

SIMULTANEOUS PHOTOTHERMAL AND DIFFERENTIAL THERMAL ANALYSIS

D. J. DAVID

Columbia Scientific Industries, 3625 Bluestein Boulevard, Austin, Texas 78702 (U. S. A.)

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ABSTRACT

Simultaneous photothermal analysis (PTA), and differential thermal analysis (DTA) curves of inorganic compounds and organic polymers are presented. While the two techniques reinforce each other and provide complementary information, light emanating from the sample and detected by a photomultiplier tube provides features in the PTA thermograms not present in the DTA thermograms.

INTRODUCTION

It is known that many different types of materials can exhibit luminescence. The luminescence may be fluorescence or phosphorescence, the former occurs almost concurrently with the absorption of the exciting light while the latter is more leisurely emitted light. When certain materials are heated to temperatures below incandescence, this phenomenon is termed thermoluminescence.

Thermoluminescence has been used at an early date by Dérivé¹ in the study of minerals and ceramics. Further studies and applications of this phenomenon have been described²⁻¹⁴. The use of this technique for geologic age determination has been reported by Zeller¹⁵, and Zeller and Ronca¹⁶. Ralph and Han¹⁷ have reported on pottery dating and Lancaster¹⁸ and Wendlandt¹⁹ have reviewed principles and applications.

These applications deal with ordered or semi-ordered materials such as crystals or inorganic glasses which have imperfections or traps. When these materials are subjected to high energy radiations, electrons are removed and due to the higher energy levels attained by the electron, it cannot be recaptured by its own ion and thus is free to wander through the crystal lattice or is trapped. An energy of about 10 eV is sufficient for electron removal. If there are imperfections or traps in these materials, upon heating, the absorbed energy is given off in the form of luminescence or light as the electrons return to their original positions from their traps. These principles have been applied in geological dating¹⁵⁻¹⁷.

It is also known that the photoluminescence process occurs in the case of aromatic compounds in the region 2500 Å–3500 Å, where the π -electrons are responsible mainly for the activity. Crystalline non-aromatic organic materials should also exhibit luminescence for reasons similar to those cited above. This particular

aspect where both aromatic and non-aromatic long-chain, high-molecular weight organic polymers are involved, has not been investigated by this technique. Ashby²⁰ has reported on another form of luminescence, *viz.*, oxyluminescence, which occurs when organic materials are heated in the presence of oxygen.

Consequently, a study was undertaken to determine whether or not photothermal analysis could be used to detect changes occurring in materials as a function of temperature and have general utility for materials investigations. Differential thermal analysis was used simultaneously in order to reinforce the data obtained from photothermal analysis and to aid in the interpretation of the photothermal data.

EXPERIMENTAL

In order to accommodate both the PTA and DTA techniques simultaneously, a standard Stone-Premco DTA cell Model SH-202-11R-Ni was modified by boring a 0.275 inch opening in the cell cap to permit sample viewing by the photomultiplier tube. A Stone-Premco Furnace, Model LTF was used and modified by boring a cavity extending from the top of the furnace through the furnace insulation terminating at the cell cap opening. With an "end on" photomultiplier mounted on the

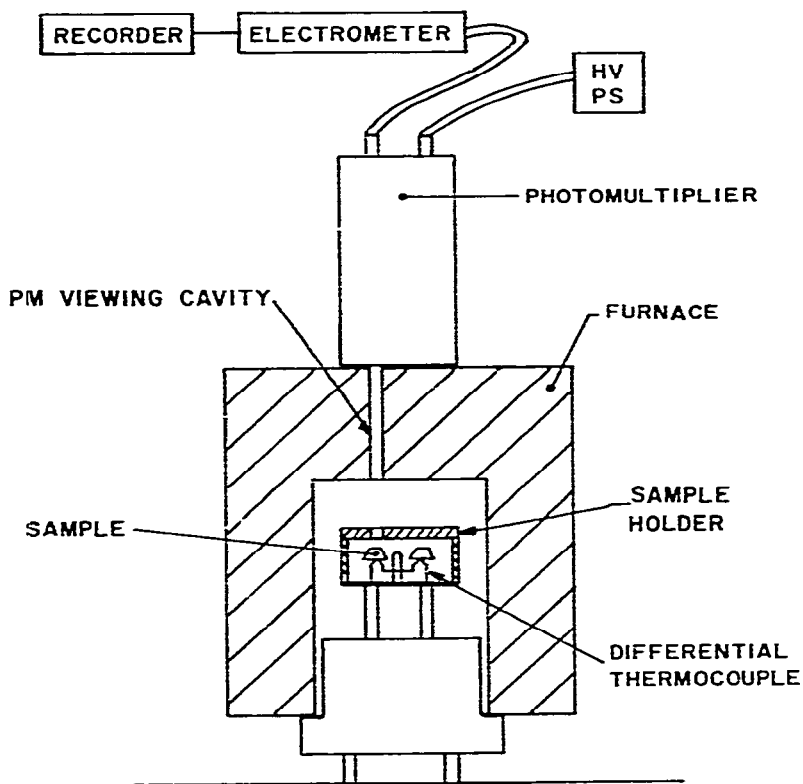


Fig. 1. Schematic diagram of simultaneous Photothermal and Differential Thermal Analysis apparatus.

