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Abstract

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CALORIMETRIC STUDY OF THE KINETICS OF RADIATION POLYMERIZATION

In a number of cases, in studying the kinetics of polymerization, a method is required that makes it possible to record the appearance of the polymer immediately, i.e., at the very moment of its formation. Meanwhile, such most widely used methods as dilatometric and gravimetric methods are practically unsuitable for studying the polymerization kinetics of viscous and solid monomers. The most universal in this respect is apparently calorimetric registration of the kinetics of heat evolution due to polymerization.

To solve a whole series of problems we designed and used a special heat-conducting calorimeter based on the principle of the Calvet microcalorimeter ([1]), which made it possible to carry out measurements directly in the radiation field.

Design of the calorimeter. The layout of the heat-conducting calorimeter is shown in Fig. 1. Two identical cuvettes made of red copper, with the sample under study (*1*) and the reference (*2*), are surrounded by jackets (*3* and *4*) identical in their thermophysical properties, through which passes practically all the heat evolved (absorbed) in the sample and in the reference. The heat flows passing through jackets *3* and *4* create temperature differences between their inner and outer surfaces, which are monitored by batteries of thermocouples (*5* and *6*) containing 500 copper–constantan thermocouples each and connected differentially to a galvanometer (*7*). The thermopiles are made of mica 0.03–0.05 mm thick in the form of rings 3–5 mm high, on which a tape rolled from constantan wire of diameter 0.1–0.2 mm is wound toroidally. To create the thermoelements, copper is electrolytically deposited onto the constantan. The jacket is assembled from two or three such thermopiles. Possible errors introduced by fluctuations of heat evolution in the sample, by changes in the geometry and thermophysical properties of the sample, etc., which are so characteristic of thermographic installations, are not significant for such a heat-conducting calorimeter. The stability of measurements on this calorimeter is determined by the stability of the properties of jackets (*3* and *4*).

The differential connection of the thermopiles makes it possible to eliminate such side heat processes as temperature fluctuations of the thermostated block

Fig. 1. Schematic of the calorimeter

Figure 1: Fig. 1. Schematic of the calorimeter

(*8*) and heat evolution due to absorption of ionizing-radiation energy. The latter circumstance is especially important: it makes it possible to carry out measurements directly under the beam.

The measuring cuvettes with jackets are placed in a massive copper block, which ensures a uniform temperature field around the thermocouple batteries. The block (*8*) is placed in a thermostating copper jacket (*9*), through which the thermostat liquid circulates (thermostating accuracy $±$0.01°). Between the thermostating jacket (*9*) and the block (*8*) there are four shields (*10*) made of copper 0.2 mm thick. Irradiation of the working cuvette of the calorimeter can be carried out both from the end of the calorimeter through channel (*11*) and radially—through the walls of the thermostating chamber. The working cuvettes of the calorimeter are copper cylinders 10 mm in diameter and 20 mm high, with a wall thickness of 0.5 mm. The cuvette is sealed at the top with foil 0.02 mm thick. Through a glass tube soldered to the bottom of the cuvette, the monomer under study is introduced and degassing is carried out.

pumping (vacuum 10^{-5} mm Hg), after which the tube is sealed. The cuvettes are inserted into copper holders (12) with a sliding fit.

Fig. 1. Schematic of the calorimeter

A calorimeter of this design, with insignificant modifications, was used for solving the three problems described below.

Study of the kinetics of radiation polymerization of polyether acrylates. The calorimeter used for these experiments had an inertia of 15 sec and a sensitivity to thermal power of $6 \cdot 10^{-5}$ W/mm of scale. Recording of heat release was carried out with an EPP-09 self-recording instrument, whose sensitivity was increased to $0.5 \cdot 10^{-3}$ mV/mm. The calorimeter was calibrated by measurements of the thermal power of an electric heater located in the cuvette. Figure 2 shows a typical kinetic curve of radiation polymerization (MBF-1). The kinetics of post-polymerization of these monomers was also studied. The use of the calorimeter described made it possible to carry out measurements up to 100% conversion of these polymerization-capable oligomers, which in practice is possible only by means of calorimetric measurements. Since for all these monomers a very considerable after-effect is observed, registration of the polymer concentration directly at the moment of its formation in the present case makes it possible to clearly separate the data on purely radiation-induced polymerization. Detailed studies of the polymerization kinetics of these monomers using this calorimeter are given in (2).

