PULSE HEATING AS A TOOL TO STUDY THE HIGH TEMPERATURE PROPERTIES OF UNSTABLE LIQUIDS[1]

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[1] Paper presented at the Thirteenth Symposium on Thermophysical Properties, June 22-27, 1997, Boulder, Colorado, U.S.A.

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ABSTRACT

We have developed the method of controlled pulse heating of a wire probe being in a good contact with liquid with respect to the temperature and the heat flux for estimation of the thermophysical properties in the region of instability of a liquid. It ensures a rapid penetration into the region of short-living states and maintenance of a given temperature regime in this region. The paper presents and discusses the character of variations of the values of the thermal activity and the lifetime of a system before its disintegration for thermally unstable liquids, such as polymeric and microheterogeneous ones, for different heating ways.

KEY WORDS: pulse heating; spontaneous boiling-up; thermal activity; unstable liquids.

INTRODUCTION

The development of pulse power methods along with the problems of simulation of extreme situations has intensified interest in studies of a system response to a powerful heat release. In real processes thermal perturbation may have a complex time distribution. Moreover, the system relaxation may proceed by several channels with different characteristic times and degrees of nonequilibrium. (For instance, the characteristics of boiling-up of polymeric liquids used as quenchants are affected by processes of thermal decomposition and microphase separation). Thus, the prediction of the system behavior under different heating conditions is a nontrivial task. The required information can be obtained in an experiment which allows for a systematic change of the heating regime and real-time control of the amplitude of the heating pulse in accordance with the current response of a system.

Our purpose is to modify the classical method of pulse heating of a wire probe [1,2] for obtaining additional data on the relaxation of complex liquids in the high temperature region, including the region of short-living states of liquid. The method in its classical form (quasilinear heating with characteristic times 10^{-5}-10^{-3} s) for an appropriate choice of regimes makes it possible: (i) to create a rapid superheat of the boundary layer with respect to the temperature of equilibrium boiling and to determine the temperature of spontaneous boiling-up [1-3]; (ii) to determine thermophysical properties of a substance at the thermostat temperature.

By introducing a high-speed control system into the circuit it proves to be possible to achieve a fine adjustment of the probe temperature variation in time. In particular, we believe that the regime of temperature plateau (see curve 1 on Fig. 1) may be important for modeling of high temperature processes. It ensures the relation between the traced property and the value T_{pl}, the registration of the response to the given heat release, and also the variation of T_{pl} value in experiment. This value may

be chosen in the region of metastability with respect to the liquid-vapor or liquid-liquid transition or in the region of thermal instability of a substance.

EXPERIMENTAL PROCEDURE

A platinum wire probe connected to the bridge circuit serves simultaneously as a heater and as a resistance thermometer. The probe diameter d is 20 μm, the length is 1÷2 cm. The current pulse length is from 10 to 1000 μs, the thickness of the heated layer of a substance is about 1÷10 μm [4]. The variation of the probe temperature in the course of its heating $T(t)$ is traced. The recorded equivalent of the resistance (and temperature) change is the potential of the bridge disbalance. The idea of the method is based on the high sensitivity of the circuit to the change of properties of a substance adjoining the probe, see curves 2 and 3 on Fig. 1. At a given heat release in the probe the rate of its heating $T(t)$ in experiments with short pulses ($\sqrt{at} < d/2$) is determined mainly by the thermal activity of a substance $\varepsilon = \sqrt{\lambda\rho c}$ [2, 5], where a, λ, ρ, and c are the thermal diffusivity, thermal conductivity, density, and heat capacity of the medium, respectively.

A kink point in the relaxation of the heated liquid is its spontaneous boiling-up. The moment of boiling-up is marked by a confined in time signal with temperature T^*, see curve 3 on Fig. 1. For a detailed resolution of a boiling-up signal the low-frequency component of the heating curve is subtracted, and the difference signal is amplified. Fortunately, the spontaneous boiling-up temperature in contrast to the case of boiling on ready and easily activated centres, is reproduced from pulse to pulse. As an example, Fig. 2 shows the superimposition of ten T^*-signals obtained on a polymer melt.[1] The spread in T^* values does not exceed 5 K at a level of about 1000 K. The amplitude noise is filtrated with the help of a standard software. In

[1] The example is given for a system which undoubtedly does not belong to the class of "well boiling liquids". The problems of boiling-up of polymeric liquids are considered elsewhere [6].

experiments with complex liquids, such as polymeric and microheterogeneous ones, the reproducibility of T^* values implies the repetition of the heating way. Its change leads to changes in the relaxation processes, and therefore, in $T^*(t^*)$ values.

