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Publisher *Taylor & Francis*

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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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To cite this Article Vogl, O. , Ivansons, V. , Miller, H. C. and Williams, H. W.(1968) 'Thermal Degradation Spectrum; Instrumentation to Record Thermogravimetric Results', *Journal of Macromolecular Science, Part A*, 2: 1, 175 – 181

To link to this Article: DOI: 10.1080/00222336808053355

URL: <http://dx.doi.org/10.1080/00222336808053355>

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Thermal Degradation Spectrum; Instrumentation to Record Thermogravimetric Results*

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Summary

Simple modification of conventional temperature-programmed thermogravimetric apparatus permits direct recording of the thermal degradation spectrum (TDS) of polymers and the rate of weight loss with rising temperature. The effect of heating rate on the TDS of poly(methyl methacrylate) is discussed.

An instrumental attachment to a TGA apparatus records directly the first derivative (rate of weight loss vs. temperature) of a temperature-programmed thermogravimetric analysis (TGA) curve—which we call the thermal degradation spectrum (TDS). It is an improved way to detect thermal stability differences in polymers.

Thermal analysis is one of the most rapidly developing areas in polymer characterization. TGA and differential thermal analysis (DTA) have been widely used [1-4], but until recently no one took advantage of the first derivative thermal-weight-loss curves to study polymer degradation. Grassie [5] measured how pressure increases with temperature during a temperature-programmed polymer degradation, manually plotted the rate and called his curves "thermal" spectra. McNeill [6] described this method in more detail and demonstrated it on several polymer samples. He called it thermal volatilization analysis (TVA) and named his curves TVA thermograms.† Examples of TGA plottings in their derivative forms are

*Contribution No. 1366.

† We wish to caution against the use of the work "thermogram" because this word has already been used for recording DTA data and for a medical technique [7] to measure the heat emitted through the skin at various points of the body. Medical thermograms are used to diagnose such disorders as tumors and to observe effects of their treatment.

mentioned also in degradation studies of epoxy polymers [8], cellulose derivatives [9], and irradiated polyethylene [10].

The maximum application temperature of organic chromatographic sorbents [11] was determined with a derivatograph [12].

Some time ago, we thought that the first derivative of the TGA curve, rather than the TGA curve itself, would demonstrate better the weight-loss characteristic during polymer degradation. Initially the first derivative curves were drawn by plotting 25 or 10°C increment weight losses against temperature. However, a faster method with direct readout was desired.

The basic instrument was an Ainsworth Model RV-AU-2 automatic recording balance. The primary variables, consisting of weight loss and temperature of the sample, were recorded as a function of time on a two-pen Bristol recorder. A sample, suspended inside an extension chamber below the balance, was heated by a manually controlled furnace.

A 10-turn 5000-ohm retransmitting potentiometer, coupled to the "weight-loss" balance motor of the Bristol recorder, provided a signal directly proportional to the displacement of the pen and therefore proportional to the loss of weight of the sample. The simple circuit for differentiating the output of the retransmitting potentiometer is shown in Fig. 1. A low-voltage offset operational amplifier (Phil-

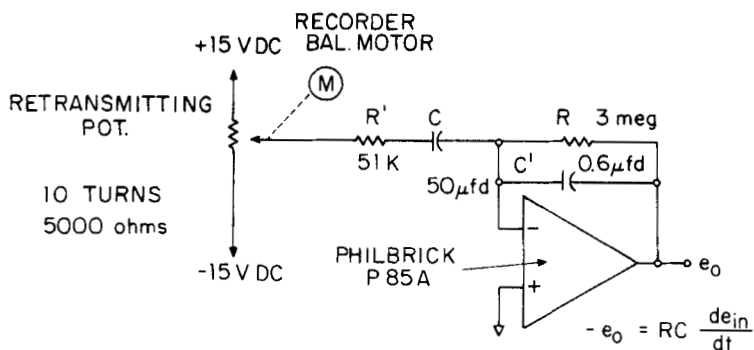


FIG. 1. Differentiator circuit.

brick P85A) connected as an active differentiator was used. At low frequencies, below 0.01 Hz ($Z_R \ll Z_C$ and $Z_{C'} \gg Z_R$), the following circuit equation holds:

$$e_o = RC(de_{in}/dt)$$

$$e_o(\text{V}) = (150 \text{ sec}) \times (\text{input rate in volts per second})$$

As an example, $e_0 = 1$ V with a 6.6 mV/sec change at the input. At higher frequencies (above 0.1 Hz, $Z_{R'} > Z_C$ and $Z_C < Z_R$), the circuit begins to function as an integrator, filtering out high-frequency noise. This differentiator output was recorded vs. temperature on a Mosely x-y recorder.