Fig. 2. Kinetics of radiation polymerization of MBF-1 ether acrylate at 20° and an intensity of 21 rad/sec. 1—thermogram, 2—kinetic curve

Fig. 2. Kinetics of radiation polymerization of MBF-1 ether acrylate at 20° and intensity 21 rad/sec. 1—thermogram, 2—kinetic curve calculated from thermogram data

Figure 2: Fig. 2. Kinetics of radiation polymerization of MBF-1 ether acrylate at 20° and intensity 21 rad/sec. 1—thermogram, 2—kinetic curve calculated from thermogram data

Fig. 3

Figure 3: Fig. 3

calculated from thermogram data

Measurement of heats of melting and phase transitions of some monomers. During the thawing of solid irradiated monomers at the points of phase transitions and during melting, effective polymerization may proceed due to active centers prepared in the course of irradiation. To test this possibility, measurements of the heats of phase transitions and melting were carried out on a somewhat modified calorimeter for irradiated and unirradiated frozen mono-

···thermocouples. The block (9) was surrounded by an electric heater, allowing uniform heating to be produced. The entire block (8), with the cuvette filled with the monomer under investigation, was frozen to −196°, after which uniform heating was carried out. A typical heating curve for irradiated (2) and unirradiated (1) vinyl acetate is shown in Fig. 3. The area under the peak is proportional to the heat of transition. Calibration was carried out using substances with a known heat of fusion. For acrylonitrile and vinyl acetate, no significant changes in the heats of fusion and phase transition of the irradiated monomers were observed. These results, described in detail in (3), are of interest for interpreting the mechanism of solid-phase polymerization of these monomers.

Fig. 3. Determination of the heats of fusion and phase transition of unirradiated (1), solid line, and irradiated (2), dashed line, vinyl acetate

Fig. 4. Kinetics of radiation polymerization of acrylonitrile at −196° and an intensity of 0.3 Mrad/min, obtained: by the gravimetric method (1), and with the aid of the calorimeter (2)

Investigation of the kinetics of solid-phase polymerization directly during irradiation. To elucidate the mechanism of solid-phase polymerization, it is necessary to know precisely when polymerization occurs—directly under the beam or as a result of post-effects. For a number of monomers this question

Fig. 4

Figure 4: Fig. 4

could be answered unambiguously with the aid of this calorimeter. The space between the block (8) and the thermostating jacket (9) was filled with liquid nitrogen, and the entire calorimeter was placed in foam-plastic insulation. Owing to the use of a differential circuit, it was possible to record only the heat of polymerization during irradiation of the calorimetric cells. As can be seen from Fig. 4, the kinetics of heat evolution in irradiated acrylonitrile at −196° correspond exactly to the kinetic polymerization curve obtained by the gravimetric method in (3). Thus, direct confirmation was obtained of the conclusion that radiation polymerization of solid acrylonitrile at −196° occurs directly during irradiation, a conclusion previously drawn in (3, 4) on the basis of the absence of additional heat evolution upon thawing of the irradiated monomer. It is interesting to note that, using a calorimeter of a different design, combined with a source of accelerated electrons, V. L. Tal' roze and co-workers (4) arrived at analogous conclusions concerning the character of the solid-phase polymerization of acrylonitrile. In subsequent work, a modification of our calorimeter will be used to determine the time of chain propagation in solid monomers at temperatures below −196°, which will make it possible to confirm or refute the possibility of the existence of a "preassigned" chain length mentioned in (3).

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