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The Attainable Superheat: From Simple to Polymeric Liquids

S. E. Puchinskis[1] **and P. V. Skripov**[1, 2]

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The phenomenon of the attainable superheat of a substance and the kinetics of nucleation of a vapor phase have been studied experimentally for liquids with molecular weight from 10^2 to 10^4. The values of the temperature of spontaneous boiling-up T^* have been measured over a wide range of parameters (pressure, heating rate, CO_2 content, molecular weight, and thermal stability of a substance) by the method of controlled pulse heating of a thin wire probe using pulse lengths from 0.01 to 4 ms. The investigation is based on a gradual increase in the molecular weight of a sample. The peculiarities of spontaneous nucleation in polymeric liquids that do not boil without decomposition are discussed. It is shown that this phenomenon is a reproducible relaxation process in a polymeric system, which accompanies the initial stage of its thermal decomposition.

KEY WORDS: controlled pulse heating; mean lifetime; polymeric liquids and oils; spontaneous boiling-up; thermal decomposition.

1. INTRODUCTION

In ordinary practice we observe boiling-up on artificial (heterogeneous) vapor formation centers. As the rate of crossing the line of liquid–vapor equilibrium $T_s(p)$ increases, a higher supersaturation of liquid $T-T_s$ is achieved, and the contribution of the bubbles of spontaneous origin to the vapor generation increases. We consider the phenomenon of spontaneous boiling-up of highly superheated liquids that occurs at sufficiently rapid heating. In this case one can break through the background of heterogeneous

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[1] Institute of Thermal Physics, Ural Branch of Russian Academy of Sciences, Pervomaiskaya St. 91, GSP-828, Ekaterinburg 620219, Russia.

[2] To whom correspondence should be addressed. E-mail: pavel-skripov@mail.ru

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nucleation and achieve the limiting values of superheat predicted by the homogeneous nucleation theory [1, 2]. It is significant that the process of spontaneous boiling-up is characterized by the reproducibility and by the high slope of the $J(T)$ dependence, where J is the nucleation rate of viable bubbles. This provides a basis for unambiguous detection of the spontaneous boiling-up moment by a certain experimental feature.

The spontaneous boiling-up kinetics and the related phenomenon of attainable superheat of a substance with respect to the liquid–vapor equilibrium temperature have been studied in detail for simple liquids and their solutions [3, 4]. For them the reliable methods of observation of the initial stage of boiling-up have been developed. The results of the experiments agree with the calculation of $J = J(T, p)$ based on the homogeneous nucleation theory with the work of the critical bubble formation written in the thermodynamic approximation. The description of this phase transition becomes less evident as a molecular chain length increases up to several tens (and hundreds) of links. The complication does not originate solely from the polydispersity typical of polymers and the difference in the properties of high molecular weight liquids and their low molecular weight analogues. It is clear that at a certain step of the chain length increment the boiling-up temperature of a substance will exceed the onset temperature of the thermal decomposition of macromolecules.

The difficulty of the very formulation of the problem is that rapid heating of a polymeric liquid transforms it into a multicomponent system with the time-dependent composition and the time-dependent value of the work of the critical bubble formation $W^* = W^*(T, p; t)$. This circumstance complicates the direct application of the homogeneous nucleation theory and the equations of state for polymer–solvent systems to the description of this phase transition. Under such conditions a systematic experimental investigation of the phenomenon of spontaneous bubble nucleation over a wide range of molecular weight of the samples appears to be timely. The emphasis is made on the elucidation of the peculiarities of this process for polymeric liquids. The specific feature of the object originates from the fact that macromolecules cannot form the vapor phase without their decomposition. This determines the principal difference of the phenomenon of spontaneous nucleation in polymeric liquids, compared to that of low molecular weight liquids, independent of their thermal stability.

An appropriate choice of the method is crucial for solving the problem. Our experience suggests that a distinct signal of vapor formation in polymeric liquids may be resolved only in the regime of sufficiently rapid heating [5]. Moreover, an investigation of the phase transition in a polymer retaining the substance individuality makes sense only at small degrees of decomposition, which are equivalent to short heating times.

