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Pulse Heating as a Tool to Study the High-Temperature Properties of Unstable Liquids[1]

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The method of controlled pulse heating of a wire probe in good contact with a liquid has been developed for estimation of the thermophysical properties in the region of instability of this liquid with respect to the temperature and the heat flux. It ensures rapid penetration into the region of short-lived states and maintenance of a given temperature in this region. This 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 systems, for different heating paths.

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

1. 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 perturbations may have a complex time distribution. Moreover, the system relaxation may proceed by several paths with different characteristic times and degrees of nonequilibrium. (For example, the characteristics of boiling-up of polymeric liquids used as quenchers 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

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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] to obtain additional data on the relaxation of complex liquids in the high-temperature region, including the region of short-lived states of liquids. The method in its classical form (quasilinear heating with characteristic times of 10^{-5} to 10^{-3} s), with 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] and (ii) to determine the thermophysical properties of a substance at the thermostat temperature.

By introducing a high-speed control system into the circuit, it is possible to achieve a fine adjustment of the probe temperature variation with time. In particular, we believe that the regime of the temperature plateau (see curve 1 in Fig. 1) may be important for modeling of high-temperature processes. It ensures a relation between the traced property and

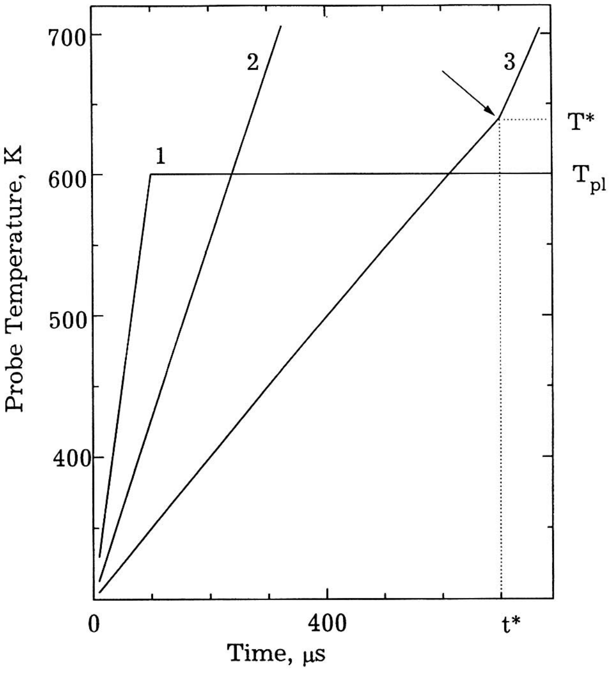

Fig. 1. Typical curves of the probe heating for the plateau regime (1) and for the linear regime (2, 3) in air (2) and in liquid (3). The arrow shows the point of boiling-up.

the value of T_{pl}, the response to the given heat release, and also the variation of the T_{pl} value in the 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.

2. 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 $20\,\mu\mathrm{m}$, and the length is 1 cm. The current pulse length is from 10 to $1000\,\mu\mathrm{s}$, and the thickness of the heated layer of a substance is about $1\,\mu\mathrm{m}$ [4]. The variation of the probe temperature with time is measured. The recorded equivalent of the resistance (and temperature) change is the potential of the bridge unbalance. The principle of the

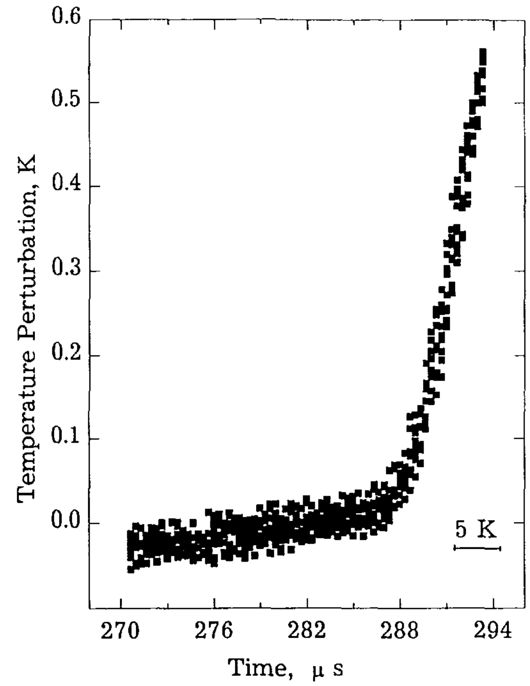

Fig. 2. Superposition of 10 boiling signals ($\Delta T = T - T_c$) for polyethylene oxide PEO-20,000 at a heating rate of $2 \times 10^6\ \mathrm{K \cdot s^{-1}}$. ΔT is the probe temperature perturbation caused by boiling-up, and T_c is the function compensating the smooth heating.