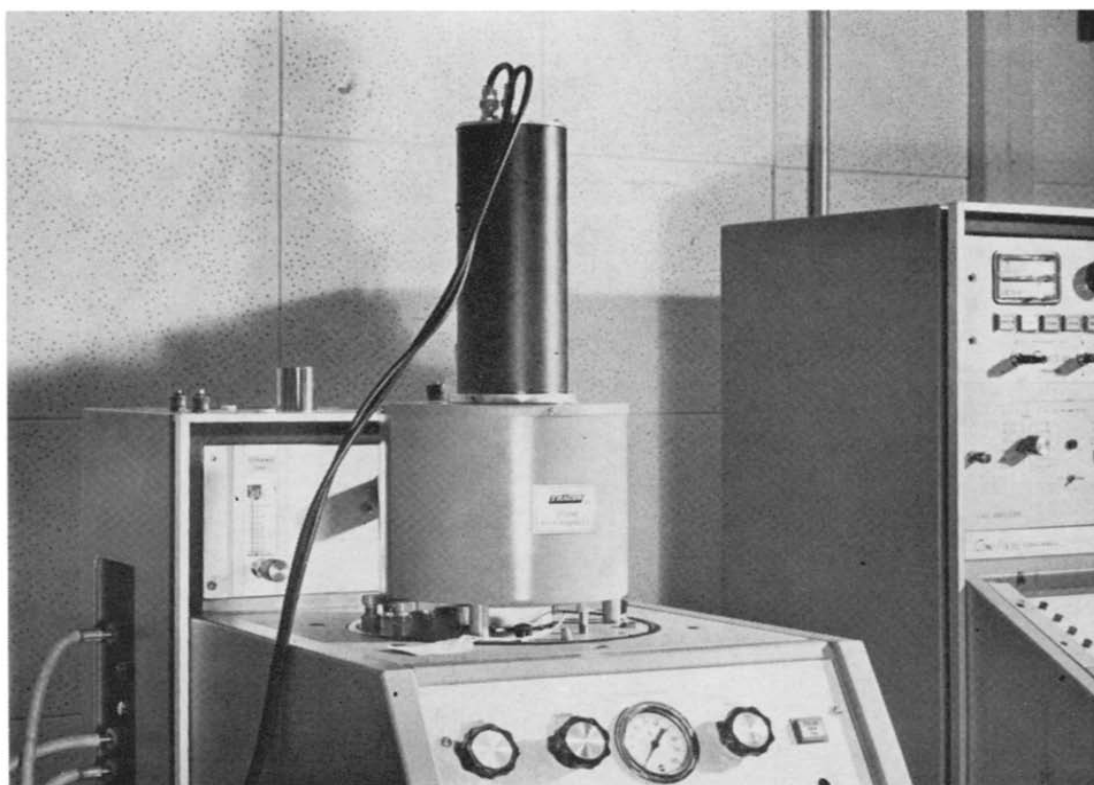


Fig. 2. Apparatus used for simultaneous PTA and DTA studies.

top of the furnace and the sample cell cap opening aligned with the furnace opening, the sample pan contained in the ring thermocouple could be viewed directly by the photomultiplier without requiring additional equipment. A schematic of this arrangement is shown in Fig. 1. Fig. 2 is a photograph of the complete system with the exception that a black photographer's cloth was placed over the photomultiplier tube and furnace platform to guard against light leaks.

In order to insure adequate spectral response at high sensitivities, the EMI photomultiplier tube, type 6256S, was chosen for these studies. This photomultiplier tube is a large two-inch diameter tube with a 1 cm cathode. It has a spectral response from approximately 2000 Å to 6000 Å and a sensitivity of 2000 amp per lumen at 1700 VDC with only 0.5 n amp of dark current. The small viewing area, high sensitivity, and suppressed red threshold to reduce thermionic effects, contribute to optimization of effective sample area viewing.

A high voltage power supply, Model 413A, manufactured by John Fluke Co., was used to provide voltage for the photomultiplier tube. A Tracor solid-state electrometer, Model No. 8169, was used to measure the current output of the photomultiplier tube. This signal was recorded on one channel of a two-channel recorder while the differential temperature was recorded on the second channel. A Stone-Premco Recorder Controller Model 202 F was used for these studies.

DISCUSSION AND RESULTS

The system was checked out by running a blank in order to observe the PTA and DTA responses which are shown in Fig. 3. These results are typical of the type of response encountered for a large number of blank runs. The rapid rise in response of