The regime of the temperature plateau includes a rapid heating of the probe to a selected value of T_{pl} and a maintenance of this value for a certain time interval. Here and below by T_{pl} we shall mean the temperature of the probe averaged over its volume. With an appropriate choice of T_{pl} value one can determine the lifetime of a system before its boiling-up. The boiling-up signal is resolved on the curve of the bridge disbalance and on the curve of the input voltage feed $U(t)$ controlled by the tracking system, see Fig. 3. The characteristic $U(t)$ curve with boiling signal is shown in Fig. 4. An increase in $U(t > t^*)$ value compensates for the additional heat loss caused by boiling.[2] By recording the value of $U(t)$ required for maintaining the probe temperature constant one can determine the density of a heat flow $q(t, T=T_{pl})$ which is connected with the thermophysical properties of a substance. In particular, the solution of the problem of a heat transfer from an infinitely long isothermal bar of radius r into a medium with a temperature T_∞ yields [5]: $q \sim \varepsilon$ at $\sqrt{at} < d/2$ and $q \sim \lambda$ at $\sqrt{at} < d/2$.

Thus, the value of $U(t, T=T_{pl})$ proves to be sensitive to variations of thermal properties. Fig. 5 shows the corresponding curves for some well-studied substances. The decrease in the voltage level from curve 1 to curve 4 corresponds to the decrease in thermal activity of these liquids. Data on $U(t, T=T_{pl})$ for vacuum are used as reference data for transition from electrical quantities measured in experiment to relative thermal properties of substances.

[2] In general case the sign of boiling signal depends on the pressure and on the molecular chain length.

APPARATUS

The block diagram of the apparatus shown in Fig. 3 combines two approaches to the problem of controlled heating which complementing each other. The first approach is realized when the feedback is switched on through the key K. The required heating function is passed from the computer through the converter DAC-DFG to the amplifier PA, which produces a current pulse of variable amplitude. The output signal from the probe corresponds to the given $T(t)$ dependence with the accuracy determined by stationary and dynamic errors of the tracking system. In particular, the value of T_{pl} is setted to within 0.1 %. The second approach is based on the relation between the heating function and a given function of current through the probe. This function is also passed from the computer and reproduced by the amplifier, but with an open key K. A combination of two approaches in different experimental stages is also possible.

RESULTS AND DISCUSSION

Originally the method was tested on simple liquids. It has been revealed that a change of 0.1 K in the temperature on the plateau (with the choice of $T_{pl} \approx T^*$) results in a shift of the moment of spontaneous boiling-up by tens of microseconds. Such a result is in agreement with the idea of nearly threshold (with respect to temperature) character of spontaneous boiling-up. The dependence of T^* values on the heating way appears for thermally unstable substances.[3] As expected, the scale of the effect increases with decreasing thermal stability.

The results of T^* measurements for trifunctional oligopropylene oxide with molecular weight $M \approx 3{,}500$ for different heating ways are shown in Fig. 6. Two different regimes were used, namely the linear heating and the "branching" one. The

[3] By thermally unstable substances we mean such substances for which the inequality $T^* > T_d$ is fulfilled. Here T_d is the temperature of thermal decomposition of a substance.

temperature of the branching point has been chosen close to the temperature T_d of the sample. The erxperimental data show the effect of a heating way on T^* values. Apparently, it is connected with peculiarities of the accumulation of decomposition products in the course of the heating. We hope that the analysis of T^* data with a systematic variation of the thermal history will clarify the character of interaction between the thermal decomposition and the boiling-up processes.

Let us next find out, what happens to the thermal properties of a system in the temperature range close to the temperature of its spontaneous boiling-up. The value of $U(t)$ was measured at different T_{pl} values for polydimethyl siloxane (PDMS, $M \approx$ 55,000) and CO_2 solution in PDMS. The content of CO_2 was about 0.5 wt.%. The results of the measurements for these samples, expressed in units of thermal activity, are shown in Fig. 7. One can see that with increasing T_{pl} , the value of ε for the solution decreases with respect to that for PDMS. We shall present the characteristic temperatures of these samples. The values of T^* at the experimental pressure of 0.1 MPa and the pulse length of 400 μs are, respectively, 840 K and 955 K, the value of T_d for PDMS being close to 600 K. The temperature in the thermostat, which is at the same time the liquid-vapor equilibrium temperature for the solution at 0.1 MPa, was 290 K. It should be noted that the solubility of CO_2 decreases with increasing T. Thus, at $T > 600$ K the samples are in the region of thermal instability, and at $T > 290$ K the solution is supersaturated with respect to the content of CO_2. When we compare the results on ε for these samples, the contribution of the first factor is essentially compensated. We ascribe the decrease in $\varepsilon(c = 0.5\%)/\varepsilon(c = 0)$ ratio with increasing T to the behavior of CO_2 in solution. The system reacts to the increase in the supersaturation degree and the approach to the boundary of spontaneous boiling

by forming subcritical nuclei of a new phase. This reduces the degree of order and the packing density of a substance and therefore its sensitivity to heat release.

The values of T^* and ε measured in experiment are structure sensitive characteristics. This circumstance gives the possibility of the use of the method for monitoring of the instantaneous concentration and physico-chemical properties of a system. The best results have been obtained on polymeric liquid + gas systems characterized by the largest scale of $T^*(c)$ changes. In particular, the resolution of CO_2 content in PDMS from the data on $T^*(c)$, see Fig. 8, in the region of $c \sim 0 \div 1$ wt.% is of the order of 0.01%. With increasing c the resolution drops.

