STUDY OF SUPERHEATED STATES OF POLYMERIC AND POLYMERIZING LIQUIDS

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The method of impulsive heating of a wire probe is used to study the high-temperature boundary of stability of the condensed state of high-molecular-weight compounds. Measurements are made of the temperatures to which several polymeric liquids can be superheated. The liquids differ in molecular weight. Similar measurements were obtained for polymerizing systems. The effect of dissolved carbon dioxide on the parameters characterizing fluctuation boiling of the system was examined.

The use of high-molecular-weight compounds in intensive thermal processes makes it necessary to study their properties under conditions of rapid heating. It is important to determine the high-temperature boundary of stability of the condensed state and to establish its relationship with the properties of the substance and the process parameters. It has been found experimentally that high-molecular-weight compounds (HMC) exist briefly at temperatures several hundred degrees greater than the equilibrium boiling point T_s (or the thermal degradation temperature T_d) [1, 2]. This is an indication of the existence of a wide range of superheated states in the coordinates p–T. By increasing the heating rate, researchers have been able to significantly alleviate the effect of thermal degradation — which disturbs the initial composition of the system — on the degree of superheating.

At normal temperatures, a polymer system can remain within the metastable region for long periods of time. Superheated states are short-lived, which to a certain extent dictates the method of study that must be chosen. Given identical external conditions, a polymer can be both nonequilibrium and metastable according to several indicators. In this case, there is a certain relaxation-time hierarchy [3]. We will assume that a well-established superheated state [4] corresponds to the inequality

$$\tau_i < \tau_x < \tau_d, \tag{1}$$

where τ_i is the relaxation time of the i-th species; τ_x is the time during which superheating is established; τ_d is the characteristic time of thermal degradation.

Discussed below are the results of tests involving measurement of the temperature corresponding to the attainable superheating T_x of HMCs of different types (T_x is the temperature corresponding to intensive fluctuation boiling of the system). We used the method of impulsively heating a substance on the surface of a wire probe [5, 6]. This technique was developed to study the kinetics of the fluctuation boiling of low-molecular-weight liquids and was subsequently used for oligomers [1], dilute polymer solutions [7], and polymerizing systems [2]. The characteristic heating rate was $5 \cdot 10^5 - 5 \cdot 10^7$ K/sec and the superheated volume was on the order of 10^{-4} mm^3. The total volume of the substance was 0.5-3 cm^3. Pressure was changed from atmospheric to a certain limiting value p_ℓ. No signal-response from boiling was obtained above this value.

We studied the following substances: molten polyethylene glycol (PEG), with a molecular weight ranging from the monomer unit to $M \simeq 2 \cdot 10^6$; polydimethylsiloxane rubber SRTN, with $M \simeq (5-6) \cdot 10^4$; polymethylmethacrylate (PMMA); an epoxy composition based on EDT-10. The substances were studied during polymerization. We also studied solutions of carbon dioxide in simple polyethers (laproles) with $M = 5 \cdot 10^2 - 3.5 \cdot 10^3$, in PEG with $M \le 1 \cdot 10^3$, and in SRTN. Studying the effect of a low-molecular-weight addition on the superheating of HMCs is important in connection with the problem of removing volatile products from molten polymers. It is also important in relation to the problem of constructing a theory of un-
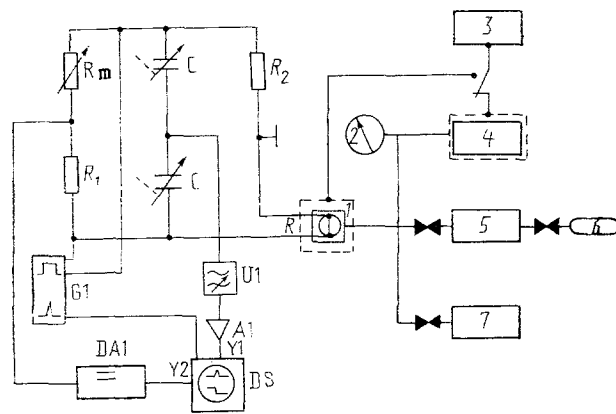

Fig. 1. Block diagram of the unit. Measuring device: G1) voltage-pulse generator; R) wire heater; R_m) resistance box R4830/1; U1) HF filter; A1) broad-band amplifier; DA1) comparator; DS) dual-beam oscillograph S9-8. Gas-saturation system: 1) thermostatted pressure block; 2) manometer; 3) temperature regulator VRT-1; 4) weighing device; 5) filter-desiccator; 6) cylinder with CO_2; 7) backing pump.

steady heat and mass transfer in rheologically complex systems [8].