2. EXPERIMENTAL

We used the method of pulse Joule heating of a thin wire probe [1, 3, 5], adapted to our problem [6–8]. This method can be used to achieve a controlled superheat of the probed layer of liquid, to detect the characteristic boiling-up signal on the heating curve, and to determine the substance temperature (by the probe resistance) at any moments in which we are interested. In our experiments the average heating rate was from 10^5 to $10^7\ \mathrm{K \cdot s^{-1}}$, which corresponded to a duration of heating of a substance before its boiling-up t^* from 10^3 to 10^1 µs.

The method is illustrated by the schematic block diagram of the apparatus presented in Fig. 1. Its main element is a platinum wire probe with a diameter of 10 µm. This probe combines a heater and a resistance thermometer. The whole processes of variation of the heat flux and the probe temperature in a continuous liquid and then in a boiling layer are recorded. The characteristic break in the time dependence of the probe temperature $T(t)$ (see Fig. 2), corresponds to the moment of formation of vapor bubbles at its surface. The heat flux into the liquid, the moment and the temperature of boiling-up, and the probe temperature perturbation caused by boiling-up are determined experimentally. These parameters are important for establishing the peculiarities of heat transfer in the pulse-heated liquid before and after its boiling-up [6, 7]. However, this is the subject of a separate discussion. Here, we concentrate on the temperature and time conditions of the spontaneous boiling-up phenomenon.

By the temperature perturbation $\Theta(t-t^*)$ (see Fig. 3), we mean the difference between the actual probe temperature and its extrapolated value into the region $t > t^*$ assuming that there is no boiling-up. To get the necessary resolution of the initial stage of the process, the useful temperature perturbation signal was separated from the background of large average values of electrical quantities tracked in the experiment, and this signal was

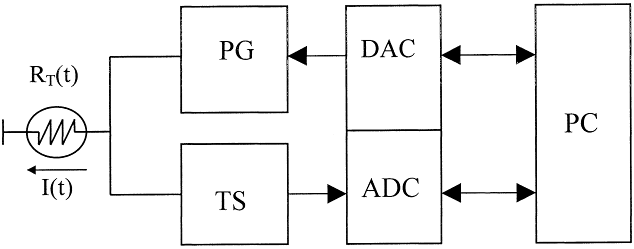

Fig. 1. Block diagram of the apparatus: PC, computer; DAC, digital-to-analog converter; G, current pulse generator; R_T, probe; TS, tracking system; ADC, analog-to-digital converter.

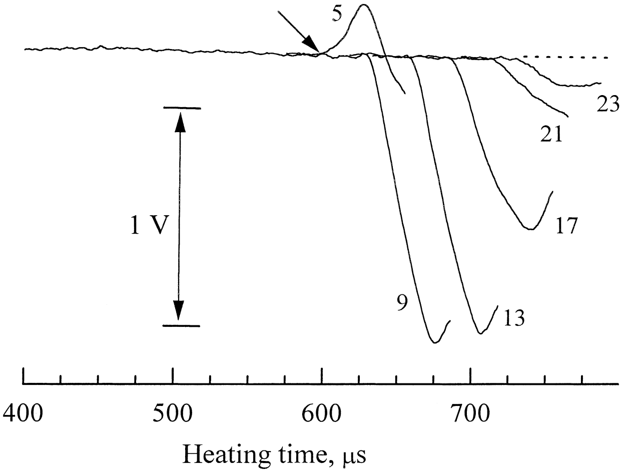

Fig. 2. Boiling-up signal separated from the background of smooth heating for a CO_2 solution (0.02 weight fraction) in the oil Mobil SAE 5W-50 at different pressures and heating rate $\dot{T} \approx 0.7$ $K \cdot \mu s^{-1}$. The indicated numbers are the pressure values in bars. The arrow shows the point of boiling-up for $p=5$ bar.