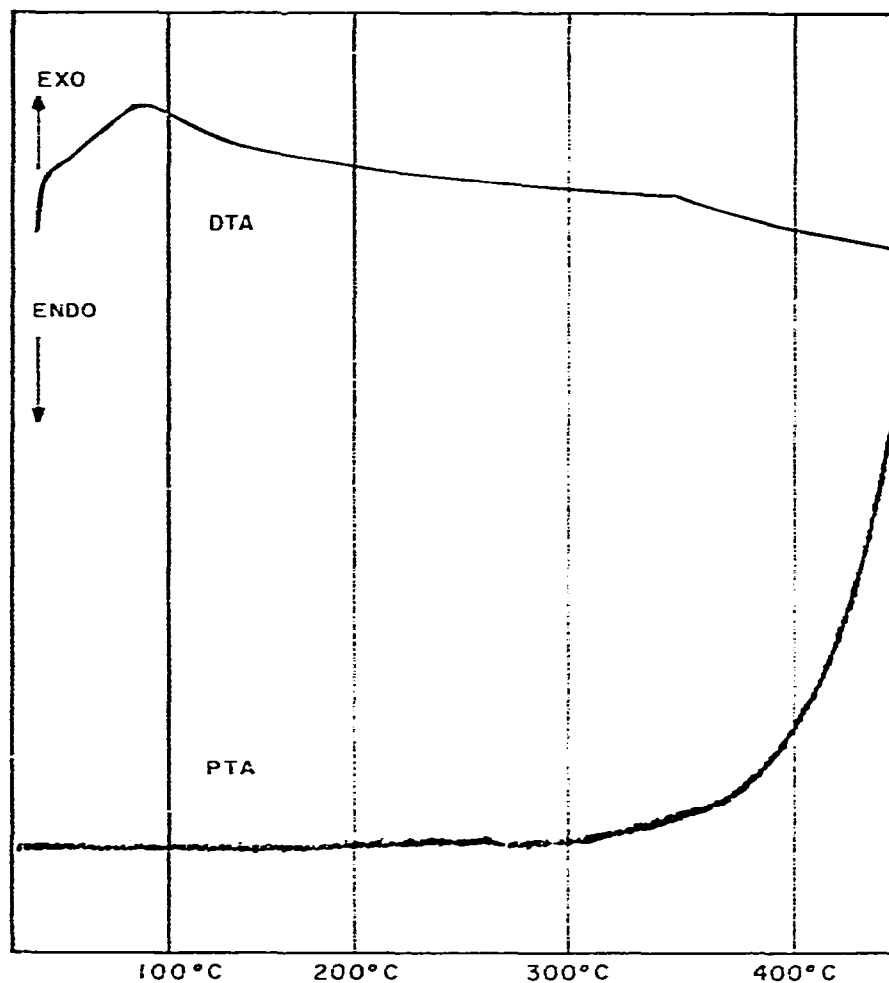


Fig. 3. Blank run; heating rate, 10 °C/min; gas flow, 0.05 standard cubic feet per hour (SCFH) N₂. DTA, 40 μV or ~1.2 °C full scale (FS); PTA, 1.6 × 10⁻⁸ amp FS at 1300 V.

the PTA side of the system that begins at about 400 °C is typical and is due to heat effects on the photomultiplier tube from the furnace.

Because carbonate rocks are known to thermoluminesce⁸ and the thermoluminescent glow curves have been used for radioactive dating^{15,16}, the first materials chosen for investigation were carbonate materials. The sample was a naturally occurring carbonate, the exact composition of which is unknown, obtained from a cave formation in Texas. This was an interesting specimen from the standpoint that

it consisted of alternate dark and white bands. One aspect of this investigation was to determine whether or not the technique could differentiate between the compositional changes responsible for the different color bands in the same specimen.

The thermograms shown in Figs. 4 and 5 indicate that there are only small differences between the thermograms of the white band and dark band samples in

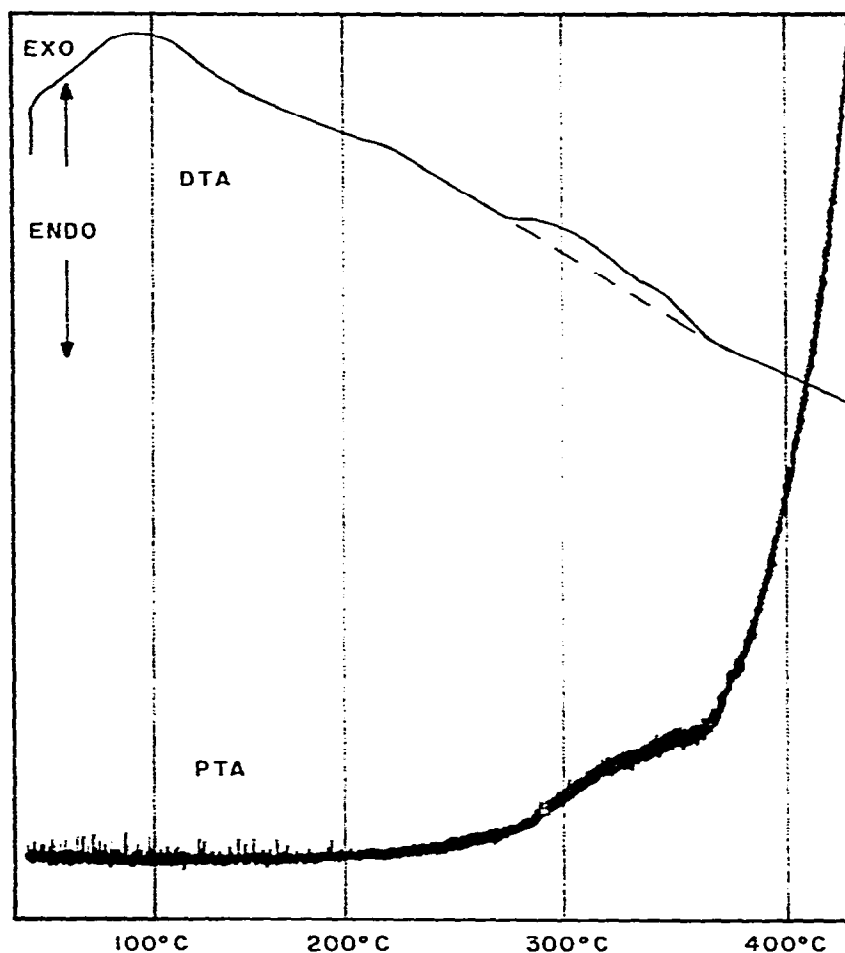


Fig. 4. Thermograms of white band limestone using simultaneous PTA and DTA: heating rate, $10^{\circ}\text{C}/\text{min}$; gas flow, 0.05 SCFH N_2 ; sample size, 8.4 mg . DTA, $150\ \mu\text{V}$ or $\sim 4.7\ \text{C FS}$; PTA, $1.6 \times 10^{-8}\ \text{amps FS}$ at $1300\ \text{V}$.

