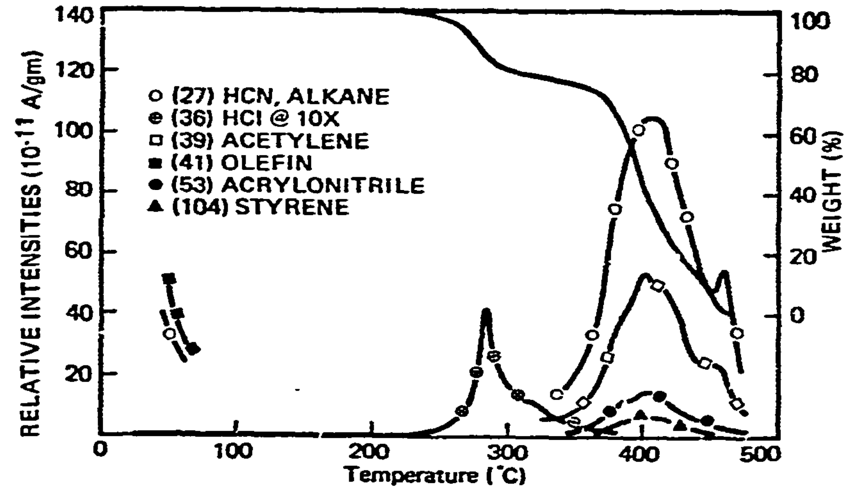

Fig. 5. Evolution of the decomposition products from ABS.

presence of impurities and additives such as fire retardants are also detected during the analysis.

Polyurethanes

Figures 6 and 7 show the chart records from the Mettler Thermoanalyzer I for the toluene diisocyanate (TDI) and methylene bis-4-phenyl isocyanate (MDI) based polyurethanes. The most obvious difference between the thermal decomposition of the two materials is their pressure behavior. The TDI polyurethane has a much greater increase in pressure than the MDI polyurethane, indicating a higher loss of low-molecular-weight fragments. This is not possible to judge from the TG curves. Such indications are of great importance when evaluating kinetics or considering mechanically similar materials for heat sensitive applications.

Figures 8 and 9 show the degradation products as a function of temperature. The symbols in these figures are used to differentiate the lines and are not actual data

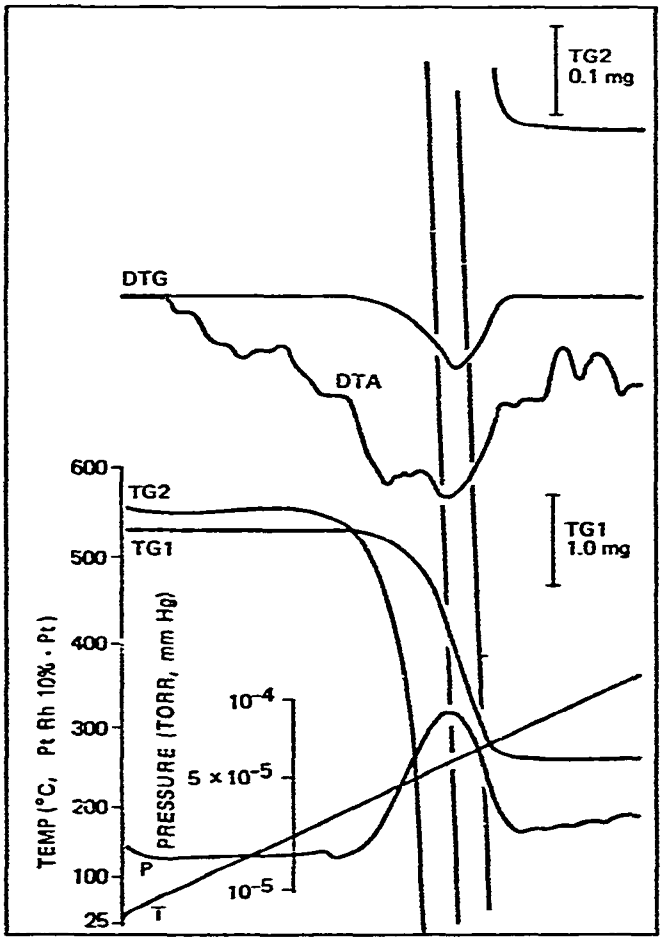

Fig. 6. Thermogram of TDI polyurethane.