CONCLUSION

The present work gives the key points of the method of controlled pulse heating. The method makes it possible to determine the lifetime of a system before its boiling-up or disintegration and to evaluate its thermal properties at a given temperature. This forms a basis for determining the absolute values of the system thermal properties in the region of short-lived states and for elucidating the relaxation mechanism of a complex system in condition of pulse action.

ACKNOWLEDGMENT

This study was supported by the Russian Foundation of Fundamental Investigations under grant 95-02-03645-a.

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FIGURE CAPTIONS

Fig. 1. Typical curves of the probe heating for the plateau regime (1) and for the linear regime (2,3) in the air (2) and liquid (3). The arrow shows the moment of boiling-up.

Fig. 2. Superposition of ten boiling signals ($\Delta T = T - T_c$) for polyethylene oxide PEO-20,000 at the heating rate of $2 \cdot 10^6$ K/s. ΔT is the probe temperature perturbation caused by boiling-up. T_c is the function compensating the smooth heating.

Fig. 3. Block diagram of apparatus: PC, computer; DAC, digital-to-analog converter DFG, driving function generator; PA, power amplifier; Pr, probe; CFG, compensating function generator; DA, differential amplifier; ADC, analog-to-digital converter Points 1 and 2 correspond to the input and output signals, respectively.

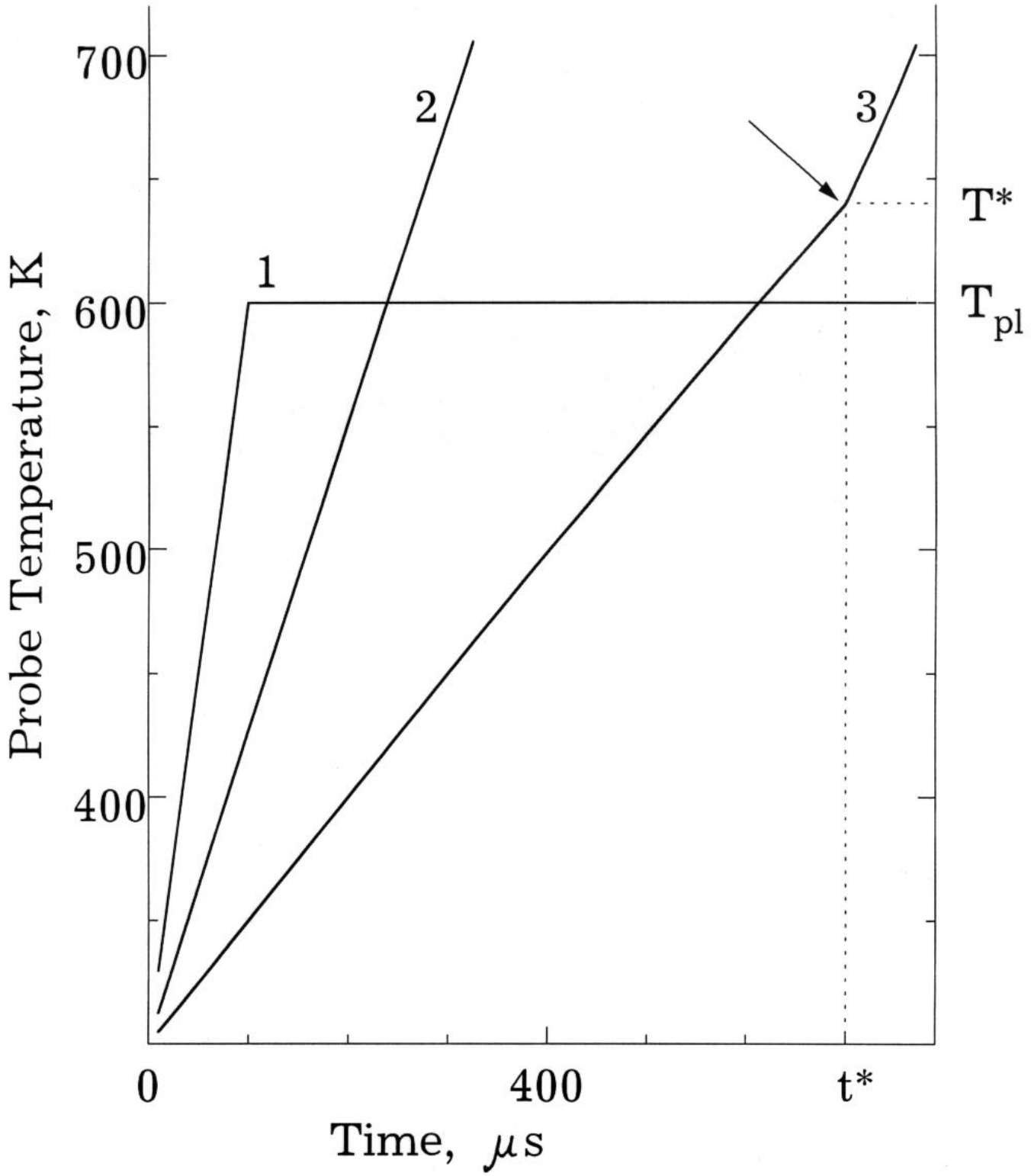
Fig. 4. Characteristic $U(t)$ curve with the boiling signal for oligoethyleneglycol PEG -400 in the plateau regime. T_{pl} = 820 K. The arrow shows the moment of boiling-up.