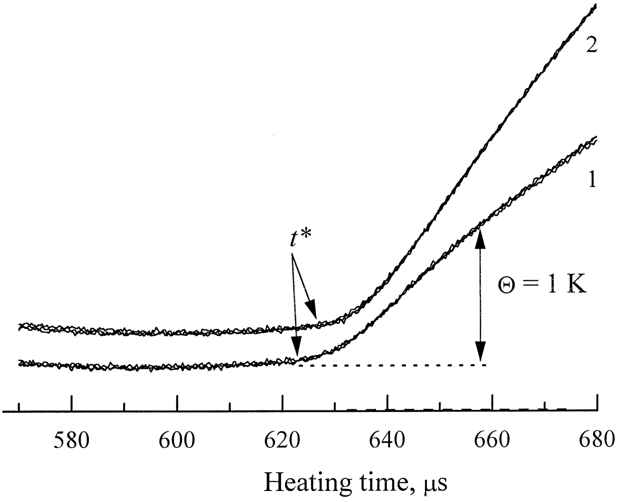

Fig. 3. The probe temperature perturbation $\Theta(t-t^*)$ caused by boiling-up of poly(dimethylsiloxane) PDMS-10000 at pressures of 0.03 MPa (1) and 0.01 MPa (2). Superposition of three sequential pulses is shown for both cases.

amplified. The details regarding the construction and operation of the measurement system are given elsewhere [7, 9].

To improve the reliability of our conclusions concerning the kinetics of spontaneous nucleation in a polymeric liquid and the contribution of the process of thermal decomposition to its onset, we are developing a procedure for setting the required (in the general case, arbitrary) regime of heating. This procedure is used to choose and finely control the probe heating profile $T(t)$ in a series of measurements taking into account a number of the thermal properties of the sample [6, 7, 10].

The objects of our studies were the following substances: homologous series of polystyrene, poly(ethylene oxide), and polydimethylsiloxane with a chain length from one to several hundreds of links; selected polymer melts of different structure and oils; and polymer solutions in standard solvents. The solutions of carbon dioxide in solvents and polymers were chosen as model systems. Measurements were made over a wide range of variables: the concentration c, the number-average molecular weight $\bar{M}_n$, and the sample heating profile. The pressure increased up to the effective critical pressure $p_c^* = p_c(t^*)$, at which the response signal was no longer resolved [11]. In our case, the computer software identifies the pressure at which the perturbation $\Theta_\Sigma(p) = 0.5 \sum_{i=0}^{19} (\Theta_i + \Theta_{i+1})$, where $i(t = t^*) = 0$, becomes equal to zero.

The investigation was carried out in order of increasing object complexity–from a simple liquid to a polymer melt. The polymer sample preparation procedure has been described earlier [5, 8]. The most important step is to provide a controllable distillation of volatile additives.

3. RESULTS AND DISCUSSION

In experiments on polymer–solvent systems, the aim was to elucidate the peculiarities of boiling-up of such systems over the full range of compositions. By solving this problem, one can make a smooth transition to measurements on pure polymers. Our approach to the interpretation of the results assumes the similarity of boiling-up conditions for the following systems: (polymer + thermodecomposition products forming in the course of pulse heating) and (nonvolatile liquid + dissolved gas). The latter is more convenient for analysis.

The results of the experiments on polymer–solvent systems are summarized in Fig. 4. Let us emphasize the essential result providing a foundation for the development of this investigation. We have revealed that for changes of the solution composition from a pure solvent to a polymer melt the characteristic signal of boiling-up retains the confinement in time and

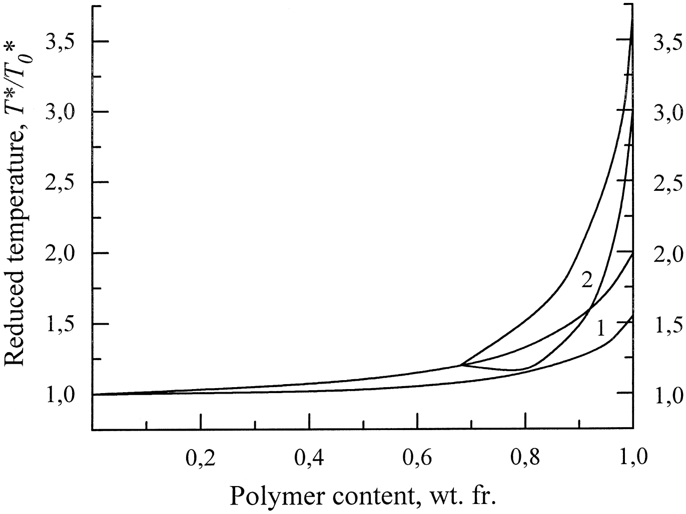

Fig. 4. Generalization of the results on spontaneous boiling-up temperature for polymer–solvent systems reduced to that of the solvent vs polymer weight fraction. The regions characteristic for standard solvents (1) and for dissolved CO_2 (2) are shown. The values of $T_0^*(p=1$ MPa) vary from 277 K for carbon dioxide to 689 K for diethylene glycol.