The possibilities of using well-known theoretical methods [5, 6] to evaluate the super-heating of an HMC are quite limited. This is connected with the "multicomponent" character of the response of the system to rapid heating. During such heating, the system may generate signals as a result of nucleation, thermal degradation, and stratification.

The method of impulsive heating makes it possible to conduct tests within a broad range of values of the important variables (p, c, τ). Measurement frequency is satisfactorily high. A key aspect of the method is separation of the useful signal from the background caused by uniform heating. The signal has the form of a characteristic perturbation on the curve describing the dependence of the resistance of the heater on time. We used a platinum wire 20 μm in diameter and 1-2.5 cm in length as the heater and low-inertia temperature sensor. In the tests, we determined the temperature of the heater at the moment boiling began. After a correction was made for radial and end effects, we took this temperature as the temperature of the boundary layer of liquid. The error of the temperature determination was 0.7% T*, K. The correction was 0.5-3.5% of $(T_* - T_0)$ and depended on the duration of the pulse and the length of the heater.

Figure 1 shows a block diagram of the unit. We will briefly discuss the principle of operation of the measurement device. The voltage imbalance on the bridge was the recorded equivalent of the change in resistance. The instrument which analyzed the signal contained two channels which worked in parallel. The first channel separated the useful signal and consisted of an HF-filter U1 and a broad-band amplifier A1. The filter consisted of the capacitive branch of a bridge (C—C) composed of a set of variable capacitors and transformers on a line with a Z-type electromagnetic coupling (1:16) [9]. To maximize separation of the useful signal, the parameters of the filter were set within the range 5-500 kHz. Such a filter design has several advantages over the ARC filters used previously [1, 2, 5, 6]. The second channel of the instrument consisted of a branch of an R_1—R_m bridge and a DA1 comparator and was used to determine the resistance (and temperature) at a given moment of time. In the event of zero imbalance on the bridge, the comparator produces a marker in the form of a voltage drop. The moment of imbalancing of the bridge coincides with the moment of the onset of boiling, thanks to the presence of resistance box R_m.

The system used to monitor gas saturation is shown schematically in Fig. 1. The solutions were prepared by saturation of the liquid with vaporous CO_2 through the free surface until the equilibrium concentration was established for the specified p and T. The kinetics of the saturation process were followed by periodically measuring the value of T_* of the solution. Cessation of changes in T_* over time and over the height of the liquid column denoted establishment of chemical equilibrium between the phases. To displace the vapor phase from the measurement volume and conduct tests to determine T_* for different pressures, we made the
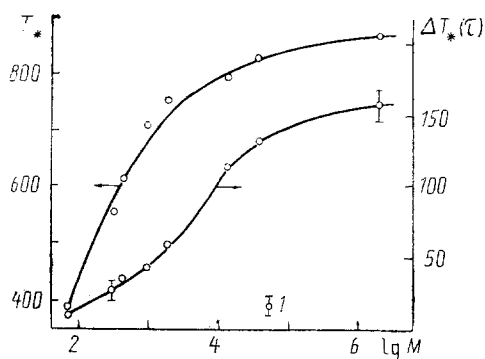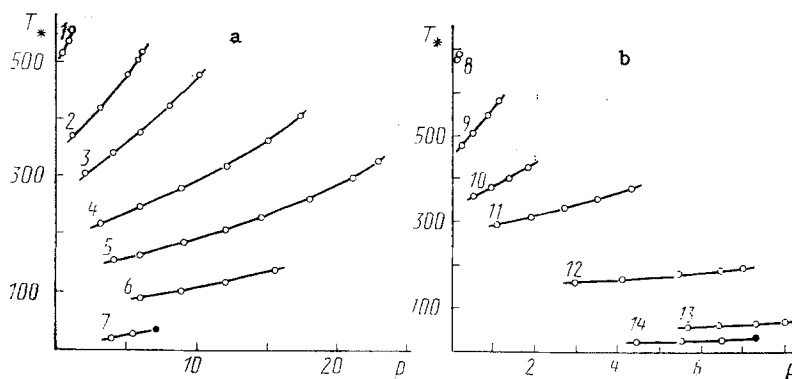
Fig. 2

Fig. 3

Fig. 2. Maximum superheating T_* (°C) of PEG at $\tau = 50$ μsec and ΔT_* (τ, μsec) = T^* ($\tau = 20$) $- T_*$ ($\tau = 800$) with different molecular weights; $p = 0.6$ MPa. Point 1) the value of $\Delta T^*(\tau)$ for SRTN, $p = 0.2$ MPa. The arrows denote the confidence interval in the series of tests.

