



## Investigation of not fully stable fluids by the method of controlled pulse heating. 2. Short-term thermal stability of polymethyl metacrylate



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### ABSTRACT

The short-time thermal stability of glassy PMMA (polymethyl metacrylate) under conditions of high-power local heating has been studied experimentally. For this purpose, a peculiar procedure in the framework of the method of controlled pulse heating of implantable probe has been developed. The procedure is based on combining the thermal shock and monitoring heating functions with characteristic pulse lengths of the order of 1  $\mu$ s and 1 ms, respectively. The value of the characteristic probe temperature  $T_{pk}^*$  was determined, a reproduction of which in a series of measurements under identical parameters of heating function resulted in irreversible changes in the thermal resistance of a polymeric sample. The depth of penetration into the region of thermal instability of polymer ( $T_{pk}^* - T_d$ ), where  $T_d$  is the onset temperature of thermal decomposition in quasi-static process, attains a few hundreds of degrees.

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### 1. Introduction

Relaxation processes in polymers subjected to powerful external impacts change their structure and therefore their properties. The electric field and the local heating may serve (sometimes simultaneously) as sources of such impacts implemented under short characteristic times scale and confined spatial scale. An electrical insulation breakdown and/or short circuit are accompanied by extremely intense and dangerous processes of energy release in the bulk of polymer material. Due to the obvious experimental difficulties, the specificity of the response of substances under similar conditions, which are far from equilibrium, is still poorly known.

One of the important practical examples from this area is the breakdown of solid dielectrics in the course of high-voltage pulses with nanosecond characteristic times [1]. To elucidate the mechanism of such a breakdown as a whole, one must solve a set of special problems complementing each other. In particular, it is important to elucidate the limits of short-term thermal stability of a polymer under significant energy release confined in time and space, and the characteristic relations between time–temperature parameters which “trigger” the process of thermal decomposition.

Our aims were defined as follows: (1) by example of glassy PMMA, to clarify the features of polymer behavior under conditions of a high-power local heating, and (2) on the basis of indirect signs, to find the characteristic value of the temperature of thermal decomposition onset in the course of step-by-step increase of the heating power with the lowest possible heating pulse length.

The problem can be approached in various ways. Considering the approaches, we have taken into account the known experience of polymers superheating with respect to the melting point using DFSC technique [2–5] and rapid heating of polymers up to the region of thermally unstable states (with respect to the onset temperature of thermal decomposition in quasi-static process  $T_d$ ) by the contact thermal analysis technique [6,7]. We took into account the experience of studying polymer melts superheated with respect to  $T_d$  value [8,9], polymer solutions superheated with respect to the temperature of liquid–liquid phase transition [10–12] and the details of pulse experiments performed exactly with PMMA [13–15] as well. The experiments [8–10] have been performed using pulse heating of implanted wire probe technique [16] and were accompanied by characteristic response signals (on the recorded curve of the probe temperature  $T(t)$  evolution) confined in time and reproducible with respect to the heating parameters. We have taken the response temperature  $T^*$  for the temperature of the polymeric liquid’s attainable superheat. Based on the suitable model of thermal equation of state and experimentally obtained  $T^*$  values, the approximation for

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liquid–vapor spinodal of a polymeric liquid has been determined allowing for the macromolecules decomposition [8]. The modern version of the technique [16], namely, the method of controlled pulse heating of a wire probe – resistance thermometer, is described in the previous paper [17]. Generally, this method corresponds to the requirements of the problem. The essence of requirements is as follows: the possibility of flexible tuning of pulse heating parameters, reliable repeatability of the results in a series of measurements under given heating parameters, sufficient resolution with respect to temperature effects related to the substance properties changes.