We have operated our derivatograph for 3 years and have routinely recorded thermal degradation spectra (TDS) with good results. TDS, like TGA, are related to the weight loss of the sample and not, as in the TVA case, to the volume of the decomposition products. Incidentally, the TDS technique is not limited to organic polymers, but it could be used for other weight-loss studies.

Various kinds of information can be obtained from TDS: (1) Maximum degradation temperature (MDT) is the temperature of maximum rate of degradation; (2) the temperature of the onset of polymer degradation shows the thermal stability; (3) if more than one peak is observed in TDS, polymer portions with different thermal stability or volatile components (e.g. monomer) are present (their relative percentage can be determined by integrating the various peaks); and (4) differences in shapes of degradation peaks reflect different types of degradative reactions in various polymers.

Figures 2-5 show TDS of a variety of polymers: polyolefins, polyamides, polyesters, and polyacetals. MDT values correlated well with the known differences in the thermal stability of these polymers

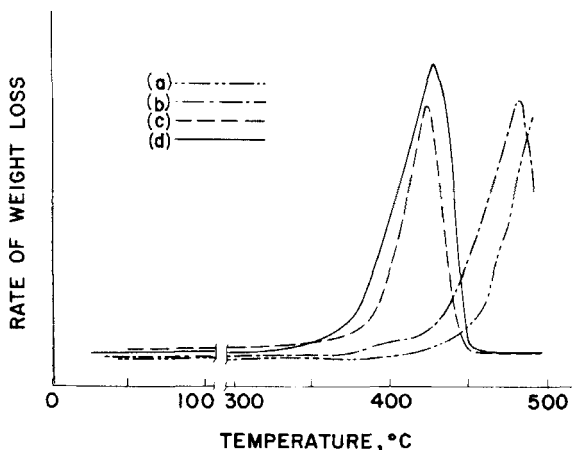


FIG. 2. Thermal degradation spectra of polyolefins: (a) polyethylene; (b) polypropylene (oriented 2002); (c) polystyrene; Fosterane 50 D AR 9100; (d) polystyrene; Bakelite BMS 601 A-1. Programmed heating rate: 6°C/min.

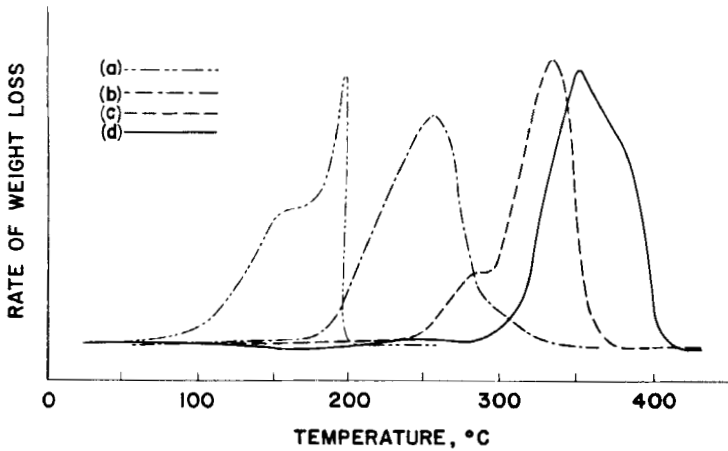


FIG. 3. Thermal degradation spectra of polyoxymethylenes: (a) Paraform; (b) experimental polyoxymethylene, uncapped; (c) experimental polyoxymethylene, acetate-capped; (d) commercial Delrin 150 and 500. Programmed heating rate: 6°C/min.