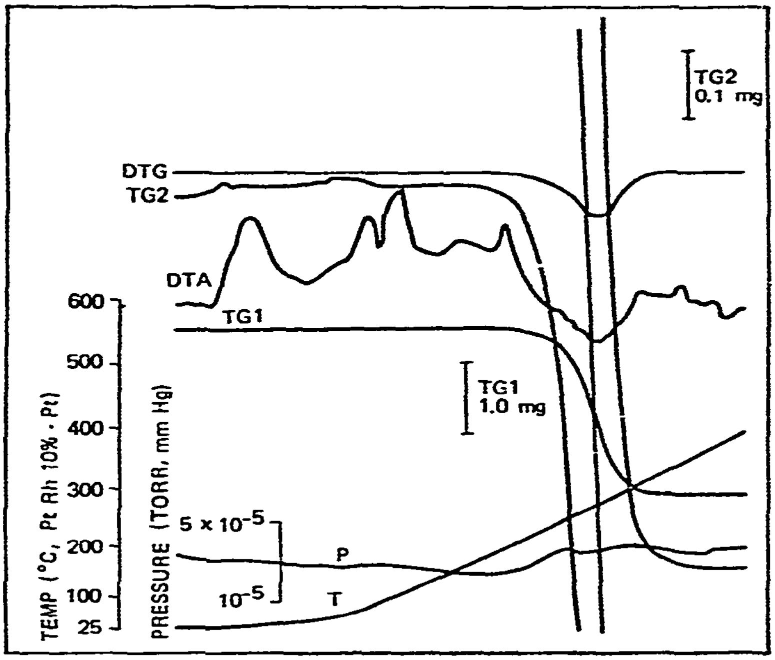

Fig. 7. Thermogram of MDI polyurethane.

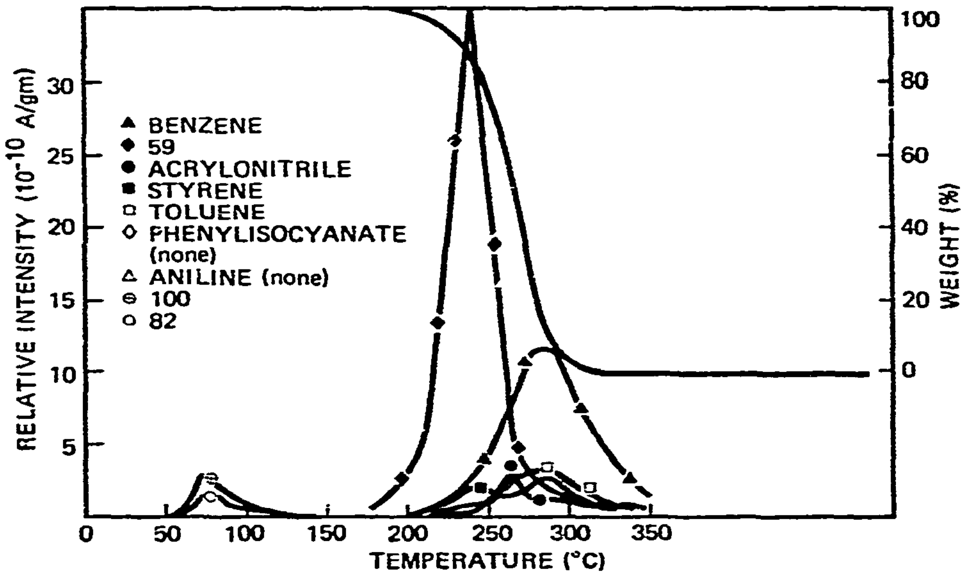

Fig. 8. Thermal degradation of TDI polyurethane.