either the case of PTA or DTA. A number of runs of each colored band of the same specimen have shown that there are consistent small significant differences by either PTA or DTA that are not readily apparent from a single scan.

One significant feature of these thermograms is the exothermic peak beginning at about 300°C and terminating at approximately 375°C as marked on the thermograms. These DTA exothermic peaks coincide with the major glow peak and are due to the release of stored energy or trapped electrons. This aspect has been confirmed by

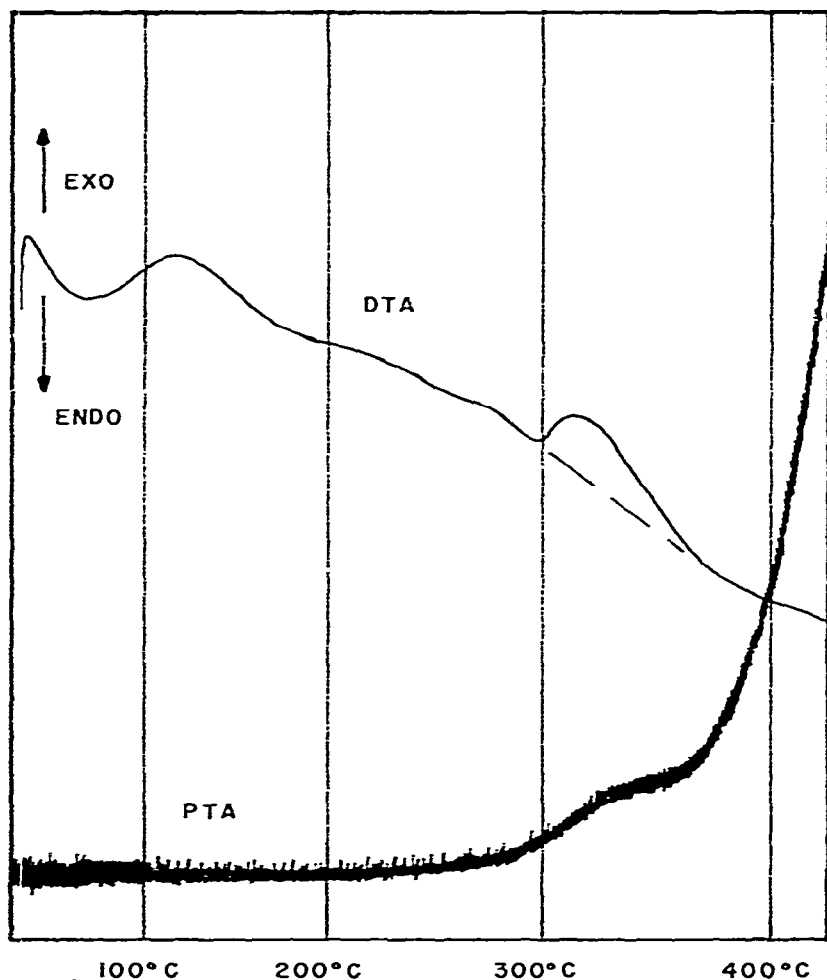


Fig. 5. Thermograms of dark band limestone using simultaneous PTA and DTA; heating rate, $10^{\circ}\text{C}/\text{min}$; gas flow, 0.05 SCFH N_2 ; sample size, 8.4 mg. DTA, $150\ \mu\text{V}$ or $\sim 4.7^{\circ}\text{C}$ FS; PTA, 1.6×10^{-6} amps at 1300 V.

irradiation of specific minerals in a nuclear reactor and subsequent examination by DTA²⁰. Kardos²¹ also observed exotherms in the same general temperature range in his study of Apollo 11 lunar samples. These exotherms were attributed to the release of stored energy based upon the study of synthetically irradiated samples and the effect of solar winds. Thus, DTA would appear to be as sensitive or perhaps more sensitive than photothermal analysis for examining these types of materials and perhaps would be better suited to studies involving geologic dating than thermoluminescent analysis.

The PTA thermograms are similar to those reported by Ralph and Han¹⁷ and Lewis¹⁴. The glow curves are known to vary widely and depend upon electron trap formation which in turn is dependent upon specimen age, imperfections, and vacancies in the crystal lattice, composition, impurities, ion dislocations or holes, statistical

imperfections due to kinetic motions, radioactive element content, and amount of exposure to all types of radioactivity^{8,18,19}.

Differences in thermoluminescent character will also be observed to change as the experimental heating rate varies. We have utilized a 10°C/minute heating rate, in general, which seems to optimize both PTA and DTA responses although for glow curve studies, a heating rate from 10°C/minute¹⁹ to 16°C/second¹⁷ has been reported.