## 2. Approach

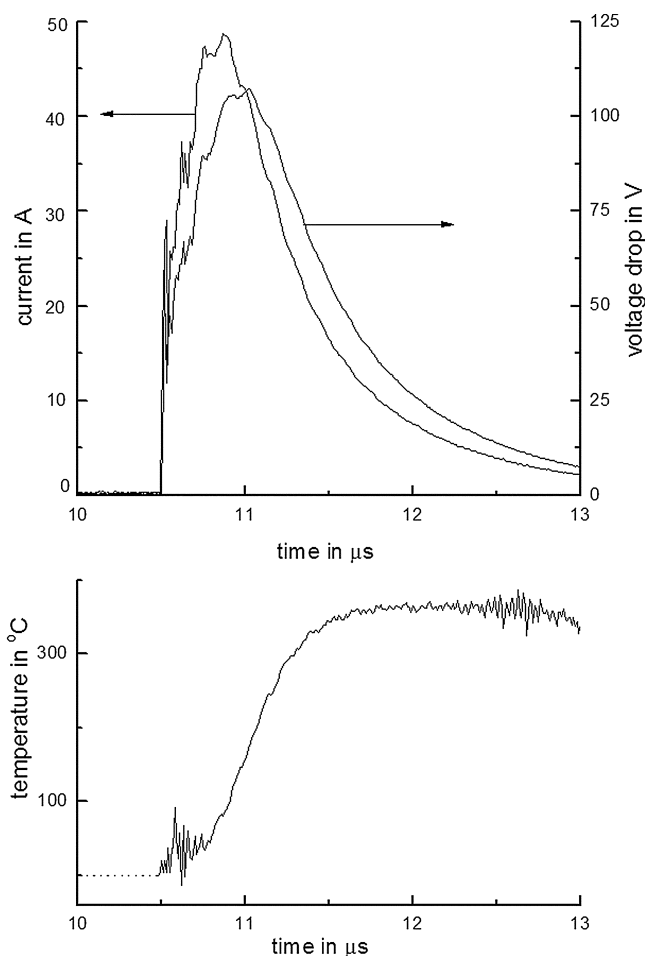
To solve the problem, we have selected the method of controlled pulse heating [17,18]. Nevertheless, it cannot be applied directly due to practical limitation on the probe heating rate. The difficulty of the very formulation of the problem is that there is no reason to expect neither an unambiguous detection of the timing of thermal decomposition, nor the possibility of the probe temperature monitoring directly in the course of rapid heating typical of the phenomenon of high-voltage breakdown (characteristic discharge time period is of the order of 10 ns). So, we were pressed to search rather “soft” approach which implies the possibility of recording an extended in time response signal to heat release. Following the conditions of our task, we attempted to reduce the pulse heating length in order to increase as much as possible the depth of reproducible penetration into the region of thermal instability ( $T - T_d$ ) of a polymer. In order to select the useful signal, the shift of the measurement stage to the “tail” of the basic heating pulse has proved to be reasonable. The similar approach was applied for investigating thermal stability and thermophysical properties of thermally unstable polymeric liquids under millisecond times scale [19].

So, increasing the heating rate in step-by-step manner, we have finally received the technique of a probe shock heating. The essential characteristics of the technique are as follows: the length of basic (shock heating) pulse is  $t_{sh} \approx 1 \times 10^{-6}$  s, the energy transferred to the probe (platinum wire 20  $\mu$ m in diameter and  $l \approx 3$  mm in length) in the course of shock heating is stepwise increased from  $10^{-1}$  to  $10^1$  mJ, the corresponding probe temperature rise attains  $10^2$  K by the order of magnitude, see Fig. 1. The length of the monitoring pulse, which is responsible for the response record, was  $t_m \sim 10^{-4}$  s by the order of magnitude, as discussed below. At the same time, the crucial prospects of the base method [17] have proved to be maintained.

In the framework of our approach, the appearance of the signs of thermal decomposition is revealed from comparison of the response curves in a series of pulses under identical parameters of the heating function. The short-term thermal stability of a polymer means that the response signal parameters remain the same in the course of repeated heat release with the fixed parameters. On the contrary, we assign a systematic drift of the response parameters in a series of pulses with the fixed parameters to thermal decomposition of a polymer as the most natural relaxation process under given experimental conditions.

## 3. Experimental

Let us start the considering of details of experimental technique with the measuring cell. The main element of the cell is a set of wire probes. The probes together with current supply construction was immersed in the cell with liquid monomer (methyl methacrylate) and implanted into the bulk of sample in the course of block polymerization. The details of polymerization have been described elsewhere [16]. The requirement to the quality of the



**Fig. 1.** The scales of shock heating characteristic time, heating power ( $P = U \times I$ ) and probe temperature rise with respect to the technique of a probe shock heating: raw signals of a voltage drop across the probe  $U(t)$ , a current in the probe circuit  $I(t)$  (above) and calculated data of the probe temperature  $T(t)$  as functions of time (below). The delay time of a circuit prior to the shock heating pulse onset was set equal to 10.5  $\mu$ s.

thermal contact between a substance and a probe was naturally met due to the essential decrease in the sample volume in the course of polymerization. In its turn, the decrease in the sample volume imposes a limitation from below on the wire diameter. Finally, selecting the diameter of 20  $\mu$ m was based on the following circumstance. For this particular diameter, both the sufficient sensitivity in our experiment and the sufficient probe's strength under polymerization conditions has been observed. A cell consists up to ten probes with similar parameters,  $l = 3 \pm 0.15$  mm, for performing subsequent measurements with the same sample, see Fig. 2. In view of the specificity of the methyl methacrylate polymerization mechanism, obtained under similar conditions samples can, however, have a different molecular weight distribution.

A voltage drop across the probe and a current in the probe circuit are traced in the course of experiment. This makes it possible to calculate the values of heating power and probe temperature averaged over the bulk in time  $T(t)$  and, finally, the actual values of heat flux density through the probe surface  $q(t)$  and the thermal resistance of the substance under given conditions of heat release  $R_\lambda(t) = \Delta T(t)/q(t)$ , where  $\Delta T(t)$  is temperature rise with respect to the initial temperature  $T_0$ , can be determined at any moment [17]. Thermal resistance appears to be the main observable for comparison of heat transfer intensity in samples in the course of high-power pulse experiments, as we discussed

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