Fig. 3. Dependence of T^* (°C) of solutions of CO_2 in laprole L-502 (a) and SRTN (b) on pressure (MPa): 1) $c = 0$; 2) 5.5 mass %; 3) 9; 4) 15; 5) 22; 6) 34; 7) 100; 8) 0; 9) 1; 10) 2; 11) 5; 12) 12; 13) 27; 14) 100. Dark point represents the critical point of CO_2; $\tau = 500$ μsec.

bottom of the mixing chamber movable. The concentration of dissolved carbon dioxide was determined in a parallel test by means of a device which worked on the "balance-rod principle" [10]. The standard deviation of the measurements for a relative scale sensitivity on the order of 10^3 was 5%.

Let us discuss the test results in Figs. 2-4 in succession. The properties of a polymer — including its maximum superheat for given external conditions — are determined mainly by its structural properties, average molecular weight, and the molecular-weight distribution (MWD). The effect of pressure and pulse duration of T_* was studied using a homologous PEG series as an example. The initial temperature was 20-40 K greater than the melting point of the substance. We chose PEG as the base system due to its narrow MWD. This allowed us to assume that the change in T_* within the series is determined only by the change in M. The relation $T_*(M)$ (see Fig. 2) is of the usual nature for the corresponding relation for the temperatures corresponding to phase transformation or the structural change into a polymer. However, given the same change in the argument, the scale of the change in T_* is an order of magnitude greater. With an increase in pressure, the curve $T_*(M)$ shifts in the direction of higher temperatures by an amount which averages 3-4 K/0.1 MPa. It is logical to connect the presence of the steep section of the curve in the low-molecular region with an increase in the work done in the formation of the critical bubble. This work is reduced due to a reduction in the vapor pressure of the polymer with an increase in M. The

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natural tendency for T_* to reach the saturation level can be judged from the stabilization of the properties which determine the maximum superheat. Also important (in addition to vapor pressure) are the kinetics of accumulation and degree of fragmentation of thermal degradation products in the heated layer and surface tension at the given temperature. The effect of thermal degradation on parameters characterizing fluctuation boiling increases with an increase in M. This is manifest in steepening of the relation $T_*(\tau)$* (Fig. 2) and the extreme character of the relation $p_\ell(M)$. The minimum value of limiting pressure $p_\ell \leq$ 0.8 MPa lies within the interval $M \sim (2\text{-}7) \cdot 10^3$. The monotonic reduction in p_ℓ — taken as the critical pressure of a thermally unstable substance [1] — is consistent with the overall change in p_c within the homologous series. The increase in p_ℓ at $M \geq 7 \cdot 10^3$ is similar to the change in the p_c of the substance when the low-molecular component is dissolved in it. It can be assumed that within the interval $M \sim (2\text{-}7) \cdot 10^3$ there is a unique change in the kinetics of relaxation of the polymer. The second inequality in relation (1) is violated. Here, τ_d is the time required for the accumulation of a "critical mass" of low-molecular products in the heated layer at the specified heating rate. In practice, this limits the possibility of observing a well-defined superheated state in PEG with a value of M that is not excessively small. The likelihood of the realization of such a state is greater for thermally stable substances. For example, in the case of SRTN, the indications of thermal degradation are an order of magnitude less intense (see Fig. 2).

To explain the aspects of boiling that can be attributed to the introduction of a low-molecular addition into HMC, we conducted a series of tests with solutions of carbon dioxide in different oligomers. Some of the results reflecting the essence of the problems are shown in Fig. 3 (also see [2]). Let us outline the general features characteristic of the systems we studied. When carbon dioxide is dissolved, the values of T_* and $\Delta T_*(\tau)$ decline more rapidly than they would in accordance with an additive law. The curvature of these characteristics decreases with an increase in concentration. The slope of the lines describing maximum superheating $T_*(p)$ change monotonically within the interval of the corresponding values for the pure components. As a result of an increase in p_ℓ, there is an appreciable broadening of the region in which two-phase equilibrium (quasiequilibrium) states exist. The uniformity of the conditions under which fluctuation boiling is manifest in the given systems suggest that, qualitatively speaking, the dependences of T_*, ΔT_*, and p_ℓ on the concentration of the addition are universal for concentrated solutions of polymers.