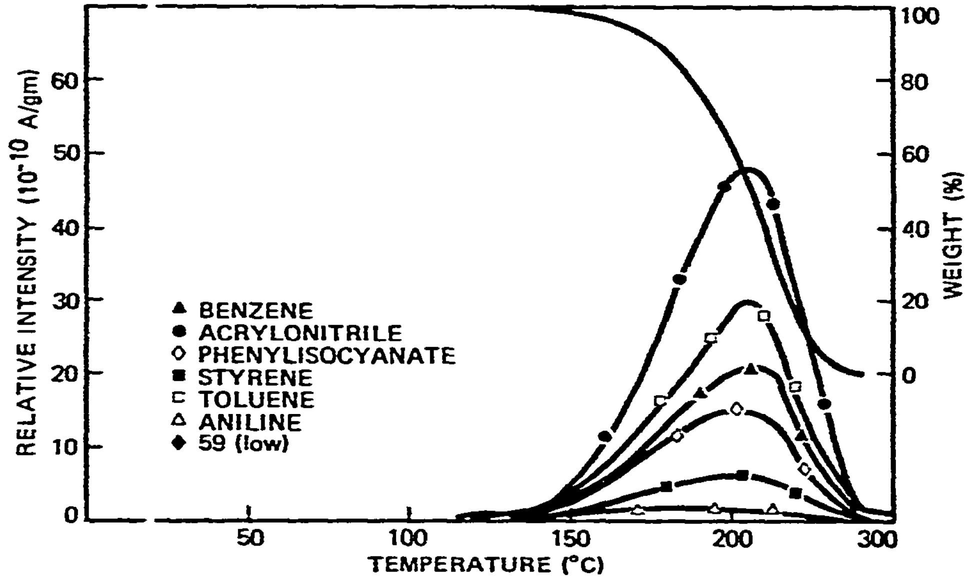

Fig. 9. Thermal degradation of MDI polyurethane.

points. The data points are more numerous, being every 12°C. TDI is characterized by the presence of phenylisocyanate and aniline fragments. On the other hand, MDI shows a strong peak at mass number 59, so far not identified. An impurity is released in the MDI from 50–125°C (Fig. 8). Such low temperature losses of volatile trace material are frequently of major importance to mechanical properties. It would be very interesting to study the effect of cure cycles on the 82 and 100 products. Given samples of different prepolymer compositions, the mass yields of the fully cured material have been shown to reflect the prepolymer composition. This is a difficult analytical problem by other methods—especially on finished products.

Polyesters

To determine whether the mechanism of decomposition for this polyester was random decomposition or unzipping, capped and uncapped polyester samples were examined.

Figure 10 illustrates the thermal decomposition of the uncapped polyester. The evolved gases exhibit the same inflection as shown in the weight-loss curve. By capping this polymer, a pronounced shift to higher temperatures occurs in the decomposition curve (Fig. 11). Therefore, the basic mechanism for the decomposition of this polymer must be unzipping through the ester group and the liberation of CO_2. The unzipping is most likely cyclic of the back biting type[11]. The presence of CO_2 as a thermal decomposition product was verified by pyrolysis GC.

A simultaneous TG–MS system has demonstrated the ease of making polymer compositional and structural determinations. It opens up new ways to study decomposition kinetics and mechanisms. The sensitivity of this method to the detection of additives and other volatiles is far greater than conventional TG. The system has a simplicity and directness which should minimize problems of vapor fractionation and condensation.