the reproducibility with respect to temperature, as typical of the spontaneous mechanism (see Fig. 3). The differences manifest themselves only in quantitative characteristics of this signal, $\Theta(p, t-t^*)$ [7, 8]. This indicates that at the heating rates $\dot{T} \sim (10^5$ to $10^7)$ $K \cdot s^{-1}$, the degree of superheat of both low molecular weight and high molecular weight systems is close to its limiting value, which corresponds to a high nucleation rate.

For low solvent contents $(1-c \rightarrow 0)$, the values of the temperature of spontaneous boiling-up T^* increase sharply, going deeper into the region of thermal instability of the components. This is accompanied by enhancement of the $T^*(\dot{T})$ and $p_c^*(\dot{T})$ dependences (see Fig. 5), as is typical of thermally unstable compounds. The slope of these dependences is determined by the kinetics of the initial stage of thermodecomposition reaction, the composition of volatile products, and the degree of their compatibility. The latter point may prove to be important. The sensitivity of T^* values to the degree of compatibility of components was first found for polymer homologue + solvent systems [12, 13] exhibiting liquid–liquid immiscibility. In the course of heating, these solutions became metastable with respect to liquid–liquid transitions as well. In this paper we study the coexistence of these two types of metastability by the measurements of

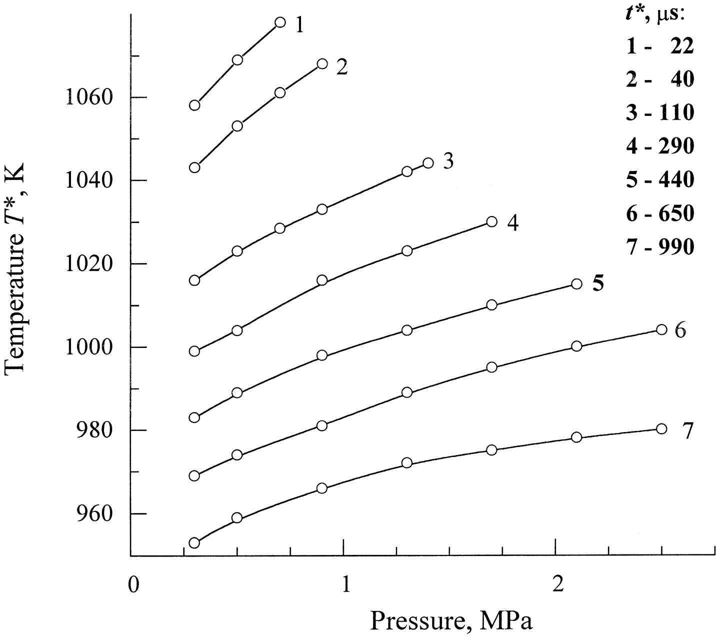

Fig. 5. Temperature of spontaneous boiling-up of oligodivinylisoprene ($\bar{M}_n = 4.5 \times 10^3$) vs pressure at different heating times (regime of approximately linear heating).

$T^*(p, \dot{T})$ for model systems (hexadecane + CO_2, tetraethylene glycol + CO_2) with systematic variations of the thermodynamic stability of the pulse-heated solution $\Delta p(p, T_v) = p(T^*) - p_s(T^*)$. Here p is the bulk phase pressure, Δp is the supersaturation with respect to the liquid–vapor binodal $p_s(T)$ for the chosen value of CO_2 content $c = c(p_v, T_v)$, and p_v and $T_v = T_s(p_v)$ denote conditions of the liquid saturation with carbon dioxide vapor. The choice of the systems is determined by the essential difference in the temperature dependence of CO_2 solubility in hexadecane and tetraethylene glycol, respectively [14]. The measurements of $T^*(\Delta p, c)$ have shown that a decrease in the stability is equivalent to an increase in CO_2 content in the initial system.