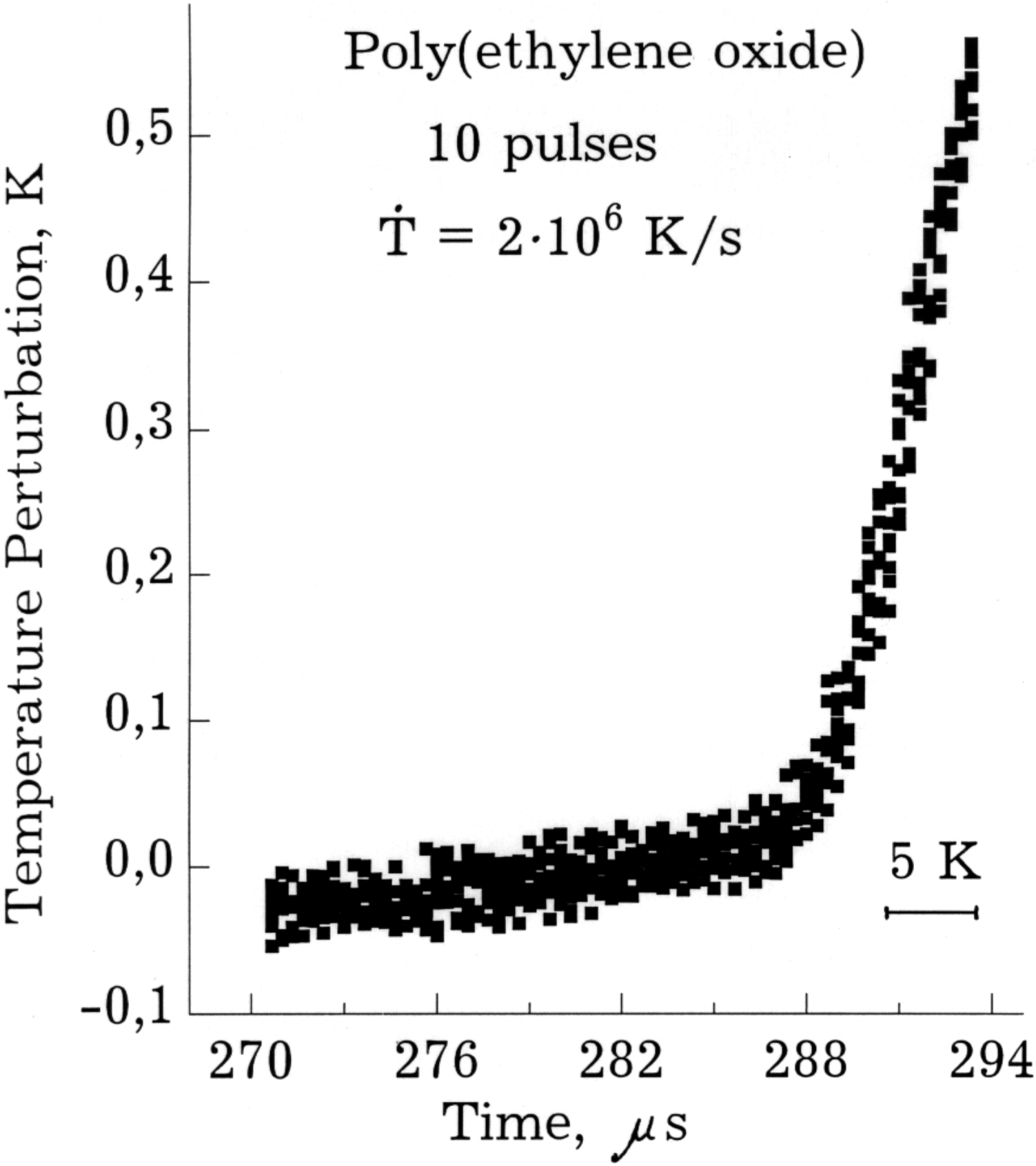
Fig. 5. Characteristic $U(t) - U_0$ curves obtained in the plateau regime (T_{pl} = 333 K) for different substances: water (1), ethanol (2), hexadecane (3), decane (4), air (5).