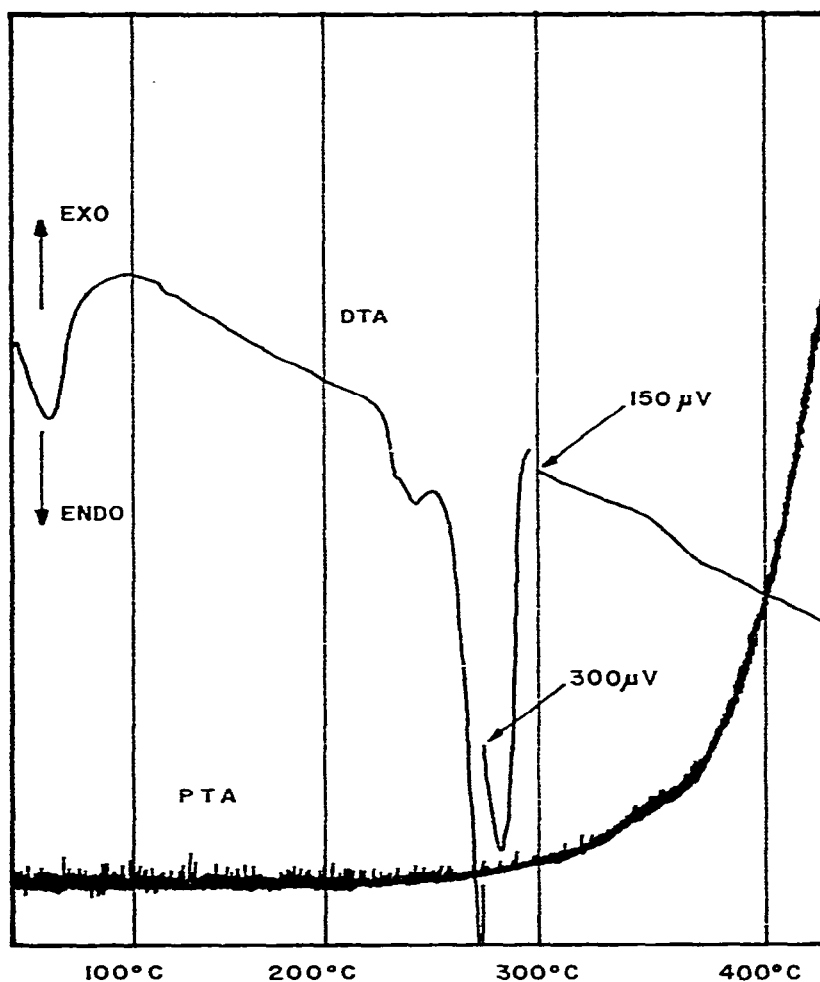


Fig. 6. Thermogram of clay using simultaneous PTA and DTA; heating rate, 10°C/min; gas flow, 0.05 SCFH N₂; sample size, 8.4 mg. DTA, 150 μV or ~4.7°C FS; PTA, 1.6 × 10⁻⁸ amps FS at 1300 V.

A sample of clay was then run (Fig. 6) in order to determine if this type of sample could be distinguished from the limestone. The DTA thermogram is quite different from the limestone in the temperature region examined due to dehydroxylation of the clay. The PTA thermogram is also distinctive, but with fewer marked differences. The DTA thermogram shows features, in general, similar to the limestone thermogram in the temperature range between 300°C and 400°C. A re-run of the clay sample corre-