Let us discuss some possible reasons for the large perturbation of T_* with dissolution of the gas. We will examine a two-component system in the coordinates p–c–T. The solubility of the gas decreases with an increase in T. For example, a change in temperature from 25 to 100°C leads to a deterioration in the solubility of carbon dioxide in SRTN. Here, solubility decreases by a factor of approximately 2.5. Thus, the heated system undergoes a dual supersaturation — with respect to both temperature and composition. Also, at p = const, the steepest section of $T_s(c)$ corresponds to the region of low concentrations. In contrast to simple liquids [12], no unambiguous relationship exists between the binodal $T_s(p)$ and the line of maximum superheating in the case of solutions. Nevertheless, it may be that the natural restriction on the width of the superheated region "constrains" the behavior of the relations $T_*(c)$ and $T_s(c)$ — they change in a similar manner. Within this context, it is useful to refer to the results obtained in [13] from the superheating of aqueous solutions of gas. Here, the shift $\Delta T_*(c) = T_*(0) - T_*(c)$ with a small value of c is an order less than the corresponding shift ΔT_s. At first glance, this conflicts with the approach described above. However, such behavior is a reflection of the nonmonotonic character of the solubility isobar. The increase in the solubility of the gas in water near the temperature T_* reduces supersaturation in terms of concentration.

In order to explore this topic more thoroughly, it is important to know the phase state of the initial solution, the character of its change with temperature, and the composition of the nucleated bubble. A sharp reduction in T_* with the addition of the second component was seen for systems with a lower critical dissolution temperature. This applies to the system water–diethyl ether [6] and, with certain stipulations, to the system zinc hexane-polystyrene [14]. Carbon dioxide can be found in the oligomer both in the form of individual molecules and in the form of clusters. Indirect data provide evidence of the condensation of CO_2 in the polymer matrix (see [15], for example). The dissolution of CO_2 increases the mobility of the molecular structures. In particular, the glass point of the polymer —

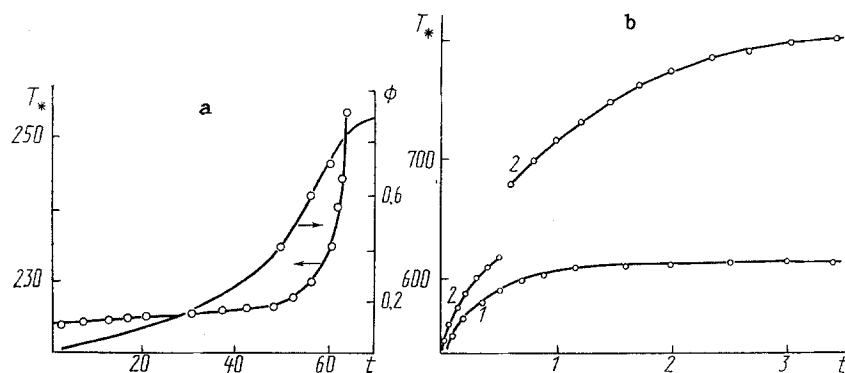*This subject was explored in detail by the authors of [11].

Fig. 4.   Change in T_* (°C) during the polymerization of MMA
(a) (t, min, $T_0 = 65$°C) and the curing of EDT-10 (b) (t, h):
$T_0 = 90$°C (curve 1) and $T_0 = 140$°C (curve 2); $\tau = 70$ μsec.

determined by segmental mobility — may decrease by 100° in the case of saturation with vapor-
ous CO_2 [16]. The decrease in solubility and viscosity which accompanies heating promotes
microphase stratification of the system into regions which consist mainly of an individual
component. The presence of CO_2 also facilitates evaporation of the oligomer molecules or
their fragments. The assumption that the contents of a bubble are 100% CO_2 is unlikely
to be valid, since boiling begins at temperatures and pressures which are supercritical
for CO_2.

The data we have obtained on the superheating of solutions allow us to present the follow-
ing simplified example, which clearly illustrates the contribution of thermal degradation
to the dependence of T_* for a HMC on heating time. Extrapolating $T_*(\tau)$ to a zero value
of τ, we will determine the maximum superheat in an approximation assuming that the substance
undergoes nondegrading evaporation. We will suppose that only one product of thermal degra-
dation — carbon dioxide — is formed during heating. Then the temperature change $\Delta T_*(\tau) =$
$T_*(0) - T_*(\tau)$ can be correlated with the change in T_* due to dissolution of a certain amount
of CO_2. For example, for polypropylene glycol with $M = 10^3$, $\Delta T_*(\tau)$ is equivalent to the
dissolution of 1% CO_2 at $\tau = 40$ μsec and 4% CO_2 at $\tau = 400$ μsec. For SRTN, the correspond-
ing values are 0.01 and 0.03%. The relation $T_*[J(\tau)]$ of the liquids — being 2-3 K per order
of change in τ for simple liquids [6] — was taken into account with the assumption that,
in the given thermodynamic coordinates, this relation is the same for different substances.