In experiments on polymer homologues with narrow molecular weight distributions $\bar{M}_w / \bar{M}_n \sim (1.01$ to $1.19)$, the aim was to elucidate the peculiarities of vapor nucleation with increasing chain length from several links to several hundreds of links. The temperature T^* and the temperature perturbation $\Theta(t - t^*)$ were measured as functions of the pressure at different heating rates.

It was found that the temperature T^* for the low molecular weight homologues increases rapidly with increasing chain length. The main increase in T^* is observed in the region $\bar{M}_n < 10^3$ or $n < 10$ links and 20 links, respectively, for polystyrene and poly(ethylene oxide). As the chain length increases further, the dependence of $T^*(\bar{M}_n)$ tends to level off [7, 8]. The limiting value of $T^*(\bar{M}_n)$ increases with increasing pressure (see Fig. 6) and with increasing heating rate. We connect the plateau in the $T^*(\bar{M}_n)$ dependence with the onset of the decomposition of macromolecules before their transition into the vapor phase. The increase in the effective critical pressure along the $T^*(\bar{M}_n)$ plateau (see Fig. 6) supports this hypothesis. According to the investigation made on model systems ($C_nH_{2n+2} + CO_2$; $n \sim 5$ to 16), this increase is caused by the formation of volatile components in the course of heating.

It is important to complement the results obtained for these series of well-defined polymers with the data for polymeric samples of different nature. For this purpose the dependence of $T^*(p, \dot{T})$ was measured for several commercial-grade polymers. The experiments have shown that the dependences of $T^*(p)$ at a given heating rate are grouped in a relatively

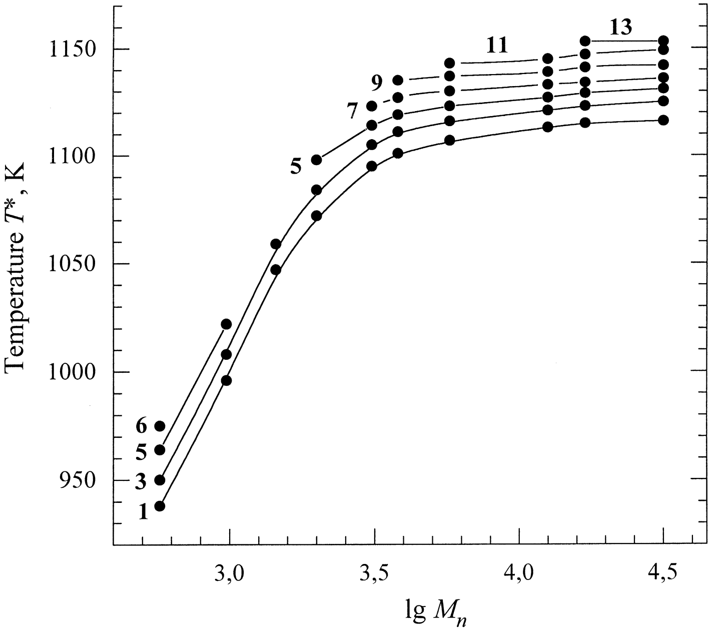

Fig. 6. Temperature of spontaneous boiling-up of poly(ethylene oxide) vs number-average molecular weight at different pressures. The indicated numbers are p values in bars. $t^* = 22$ µs.

