An improved pyrolytic device suitable for the study of polymer microstructure by pyrolysis gas chromatography

A pyrolytic device for investigation of polymer microstructure and for studying the thermal decomposition mechanism by pyrolysis gas chromatography has to meet very severe requirements with regard to temperature control, the mode of sample heating and the determination of the quantity of the specimen.

In addition it is necessary to remove any residue after pyrolysis in order to keep the pyrolytic system completely clean. This is particularly important for polymers with a whole series of decomposition products such as polyolefins.

In view of the above requirements it is now well known that the pyrolytic furnace has great advantages over the filament type pyrolyzer[1–5]. In order to maintain high reproducibility of experimental conditions in investigation of the microstructure of polyolefins we have designed a pyrolytic furnace with the following features:

samples can be pyrolyzed at any temperature up to 1000°;

the temperature of thermal decomposition can be maintained within the close range of $\pm 0.5°$;

the pyrolysis temperature is measured near to the sample;

the sample is quickly inserted in the hot zone of the pyrolyzer (for 1 sec) and always at exactly the same spot;

the heating-up of the sample is instantaneous;

the pyrolysis time can be controlled accurately;

the samples to be examined are taken in their natural form (granule, film, powder, liquid);

the amount of sample is accurately known;

there is no need to interrupt the carrier gas flow through the system during loading and unloading of the samples;

the fractions of the pyrolyzate can be controlled by selection prior to their admission into the chromatographic column by putting a short precut column between the pyrolytic furnace and the chromatograph;

the residue of the sample after pyrolysis can be measured (by quantity) and easily removed;

the cleansing of the system, from the heavier fractions encountered, is very simple and thorough;

the reproducibility of data is high.

Descriptions of design

The pyrolytic device is shown in Fig. 1. The thermal decomposition of the sample is achieved in the hot zone of a quartz tube (1) which is provided with an electrical heater (2). The sample boat (3) is fixed on to a thin rod on a pusher (5), which enables the sample to be inserted or withdrawn from the furnace. The quartz tube is 200 mm long and 14 mm in diameter, but at the inlet end, in order to allow connections to the metal block (4), the diameter is increased to 20 mm. In addition to the pusher orifice, the block has connections for the carrier gas (6), the thermocouple (7), as well as the teflon tap (8), which is used for opening and closing the furnace.

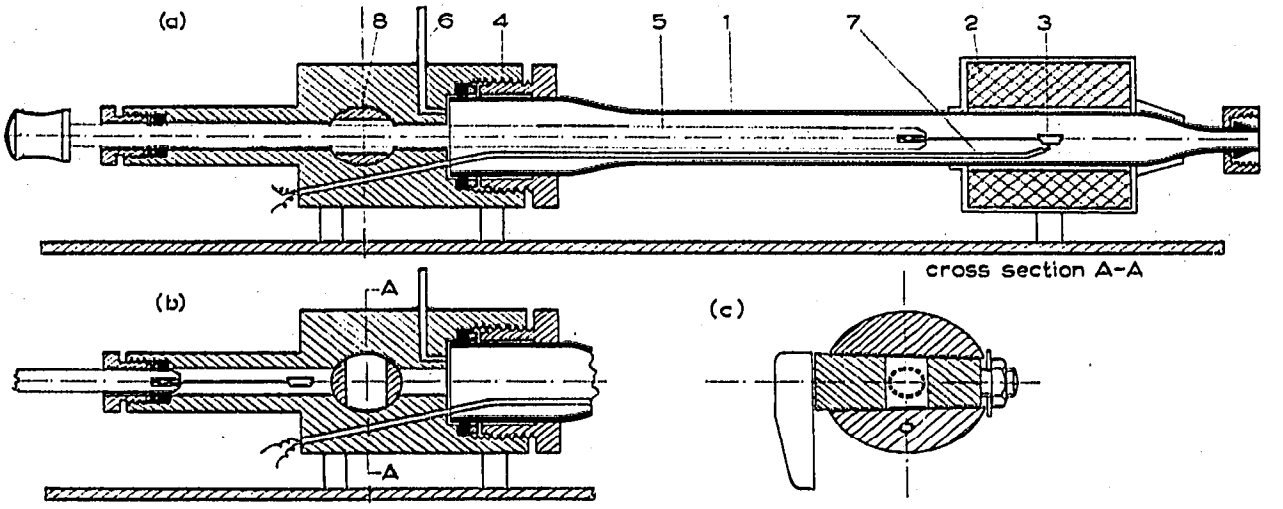

Fig. 1. Diagram of the pyrolytic device. (a) Complete device in operating position; (b) the connecting block with the tap closed; (c) detail of the teflon tap. For explanation of figures, see text.

A heater and ceramic isolator surround the tube along 7 cm of its length. The temperature of the furnace is controlled by a 3 A Variac. In order to control the pyrolysis temperature to within such a narrow range as $\pm 0.5°$, the electric current is stabilized and the heater is properly isolated.

It is also possible to connect the pyrolyzer directly to the injection port in order to prevent the heaviest fractions from entering the chromatographic column.

The method of connecting the quartz tube and the metal fittings, as well as other connections, is shown in Figs. 1a and b. The small platinum boat (3 × 5 mm) is easily attached to the pusher by inserting the platinum wire into the slot on the pusher.

Procedure

The pusher and boat, with a measured amount of sample (1–5 mg), are inserted in the opening of the block, and the pusher is pushed up to the mark on the rod, in other words to the point where the boat reaches the teflon tap. Then the tap is opened and the boat pushed into the cold zone of the quartz tube. After conditioning the sample in the stream of carrier gas, it is pushed into the hot zone of the pyrolyzer. The position of the boat in the furnace is shown in Fig. 1a. The sample can be left in the furnace as long as desirable.

The withdrawal of the boat from the apparatus consists of a single movement. When the boat is in the position as shown in Fig. 1b, the teflon tap is closed and the boat can be taken out from the device. The boat can be weighed and cleaned by burning, if necessary. The tube outlet is cleaned by burning off the residue in an air stream whilst firing the quartz tube with a burner.

Discussion of results and advantages of the improved device

A check on the reproducibility of the pyrolyzer described, connected to a Perkin-Elmer chromatograph Model 800, gave very good results. The samples to be pyrolyzed are weighed on a semimicrobalance with an accuracy of ± 0.02 mg.

Quantitative evaluation of pyrograms by peak-height measurements shows a

reproducibility with a standard deviation of 1.7 or, as a percentage of the mean, 2.0 %. The value obtained is well within the accuracy limits gained with the peak height measurement technique[6,7].

The high reproducibility obtained is the result of the operating conditions, such as temperature control, the rate of heating, the method of sample insertion and the maintenance of a thoroughly clean system as described, and thus meets the principal requirements for the determination of polymer microstructure. The results of polymer microstructure investigation will be described in another paper.

Additional advantages of this device, *viz.*, the feasibility of pyrolysis at a desired temperature, accurate measurement of the decomposition temperature, quick transport of pyrolyzate and the possibility of quantitative analysis, fulfil the requirements for the study of a thermal decomposition mechanism.

The continuous flow of carrier gas is ensured in a new, suitable way. The carrier gas passes continuously through the pyrolyzer without any changes in flow rate while the new sample is being inserted. Constant temperature can be maintained over a long period of time without any changes. The four-way valve system which is generally used and is a source of contamination with heavier fractions of the pyrolysate is avoided.

The simple and cheap performance of device, as well as adaptability to practically any chromatograph are additional advantages of the improved pyrolyzer.

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