

Modified Dilatometer for Polymerization

Sources of error in dilatometry have to be taken into account, especially in the case of fast reactions or if the polymerization is performed at high temperature.

In most dilatometers, the surface-to-volume ratio of the vessel is small and the time needed to reach thermal equilibrium may be long. The heat dissipation is slow, and for fast reactions, the temperature of the medium is not homogeneous.

This problem of heat dissipation has been discussed many years ago by Tiselius in the case of the electrophoresis cell.^{1,2} The difference in temperature between the center of a cylindrical electrophoresis tube and its periphery is proportional to Qr^2/K , where Q is the load, r is the radius of the tube and K the thermal conductivity of the medium. The use of narrow tubes should therefore be advantageous; the small liquid volume does not, however, allow accurate measurements of the contraction.

Flattened tubes as used in electrophoresis accommodate larger liquid volumes but are not practical in dilatometry.

Burnett devised a mushroom-shaped reaction vessel filled almost completely with mercury so as to have a thin layer of monomer solution and a large surface;³ magnetically stirred dilatometers have also been described.⁴

We have been using for many years a very simple dilatometer with excellent results. The ordinary cylindrical vessel is replaced by a long helicoidal tube with a thin wall (± 1 mm thick), the diameter being 10 mm or less (Fig. 1); total volume is between 25 and 50 ml.

As usual, the monomer solution is transferred to the dilatometer after freezing and melting under vacuum in the vessel (A), which is conical in order to prevent breaking as often occurs with a round vessel during the melting process.

We mention here that we use the same type of vessel, but of larger dimensions, for batch polymerizations. The following results demonstrate the efficiency of this modified dilatometer. Figure 2 shows the difference in thermal equilibration times for a classical dilatometer (7 minutes) and the helicoidal type (2 minutes) at 60°C. The rate of polymerization of ethylacrylate at 60°C in the presence of different amounts of benzoyl peroxide has been determined with the two types of dilatometers (classical or helicoidal) (Fig. 3). For a high rate of polymerization (curves A), the effect of slow heat dissipation is very pronounced and the apparent rate of reaction obtained with the classical dilatometer is too high; curves B show the same discrepancy but less pronounced.

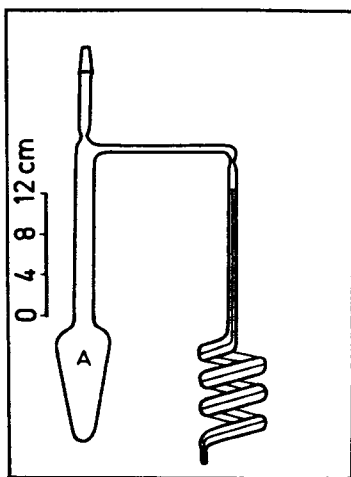


Fig. 1. Modified dilatometer.

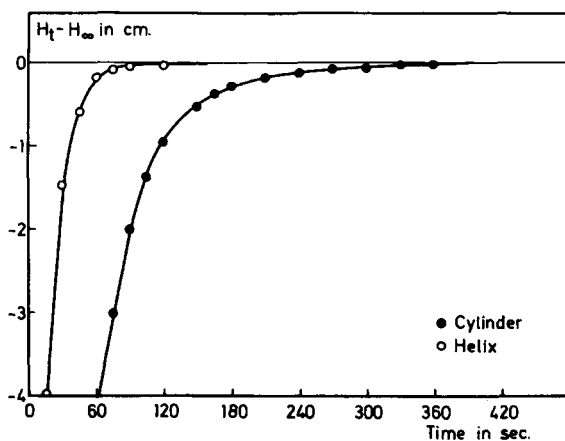


Fig. 2. Thermal equilibration at 60°C with classical (●) and modified (○) dilatometer.

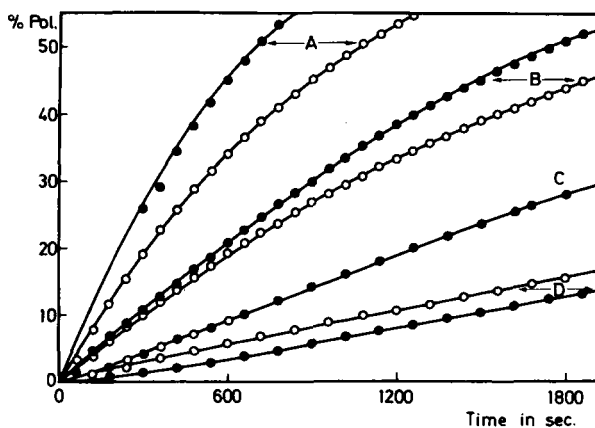


Fig. 3. Polymerization of ethyl acrylate at 60°C with different amounts of benzoyl peroxide in the two dilatometers: classical (●); modified (○).

At a low rate of polymerization (curves D), only the time of thermal equilibration affects the shape of the curves in the first part and their relative position. The curve obtained with the helicoidal dilatometer this time is situated above the one obtained with the classical type; the slopes of the two curves are, however, practically identical after a certain time of reaction. Curve C shows an example of compensation between the two effects.

These results illustrate the necessity of adequate choice of the type of dilatometer and of its dimensions in order to obtain accurate reaction rates.

References

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