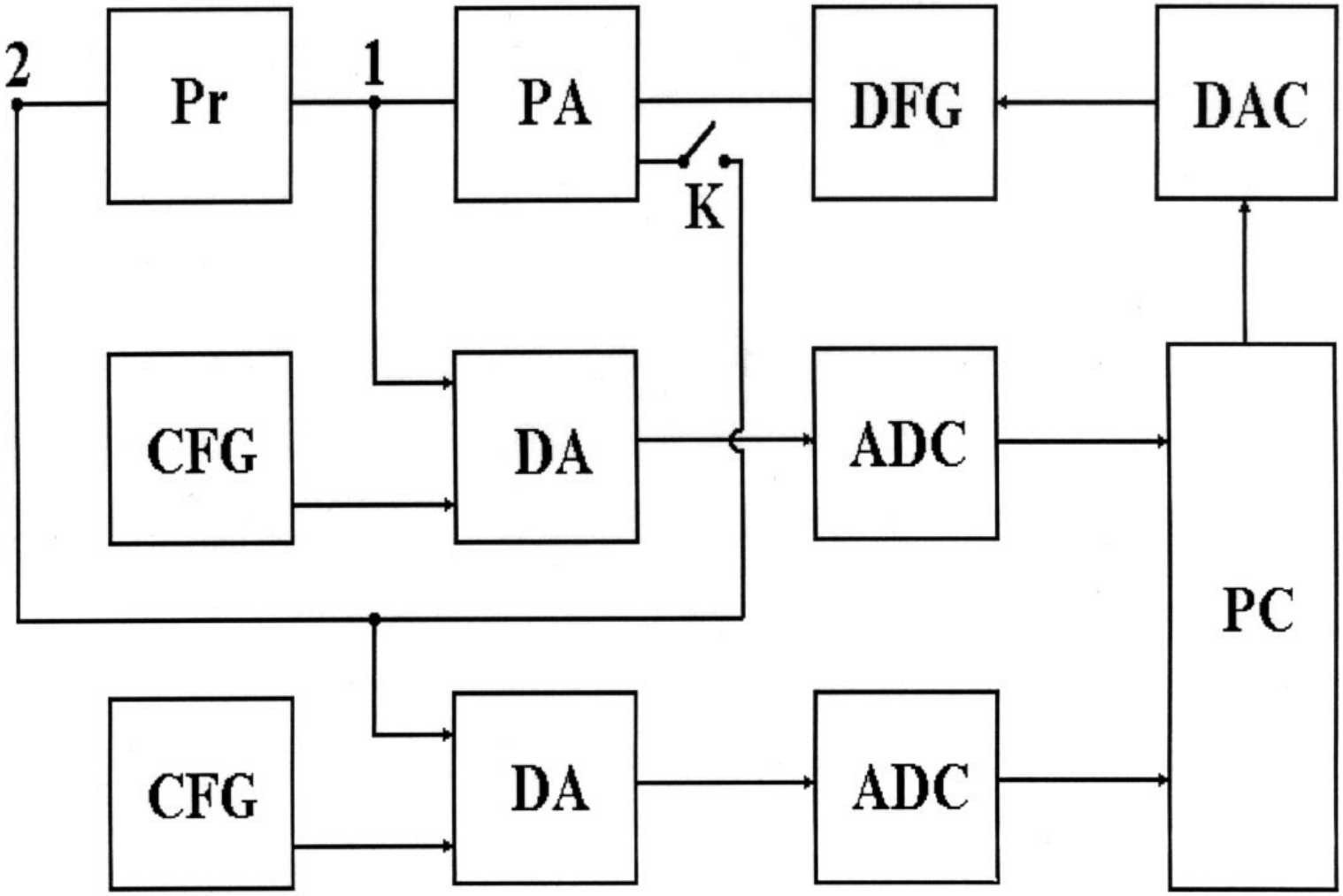
Fig. 6. Temperature of spontaneous boiling-up of oligopropylene oxide versus the heating way. Open circles correspond to the linear regime of heating, solid circles - to the brunching one. The insert shows the scheme of brunching heating. Coordinates of the brunching point are {60 μs; 573 K}.