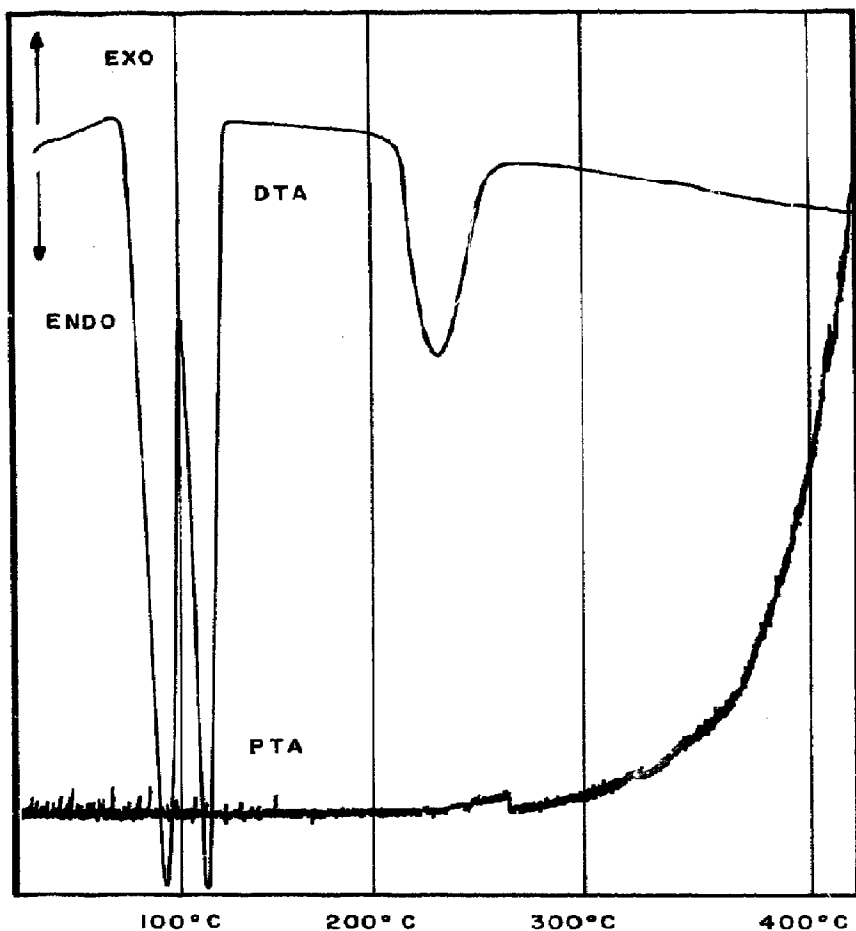


Fig. 7. Thermogram of copper sulfate pentahydrate using simultaneous PTA and DTA; heating rate, $10^{\circ}\text{C}/\text{min}$; gas flow, $0.05 \text{ SCFH } \text{N}_2$; sample size, $\sim 8 \text{ mg}$. DTA, $500 \mu\text{V}$ or $\sim 15.5^{\circ}\text{C FS}$; PTA, $1.6 \times 10^{-8} \text{ amps FS}$ at 1300 V .

sponded to the blank run shown in Fig. 3.

Copper sulphate pentahydrate was then examined by this technique (Fig. 7) since it is a material whose thermal response is well known. The PTA thermogram shows slightly increased response in the $300\text{--}400^{\circ}\text{C}$ temperature region as compared to the blank, but the interesting temperature region is from 225°C to 275°C . During the loss of the fifth water of hydration, a distinctive photometric response was observed which was confirmed on subsequent runs. The origin of this response was suspected to be due to a change in color of the specimen since a blue to white color change accompanies complete dehydration which may be sensed due to reflected light as a result of light leakage into the sample cell. This aspect was checked by running a fresh sample at night in a completely darkened room with the light cloth still in

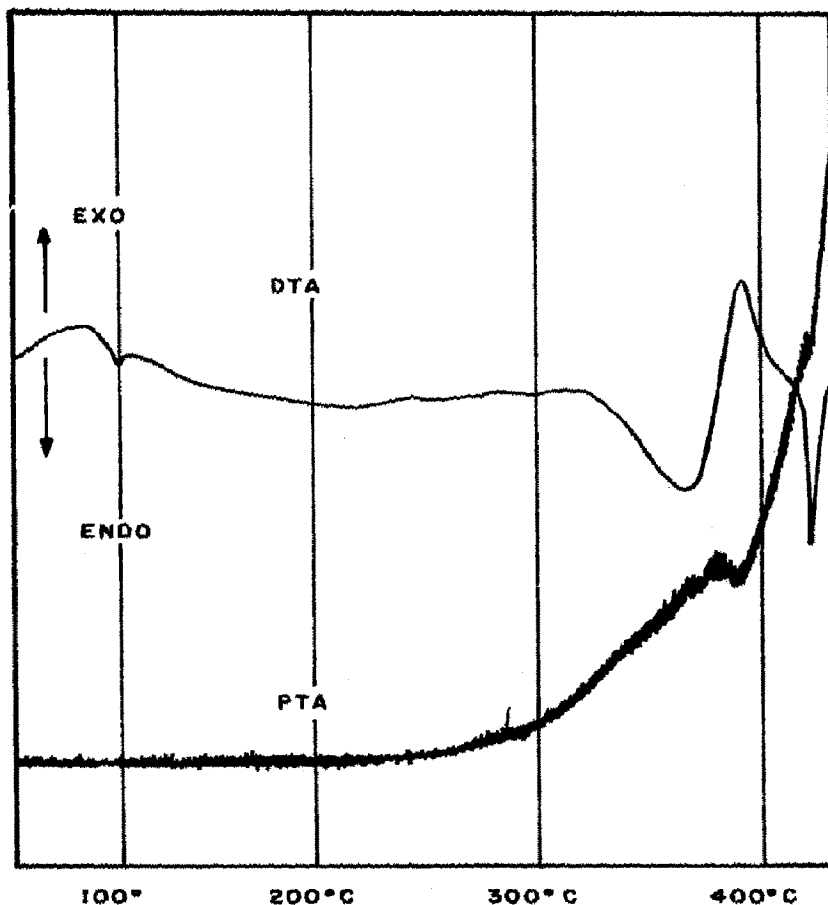


Fig. 8. Thermogram of polystyrene, MW 10,300 using simultaneous PTA and DTA; heating rate, $10^{\circ}\text{C}/\text{min}$; gas flow, 0.05 SCFH N_2 ; sample size, ~ 8 mg. DTA, $300\ \mu\text{V}$ or $\sim 9.4^{\circ}\text{C}$ FS; PTA, 1.6×10^{-8} amps FS at 1300 V.

place over the photomultiplier-furnace system. Identical results were obtained so that the photothermal origin is not clear at this time.

A number of polymers were then run in order to see whether or not this technique would have any relevance. For these purposes, a number of representative commercial polymers were chosen for analysis. These results are shown in Figs. 8–11. In each thermogram a distinctive and characteristic PTA thermogram resulted for each organic polymer examined.