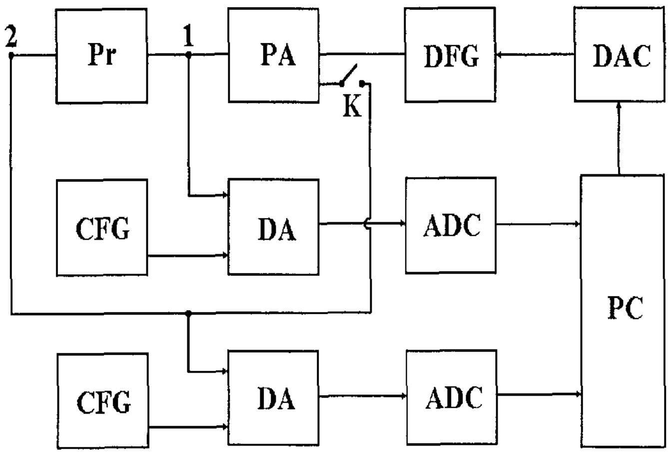

Fig. 3. Block diagram of the apparatus: PC, computer; DAC, digital-to-analog converter; DFG, driving function generator; PA, power amplifier; Pr, probe, connected to the bridge circuit; CFG, compensating function generator; DA, differential amplifier; ADC, analog-to-digital converter. Points 1 and 2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

method is based on the high sensitivity of the circuit to the change of properties of a substance surrounding the probe; see curves 2 and 3 in 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 $\varepsilon = \sqrt{\lambda \rho c_p}$ [2, 5], where a, λ, ρ, and c_p are the thermal diffusivity, thermal conductivity, density, and heat capacity of the medium, respectively.

A break point in the relaxation of the heated liquid is its spontaneous boiling-up. The point of boiling-up is marked by a characteristic signal with temperature T^* (see curve 3 in 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 centers, is reproducible. As an example, Fig. 2 shows the superimposition of 10 T^* signals obtained on a polymer melt.[4] The spread in T^* values does not exceed 5 K at a level of about 1000 K. In

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[4] 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].

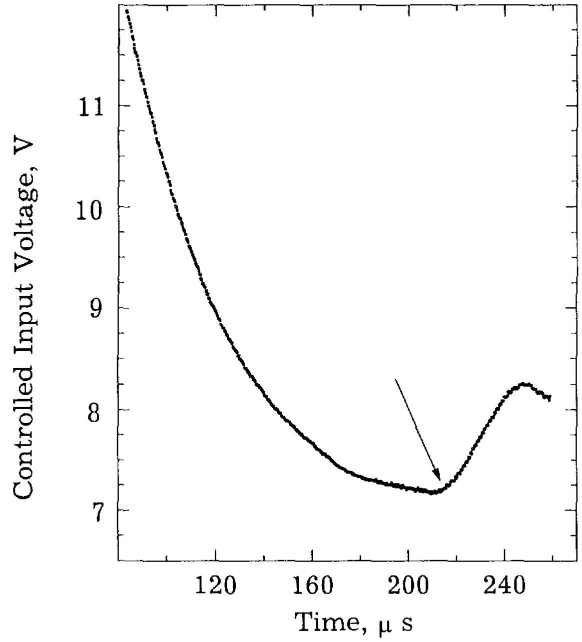

Fig. 4. Characteristic $U(t)$ curve with the boiling signal for oligoethyleneglycol with a molecular weight of $M \approx 370$ (PEG-400) in the plateau regime. $T_{\mathrm{pl}} = 820$ K. The arrow shows the point of boiling-up.

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

The regime of the temperature plateau includes rapid heating of the probe to a selected value of T_{pl} and maintenance of this value for a certain time interval. T_{pl} is the temperature of the probe averaged over its volume. With an appropriate choice of T_{pl}, one can determine the lifetime of a system before its boiling-up. The boiling-up signal is resolved on the curve of the bridge unbalance 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 $U(t > t^*)$ compensates for the additional heat loss caused by boiling.[5] By recording the value of $U(t)$ required for maintaining the probe temperature, one can determine

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

the density of a heat flow $q(t,\ T=T_{\mathrm{pl}})$ which is connected with the thermophysical properties of a substance. In particular, the solution of the problem of heat transfer from an infinitely long isothermal bar of diameter d into a medium with a temperature T_{∞} yields [5]: $q \sim \varepsilon$ at $10\sqrt{at} \leqslant d$ and $q \sim \lambda$ at $\sqrt{at} \gg d$.