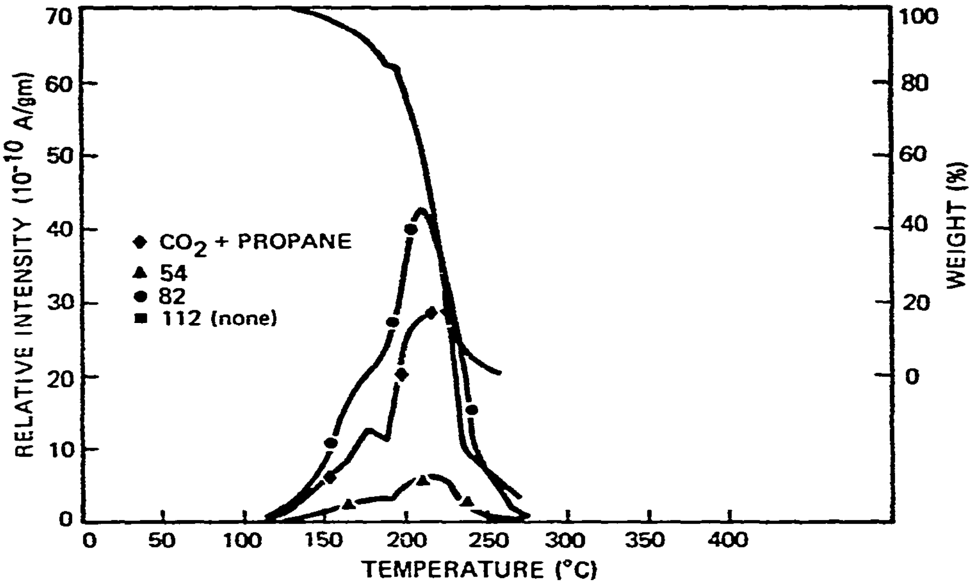

Fig. 10. Thermal degradation of polyester (uncapped).

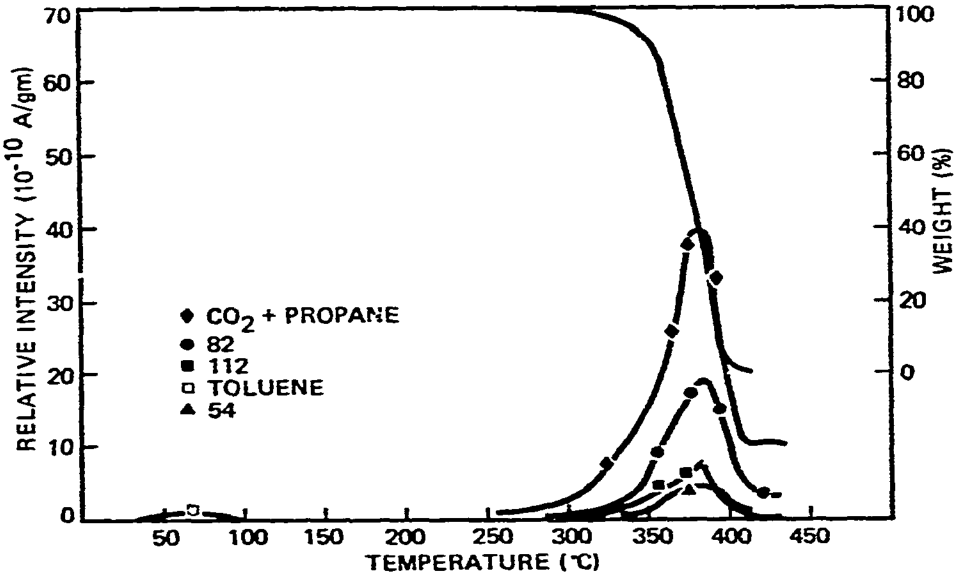

Fig. 11. Thermal degradation of polyester (capped).

ACKNOWLEDGEMENTS

The author is indebted to Edward M. Barrall, II, for reviewing this note and D. Johnson for preparing the polyurethane and polyester samples.

REFERENCES

1 J. Chiu, *Appl. Polym. Symp.*, 2 (1966) 25.
2 S. L. Madorsky, *Thermal Degradation of Organic Polymers*, John Wiley—Interscience, New York, 1964.
3 W. W. Wendlandt, *Thermal Methods of Analysis*, Interscience, New York, 1964, p. 50 et sequi.
4 P. E. Slade, Jr. and L. T. Jenkins, *Techniques and Methods of Polymer Evaluation—Thermal Analysis*, Vol. 1, Marcel Dekker, New York, 1966, p. 231.
5 J. Chiu, *Anal. Chem.*, 40 (1968) 1516.
6 F. Zitomer, *Anal. Chem.*, 40 (1968) 1091.
7 T. Chang and T. E. Mead, *Anal. Chem.*, 43 (1971) 534.
8 P. Cukor and E. W. Lanning, *J. Chromatogr. Sci.*, 9 (1971) 487.
9 E. K. Gibson, Jr. and S. M. Johnson, *Thermochim. Acta*, 4 (1972) 49.
10 H. G. Wiedemann, in R. F. Schwenker, Jr. and P. D. Garn (Eds.) *Thermal Analysis*, Vol. 1, Academic Press, New York, 1969, p. 229.
11 R. Simha, *Advan. Chem.*, 34 (1962) 157.