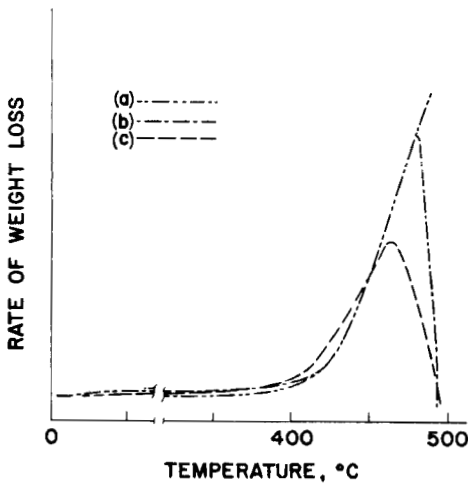


FIG. 4. Thermal degradation spectra of polyamides: (a) nylon 6-6, Polyenco 101; (b) nylon 6, "Capran" 77; (c) nylon 6-10. Programmed heating rate: 6°C/min.

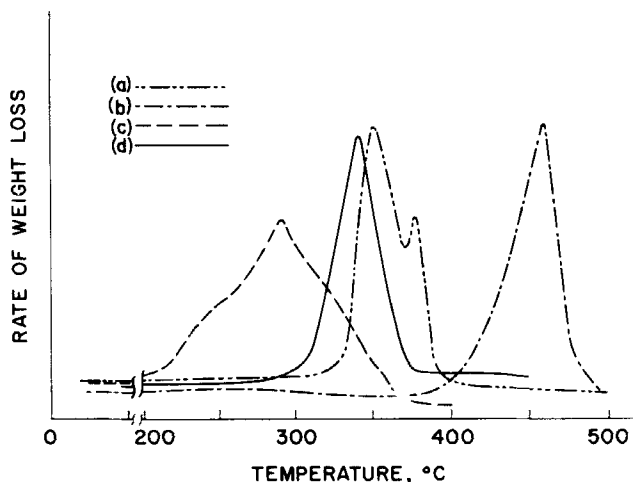


FIG. 5. Thermal degradation spectra of various polyesters: (a) poly(methyl methacrylate), Lucite HM 129; (b) polyethylene terephthalate, Mylar, type D; (c) n-butyl- and isobutylmethacrylate copolymer, Lucite 2046; (d) poly(vinyl acetate), Gelva 1. 5. Programmed heating rate: $6^{\circ}\text{C}/\text{min}$.

as shown in Table 1. At a given heating rate, MDT is believed to be as characteristic as is its T_g , or melting point, for a given polymer.

Most of this work was done with 50-mg samples at heating rates of $6^{\circ}\text{C}/\text{min}$ in a nitrogen atmosphere. Under these conditions, the MDT can be reproduced within 2°C . At an increased heating rate of

TABLE 1. Maximum Degradation Temperatures of Various Polymers, $^{\circ}\text{C}$ (heating rate $6^{\circ}\text{C}/\text{min}$)

Polyethylene	>500	Polystyrene	430
Nylon 6-6	~500	Poly(methyl methacrylate)	351, 377
Polypropylene	485		
Nylon 6	478	Polyoxymethylene	343
Nylon 6-10	463	Poly(vinyl acetate)	342
Polyethylene terephthalate	460	Copolymer n-butyl-isobutyl methacrylate	290

TABLE 2. Influence of Heating on Maximum Degradation Rate Temperature of Poly(methyl methacrylate)

Heating rate, °C/min	3	6	10	12	15
Maximum degradation rate temp., °C	331, 372	351, 377 361 ^a	385	387	390

^aProjected composite peak.

15°C/min, MDT was slightly higher (as seen in Table 2); poly(methyl methacrylate) is shown as the example. At a decreased heating rate, MDT was lower, and the thermal degradation peak was also split into a double peak. Even at 6°C/min, the two peaks were fairly well resolved. The lower-temperature peak was more influenced by the change of the heating rate than the higher-temperature peak.

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Accepted by editor October 13, 1967

Submitted for publication January 2, 1968

Zusammenfassung

Ein einfaches Zusatzgerät für die üblichen thermogravimetrischen Geräte mit linear Temperaturanstieg ermöglicht die Direktregistrierung des "Thermischen Zersetzungsspektrum" (TZS) von Polymeren, der Gewichtsabnahmegeschwindigkeit mit steigender Temperatur. Der Einfluss der Aufheizgeschwindigkeit auf das TZS wird an Hand von Polymethylmethacrylat beschrieben.

Résumé

Modification simple d'un appareil thermogravimétrique d'un programme de chauffe linéaire permet l'enregistrement automatique du spectre de décomposition thermique (SDT), c'est-à-dire la vitesse de la perte de poids en fonction de la température croissante. L'effet de la vitesse de chauffage sur le SDT du polyméthacrylate de méthyl est examiné.