Thus, the value of $U(t,\ T=T_{\mathrm{pl}})$ proves to be sensitive to variations of thermal properties. Figure 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 $U(t,\ T=T_{\mathrm{pl}})$ for vacuum are used as reference data for transition from electrical quantities measured in experiment to relative thermal properties of substances.

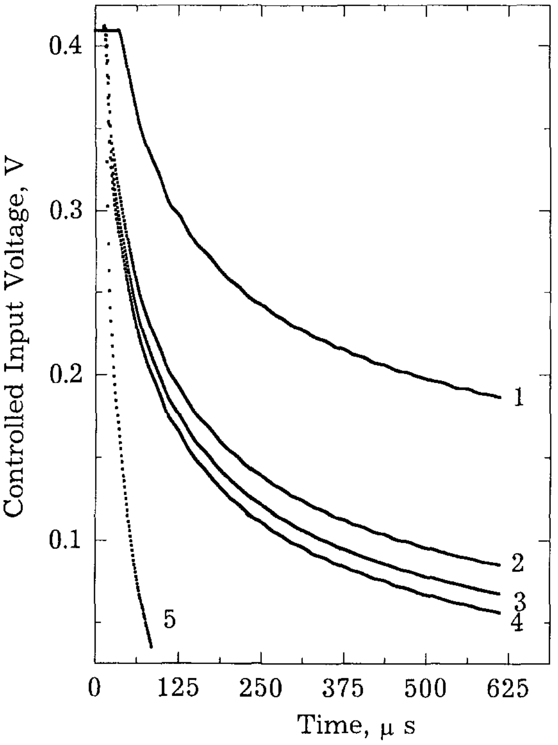

Fig. 5. Characteristic $U(t)-U_0$ curves obtained in the plateau regime ($T_{\mathrm{pl}}=333$ K) for different substances: water (1), ethanol (2), hexadecane (3), decane (4), air (5). U_0 is the bias voltage.

3. APPARATUS

The block diagram of the apparatus shown in Fig. 3 combines two approaches to the problem of controlled heating which complement each other. The first approach is realized when the feedback is switched on through the key K. The required heating function is fed 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 determined 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 fed 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.

4. 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 $T_{\mathrm{pl}} \approx T^*$) results in a shift of the point of spontaneous boiling-up by tens of microseconds. Such a result is in agreement with the idea of a nearly threshold (with respect to temperature) character of spontaneous boiling-up. A dependence of T^* values on the heating method is observed for thermally unstable substances.[6] As expected, the scale of the effect increases with decreasing thermal stability.

The results of T^* measurements for trifunctional oligopropylene oxide with a molecular weight of $M \approx 3500$ for different heating paths are shown in Fig. 6. Two regimes were used, namely, linear heating and the "branching" ones. The temperature of the branching point was chosen close to the temperature T_d of the sample. The experimental data show the dependence of the heating path 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 determine 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 a polydimethyl siloxane (PDMS; $M \approx 55{,}000$) and CO_2 solution in

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[6] 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.

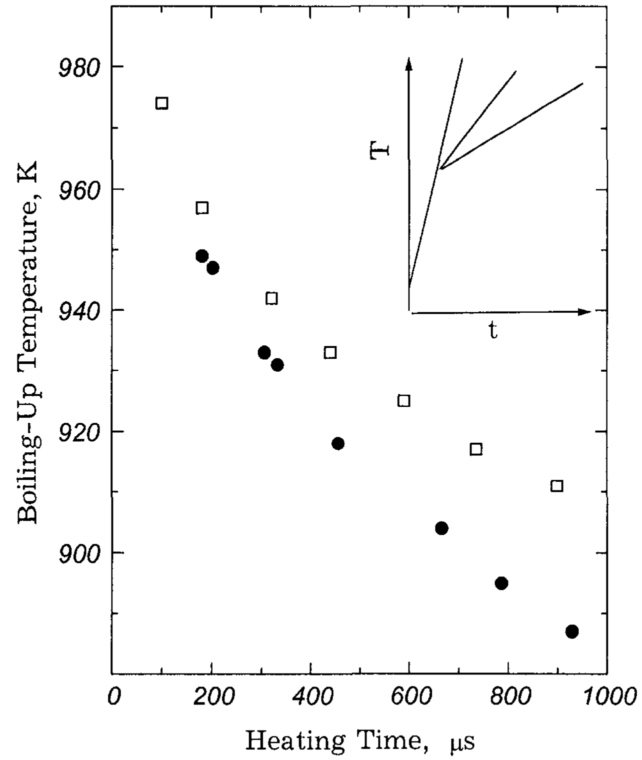

Fig. 6. Temperature of spontaneous boiling-up of oligopropylene oxide versus the heating path. Open circles correspond to the linear regime of heating; filled circles, to the branching regime. The inset shows the scheme of branching heating. Coordinates of the branching point are 60 μs and 573 K.