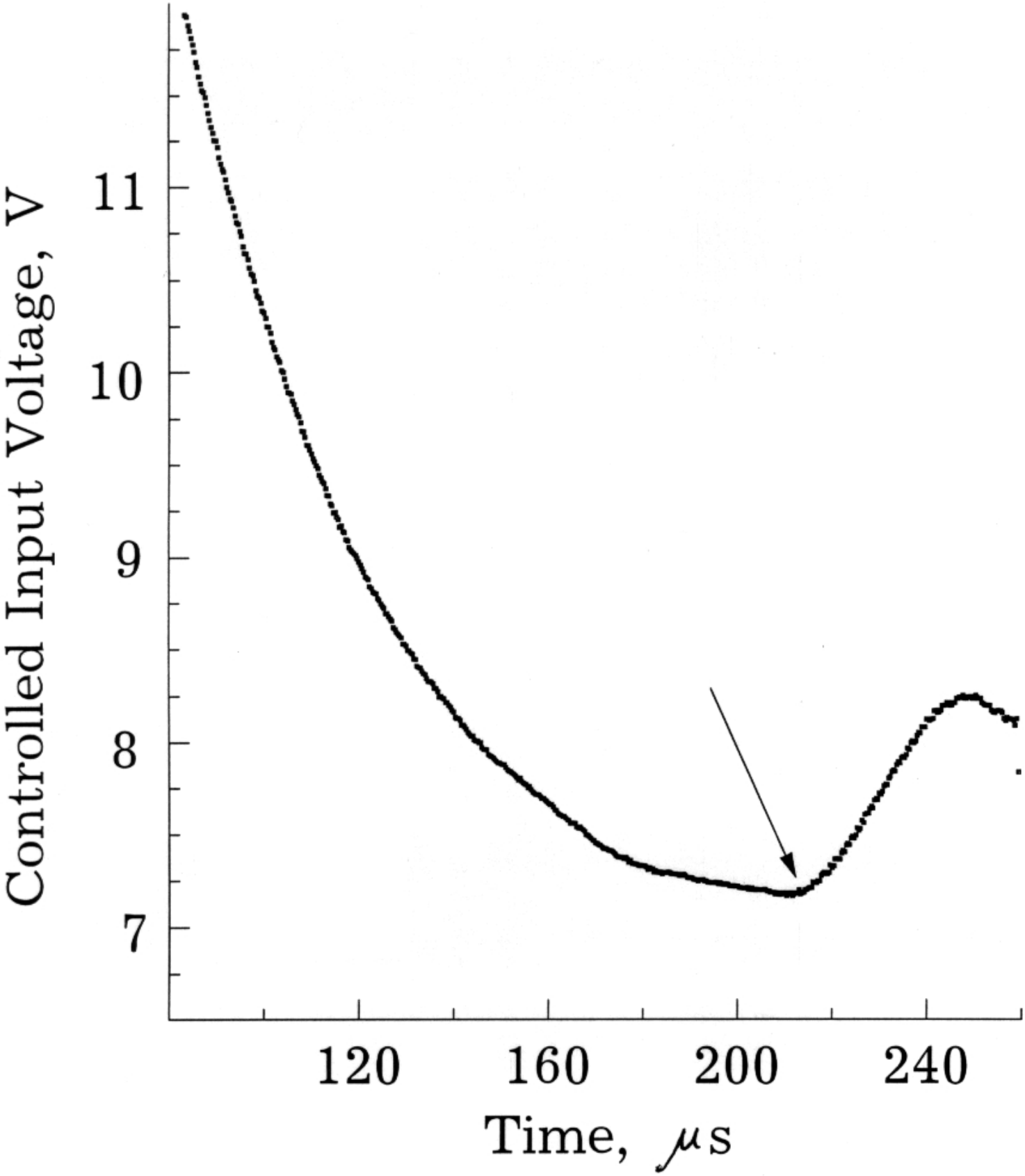
Fig. 7. Thermal activity of PDMS + CO_2 solution reduced to that of PDMS versus temperature of the plateau. CO_2 content is c = 0.5 wt.%.

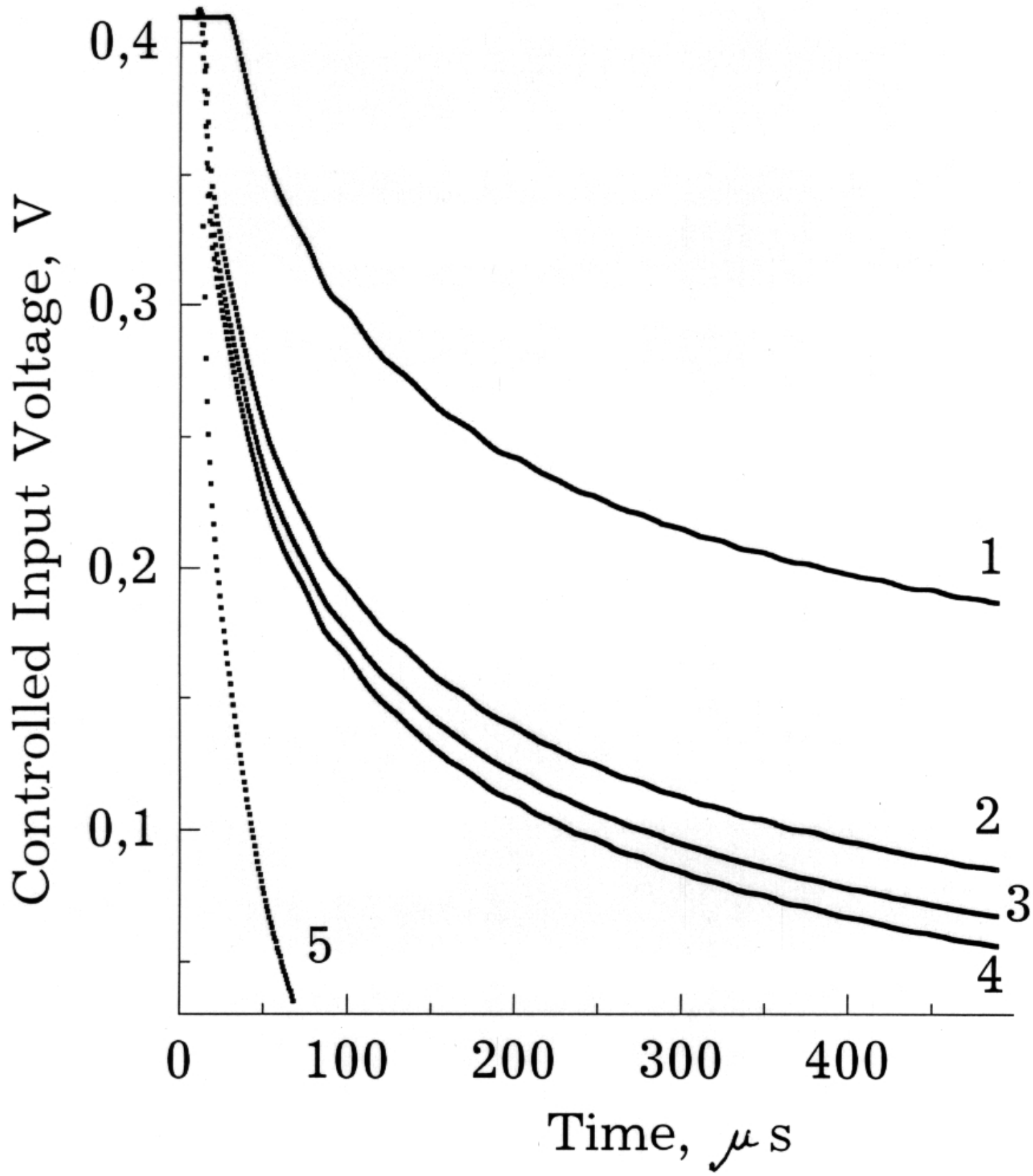
Fig. 8. Temperature of spontaneous boiling-up of PDMS + CO_2 solution versus pressure and CO_2 content.