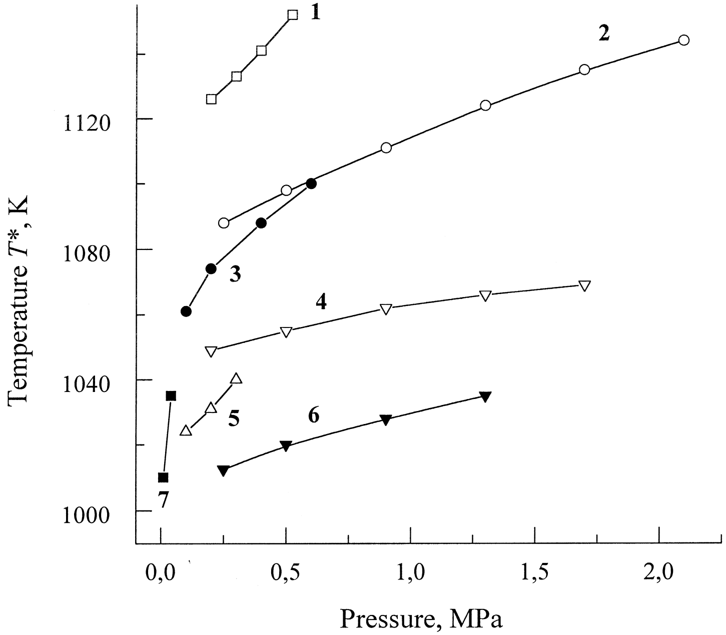

Fig. 7. Temperature of spontaneous boiling-up of polymer melts vs pressure for heating time $t^* = 110\ \mu s$. (1) Polyethylene; (2) polyurethane; (3) polypropylene; (4) polystyrene PS-35000; (5) polypropylene oxide ($\bar{M}_n = 5 \times 10^3$); (6) oligobutadiennitril (OBD-resin; $\bar{M}_n = 3.5 \times 10^3$); (7) poly(dimethylsiloxane) PDMS-10000.

narrow temperature range (see Fig. 7). For comparison, the corresponding values for low molecular weight analogues are scattered over several hundreds of degrees.

In spite of the known differences in quantitative characteristics of the thermal decomposition of polymers and in the T^* values of their low molecular weight analogues, the differences in the values of $T^*(\dot{T} = \text{const})$ for the studied polymers appear to be small. The temperature T^* of a polymeric liquid is determined mainly by the slope of the temperature dependence of the thermodecomposition process under the temperature and time conditions characteristic of our experiments; the dependence of T^* on the thermodynamical properties of a monomeric link is weak. Evidently, a considerable decrease in the characteristic time of the thermal decomposition with increasing temperature sets a practical limit on the upper value of $T^*(p, \bar{M}_n)$ for a polymer that can be reached experimentally.

The decrease in the heating rate of a polymer has proved to lead to similar effects on the characteristics of boiling-up as the addition of a volatile component to the system. The qualitative similarity of the dependences $T^*(p, \dot{T})$ for a polymer and $T^*(p, c;\ \dot{T} = \text{const})$ for a model solution (see Fig. 8) suggests using the results obtained for boiling-up of ordinary solutions for a description of the nucleation of the vapor phase in polymeric liquids. Taking into account the difficulties of a quantitative description of the decomposition process under the temperature and time conditions of our experiments, it has proved possible to model the boiling-up characteristics $T^*(\dot{T})$ of a polymer by introducing a certain quantity of a volatile additive into the melt. The use of carbon dioxide vapor for this purpose appears to be convenient, since the CO_2 content can be controlled precisely in the course of a experiment by changing the vapor pressure or the solution temperature. We have revealed that a quite low CO_2 content (~ 0.01 weight fraction) may lead to the same reduction in the T^* value of a polymer as that caused by an order of magnitude decrease in $\dot{T}$. The low value of this content allows us to assume that in our experiments a polymer mainly retains its structure at the moment of spontaneous boiling-up. Therefore, the temperature $T^*(t^*)$ for a polymeric liquid may indeed be regarded as its individual characteristic.