PDMS. The concentration of CO_2 was about 0.5 wt%. The results of the measurements for these samples, expressed as units of thermal activity, are shown in Fig. 7. One can see that with increasing $T_{\rm pl}$, the value of ε for the solution decreases with respect to that for PDMS. We present the characteristic temperatures of these samples. The values of T^* at an experimental pressure of 0.1 MPa and a pulse length of 400 μs are, respectively, 840 and 955 K, the value of T_d for PDMS being close to 600 K. The temperature in the thermostat, which is the same as 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

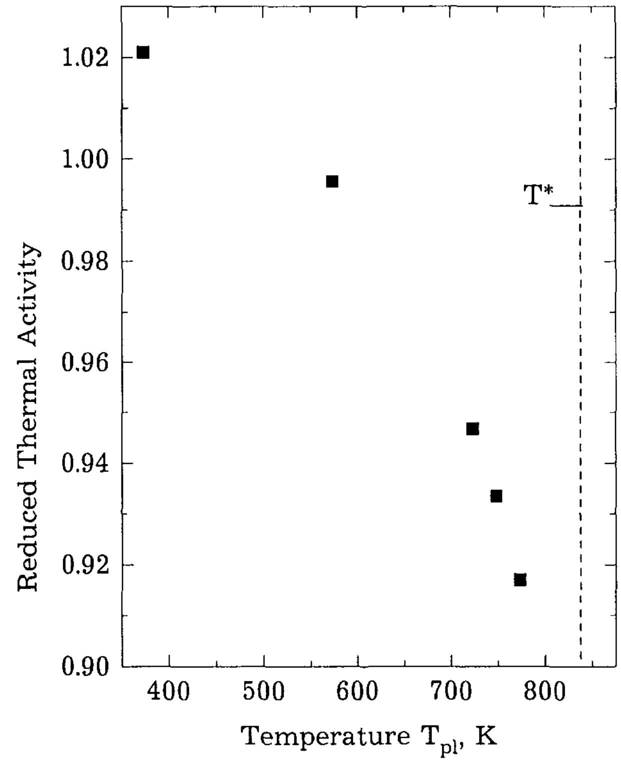

Fig. 7. Thermal activity of PDMS + CO_2 solution reduced by that of PDMS versus temperature of the plateau. CO_2 concentration, 0.5 wt%.

the results for ε for these samples, the contribution of the first factor is essentially compensated. We ascribe the decrease in the $\varepsilon(c=0)/\varepsilon(c=0.5\%)$ 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 experimental values of T^* and ε are structure-sensitive characteristics. This circumstance enables the use of the method for monitoring of the instantaneous concentration and physicochemical 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)

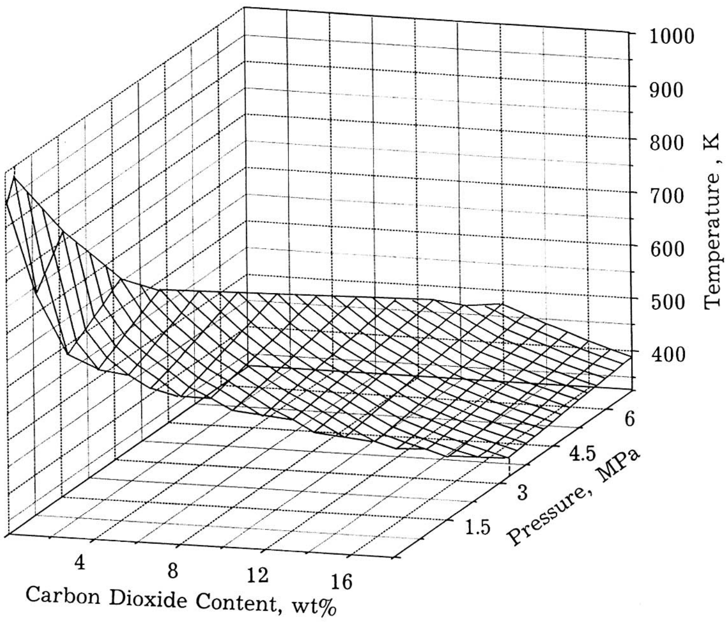

Fig. 8. Temperature of spontaneous boiling-up of PDMS + CO_2 solution versus pressure and CO_2 concentration.

in the region of $c \sim 0$ to 1 wt% is of the order of 0.01%. With increasing c, the resolution drops.

5. CONCLUSION

The present work demonstrates the key aspects 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 a condition of pulse action.

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