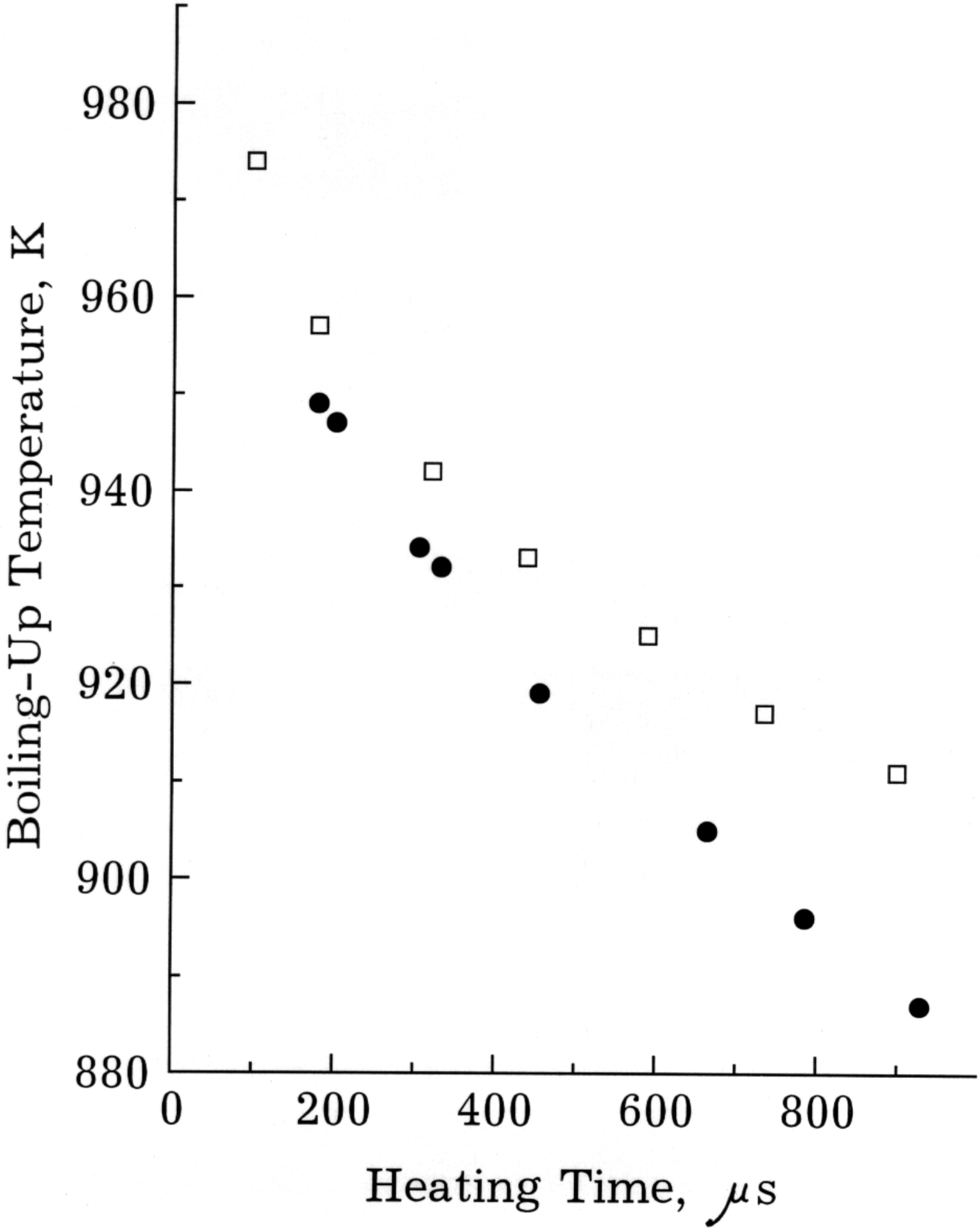

700
600
500
400
Probe Temperature, K
1
2
3
T*
T_pl
0
400
t*
Time, μs

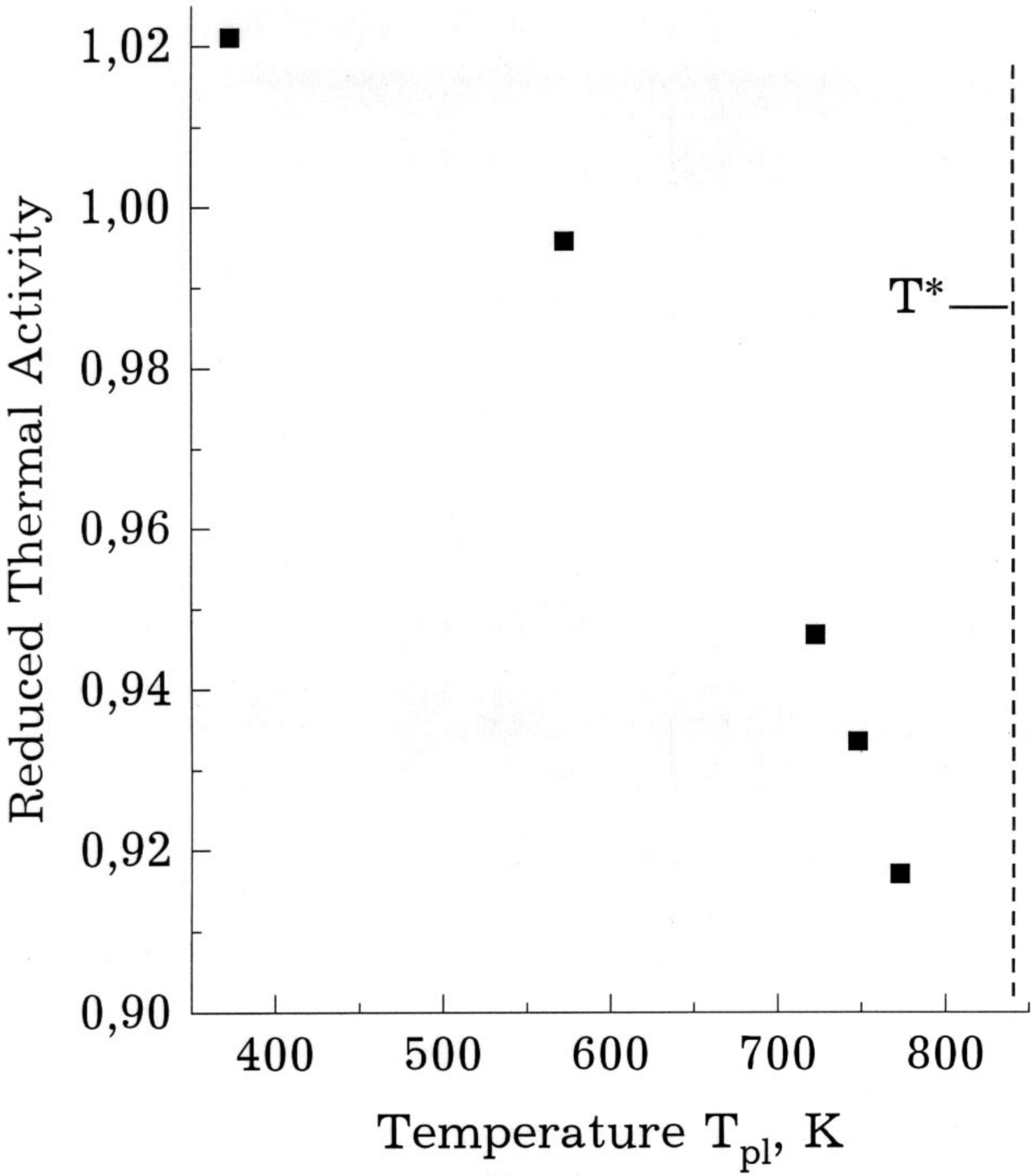

Poly(ethylene oxide)
10 pulses
$\dot{T} = 2 \cdot 10^6$ K/s
5 K
Temperature Perturbation, K
0,5
0,4
0,3
0,2
0,1
0,0
-0,1
270
276
282
288
294
Time, μs


2
Pr
1
PA
DFG
DAC
K
CFG
DA
ADC
PC
CFG
DA
ADC


Controlled Input Voltage, V
11
10
9
8
7
120
160
200
240
Time, μs


0,4
0,3
0,2
0,1
Controlled Input Voltage, V
1
2
3
4
5
0
100
200
300
400
Time, μs


980
960
940
920
900
880
Boiling-Up Temperature, K
0
200
400
600
800
Heating Time, μs


1,02
1,00
0,98
0,96
0,94
0,92
0,90
Reduced Thermal Activity
T*
400
500
600
700
800
Temperature T_{pl}, K

Spontaneous Boiling-Up Temperature for PDMS+CO_2 Mixture