Melting and/or glass transitions are not detected by PTA whereas decompositions are observed. Thus, simultaneous PTA and DTA allow differentiations between transitions such as melting or glass transitions from those accompanied by decomposition. Although effluent gas analysis (EGA) is capable of providing the same type of information, the EGA thermograms are generally featureless compared to the

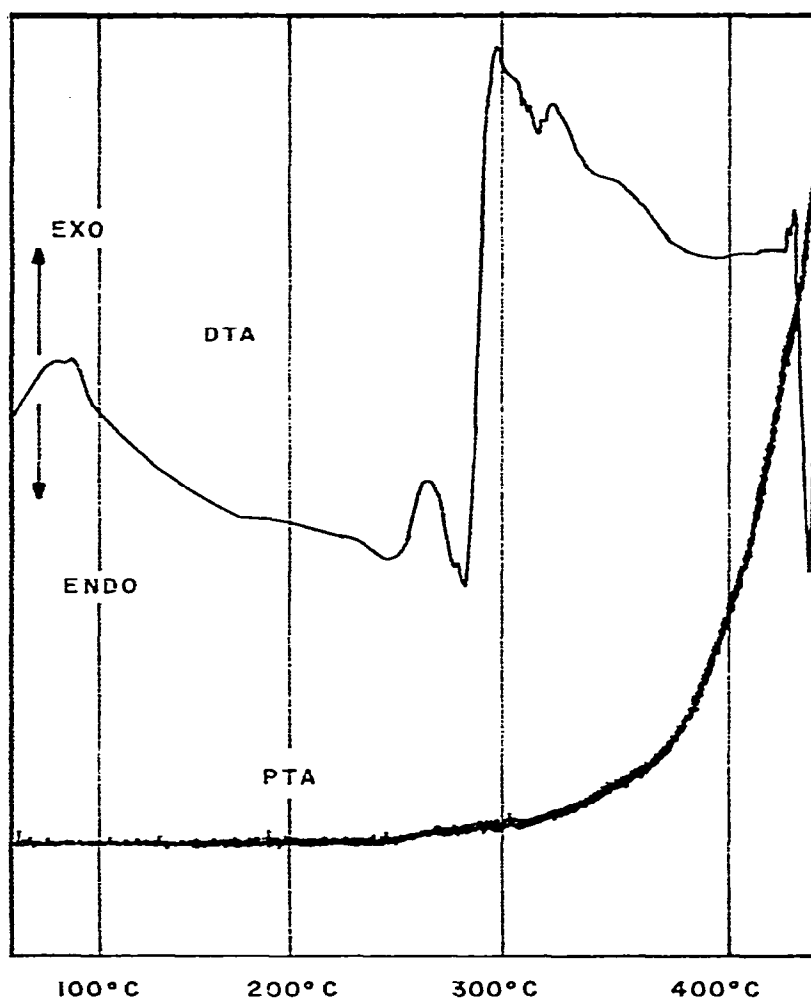


Fig. 9. Thermogram of polyvinylchloride using simultaneous PTA and DTA; heating rate, $10^{\circ}\text{C}/\text{min}$; gas flow, 0.05 SCFH N_2 ; sample size, $\sim 7.5\text{ mg}$. DTA, $150\mu\text{V}$ or $\sim 4.7^{\circ}\text{C FS}$; PTA, 1.6×10^{-8} amps FS at 1300 V .

PTA thermograms and cannot be used for identification purposes as the PTA thermograms can be. In addition, the PTA response is not necessarily a result of active decomposition.

The PTA response is unusual and was unexpected since the phenomenon of thermoluminescence should not be operable during these scans because the PTA response occurred a considerable while after any order in the polymer had been destroyed, as in the case of polyethylene (Fig. 10). The PTA response begins approximately where oxidation commences and may be a result of oxyluminescence²¹ although all samples were run with N_2 as the dynamic gas. However, there may have been sufficient oxygen present due to (1) back diffusion since the pressure dome could not be used, or (2) oxygen impurities in the nitrogen, so as to permit oxyluminescence. Light leakage may have occurred in spite of the precautions taken, as previously