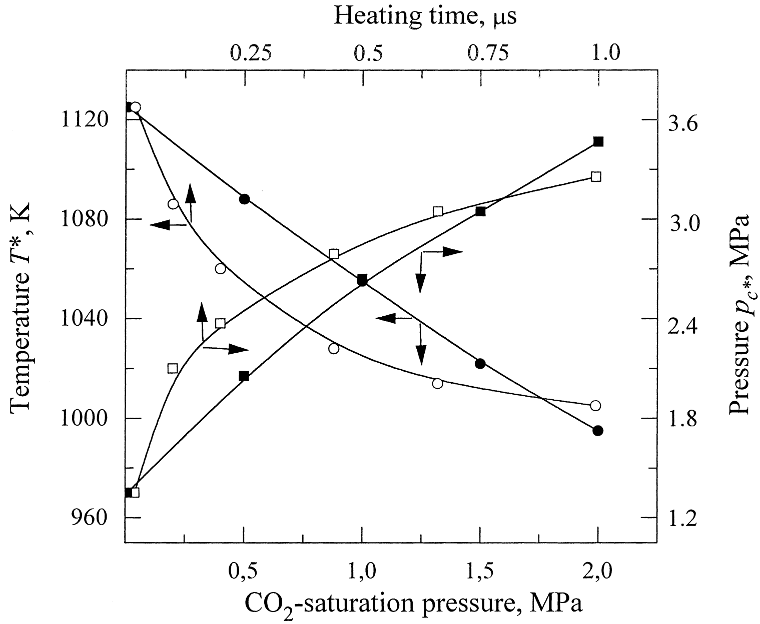

Fig. 8. Temperature of spontaneous boiling-up and effective critical pressure of poly(ethylene oxide) PEO-35000 vs CO_2-saturation pressure (filled circles) and heating time (open circles).

To clarify the relation between the phenomenon of spontaneous boiling-up of a polymeric liquid and the process of its thermal decomposition, we performed the experiments employing systematic changes of the heating profile in the region of thermal instability of a substance. The value of T^* proved to be sensitive to the change in the heating function form (function of the current $I(t)$ through the probe R_T, where $T^* = T^*[P(t)]$, $P = I^2 R_T$, $R_T = R(T)$) in the region of $T \to T^*$.

Let us consider, in particular, the regime corresponding to a heating profile that consists of linear pieces. It provides the possibility of rapid penetration into the region of thermal instability of a substance and the detailed analysis of the behavior of the system in this region (see Fig. 9, curve 1). The limiting cases are the regimes of the linear heating and the temperature plateau $T(t > t_{\text{pl}}) \approx T_{\text{pl}}$, where $t_{\text{pl}} \sim 10\ \mu\text{s}$ is the time of uncontrollable heating from the bulk phase temperature T_0 to the selected value $T_{\text{pl}} \gg T_0$ (see Fig. 9, curve 3). The latter regime is of interest, since it allows the creation of nearly isothermal conditions and the determination of the

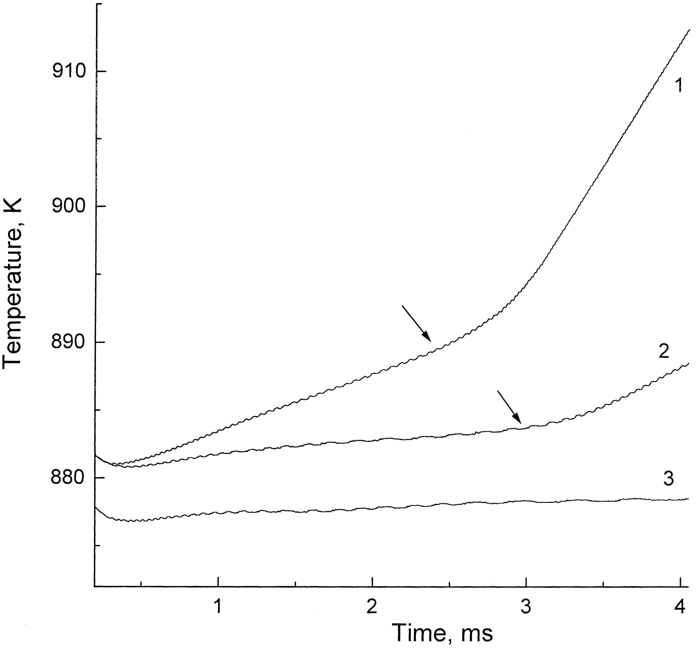

Fig. 9. Characteristic heating curves in the linear-pieces regime (curve 1) and plateau regime (2 and 3). The arrows show the point of oligomer boiling-up. The initial part of the heating curve (relatively rapid heating) is not shown.

mean lifetime of a substance $\bar{t} = \bar{t}(T_{\mathrm{pl}})$ before its decomposition (boiling-up) at a given probe temperature T_{pl} (see Fig. 9, curve 2). An expected increase in the slope of the dependence $\bar{t}(T_{\mathrm{pl}})$ with increasing thermal stability of a sample has been revealed.

Characteristic results of the T^* measurements values for a polymer corresponding to different heating profiles are given in Fig. 10. The changes in the probe temperature in the time interval preceding the boiling-up are shown by the dashed lines. The boiling-up points for heating profiles of the same type are connected by the solid lines. The increase in the spontaneous boiling-up temperature with increasing heating rate in the region $T > T_{\mathrm{d}}$, where T_{d} is the effective temperature of thermal decomposition onset at a given heating rate (see, e.g., Ref. 15), may be written as follows

$$T^*(0) - T^*(t^*) = \left[\frac{\alpha}{t^* - t_{\mathrm{d}}} \int_{t_{\mathrm{d}}}^{t^*} (T^* - T_{\mathrm{d}})^{\beta}\, dt \right]^{1/\beta}$$

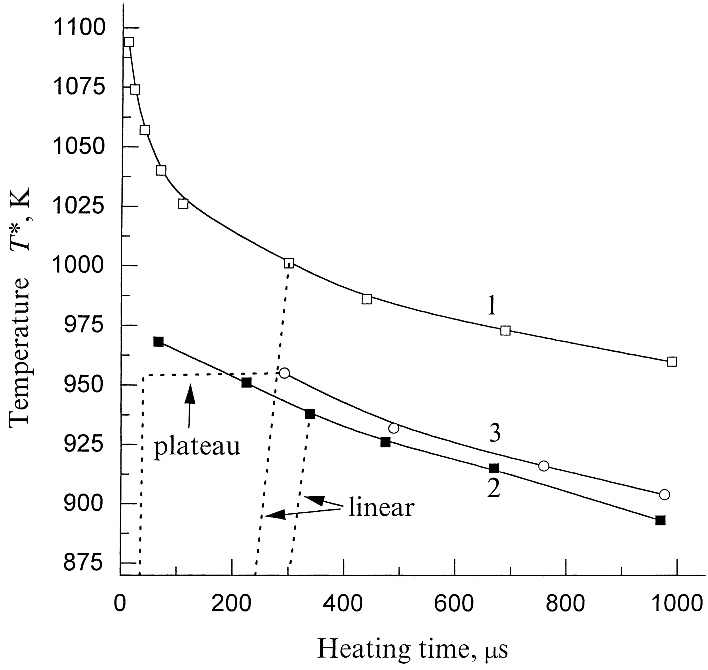

Fig. 10. Temperature of spontaneous boiling-up of OBD-resin (points 1 and 3) and CO_2 solution (~ 0.01 weight fraction) in this resin (point 2) vs heating time for two heating regimes: the linear regime (1, 2) and the plateau (3). Dashed lines show the heating profiles.

where $T^*(0) = T^*(t^* \to 0)$, $0 < \beta < 1$. Further studies are required to determine the quantitative parameters α and β of this relation.

The set of experimental results obtained in our experiments on systems of different nature gives the basis for the following conclusions. The spontaneous nucleation of vapor phase in polymeric liquids at the rapid heating is a reproducible process which accompanies the initial stage of the thermal decomposition of a system. Its characteristic time is much shorter than that of chemical reactions proceeding under these conditions. The reproducibility of T^* values at the given values of $p, \dot{T}$ implies the reproducibility of relaxation processes preceding a macroscopic phase transition as well as the steepness of their temperature dependence.

4. CONCLUSIONS

The high-temperature part of the liquid–vapor phase diagram of substances with different molecular chain lengths has been investigated experimentally. A phenomenon of the spontaneous boiling-up of a polymeric liquid marked by a characteristic perturbation of the time dependence of the heat flux has been revealed. It is shown that this phenomenon is a reproducible relaxation process in an essentially thermally unstable system, which accompanies the initial stage of its thermal decomposition.

The set of the experimental data $T^*(p, c, \dot{T}, \bar{M}_n)$ agrees with the prediction of the model of rapid phase transition in pulse-heated polymers [16]. The model allows for the process of thermal decomposition, which is responsible for the very possibility of the polymer boiling-up. It describes the changes in the spinodal temperature (taken as an approximation for the T^* value of a polymer) and of the critical-point coordinates caused by changes in the process conditions, the chain length, and, the thermal stability of macromolecules. The combined analysis of the model and experiments will help to elucidate the picture of a phase transition in thermally unstable systems and to generalize the results to a wide class of polymeric compounds.

5. ACKNOWLEDGMENTS

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