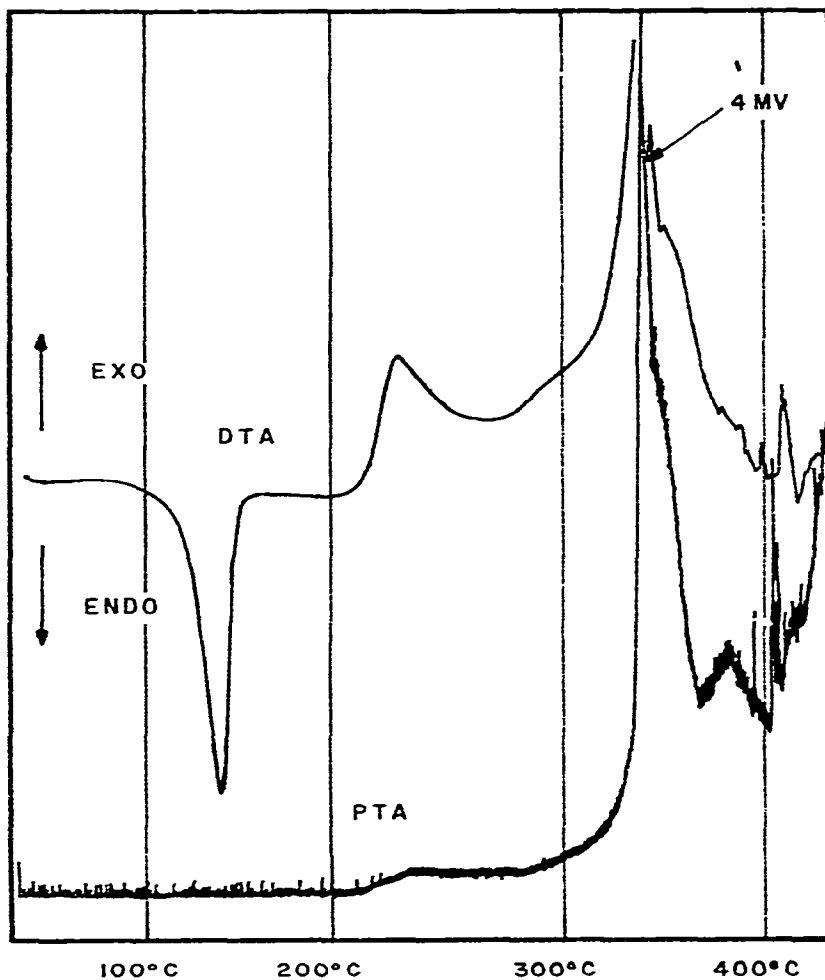


Fig. 10. Thermogram of polyethylene using simultaneous PTA and DTA; heating rate, $10^{\circ}\text{C}/\text{min}$; gas flow, 0.05 SCFH N_2 ; sample size, $\sim 7.5 \text{ mg}$. DTA, $500 \mu\text{V}$ or $\sim 15.5^{\circ}\text{C FS}$; PTA, $1.6 \times 10^{-8} \text{ amps FS}$ at 1300 V .

pointed out, so that the PTA curves may be the result of color changes of the sample. The PTA peak obtained in the polyethylene scan at about 325°C would seem to discount the curve emanating from a color change since polyethylene becomes progressively darker as oxidation proceeds.

The difference in PTA response between polyvinyl chloride and polyethylene is most marked even though identical experimental conditions were employed. Again, this would seem to negate the color change possibility. This difference may be explained on the basis of different chemical configuration so that oxyluminescence, chemiluminescence, or possibly some other mechanism is operating to produce the PTA thermograms.

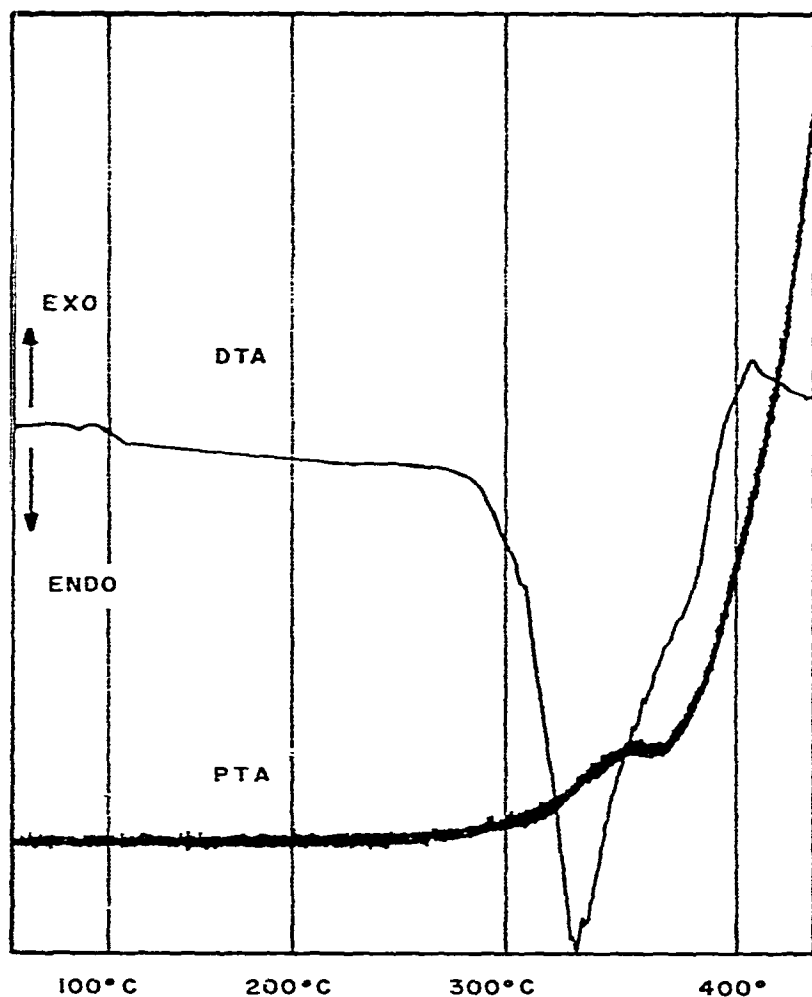


Fig. 11. Thermogram of polymethylmethacrylate using simultaneous PTA and DTA; heating rate, $10^{\circ}\text{C}/\text{min}$; gas flow, 0.05 SCFH N_2 ; sample size, ~ 8.0 mg. DTA, $300\ \mu\text{V}$ or $\sim 9.4^{\circ}\text{C}$ FS; PTA, 1.6×10^{-8} amps FS at 1300 V.

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