The appreciable effect of dissolved CO_2 on T_* for HMCs makes it necessary to critically
examine the use of gas as a means of transferring pressure in tests involving the superheat-
ing of polymer systems. In connection with this, let us examine data on the boiling of
solutions of polystyrene (PS) in toluene with an isothermal pressure release [17]. The
characteristic time of the experiment was 0.3 sec. The temperature in the thermostat T_0
ranged from 150 to 180°C. The investigated concentration interval was 40-60 mass %. The
moment at which vapor began to form in the solution t_* was determined by the method of light-
scattering. It was assumed that the pressure $p_* = p(t = t_*)$ corresponded to the maximum
supersaturation of the soluton at the given T_0, c, corresponding to the homogeneous mechanism
of nucleation. Such an interpretation of the test results is unsubstantiated, since the
temperature T_0 turns out to be 100 K below the values of T_* for pure toluene at the same
$p = p_*$ [12]. Dissoluton of the higher-temperature component in toluene should lead to an
increase in T_* [2, 11, 14]. However, one of the reasons for the underestimation of supersatura-
tion is the use of helium to create pressure in the solution. The authors of [17] proceeded
on the basis of the assumption that the solubility of helium is negligibly low. However,
even a small amount (<1 mol. %) helium can significantly reduce the value of T_* of the
liquid [18]. The value of T_* measured by our method for toluene saturated with helium
at $T_0 = 150$°C and $p_0 = 2.85$ MPA (i.e., under the same conditions as in the tests in [17])
turned out to be 15 K lower than $T_*(p = p_0)$ for pure toluene. When supersaturation is
created under quasistatic conditions, the effect of dissolved helium may be even more sharp-
ly manifest. Thus, it is more appropriate to discuss the results in [17] from the viewpoint
of the kinetics of degasification of the system helium—toluene—PS.

The sensitivity of T_* to the molecular weight of polymer homologs and to the content
of the low-molecular component implies the possibility of a significant change in T_* during

conversion of a monomer or a moligomer to a polymer. To establish the laws governing such a change, we conducted tests involving the superheating of several reactive systems with different kinetic schemes. An analysis of the test results showed that the scale and rate of change in T_* depend mainly on the nature, quantity, and kinetics of consumption of the low-molecular component (monomer or reactive addition). Figure 4 shows results of measurement of T_* during the polymerization of methylmathacrylate (MMA) by benzoyl peroxide (0.2%) and the curing of epoxide oligomer EDT-10 by triethanolaminotitanate (TAT, 10%). The method used for working with the polymerizing systems was described in [2].

During the formation of PMMA, the system is a solution of stable macromolecules in the natural monomer. This fact makes it possible to duplicate the results of tests by measuring the T_* of PMMA solutions of different concentrations. We measured values of T_* of solutions with PMMA contents from 0 to 70%. The form of the relation $T_*(c)$ is typical of systems composed of an HMC and a low-molecular-weight substance. As T_* (c = 100%) $\simeq$ 510°C, we took the temperature corresponding to the maximum superheating of PMMA with M $\simeq$ 10^6 measured by the method of replica vaporization [19]. Comparison of data on $T_*(t)$ and $T_*(c)$ allowed us to construct the kinetic curve for the degree of conversion of the monomer (Fig. 4a). The character of the change in Φ is typical of the copolymerization of PMMA. A signal-response stops being received after a high degree of conversion is attained.

The situation is less clear in regard to the curing of EDT-10 (Fig. 4b). Here, we are dealing with a two-stage process which includes five concurrent-consecutive reactions [20]. Two sections can be discerned on the graph $T_*(t)$. On the first, there is a monotonic increase in T_* with a decrease in the derivative $(\partial T_*/\partial t)_\tau$. The character of this curve can be attributed to two factors: a decrease in the content of the relatively low-boiling component TAT and an increase in the degree of conversion of the epoxy groups (reaction of the groups with TAT hydroxyl groups), as well as with slowing of the reaction as the degree of transformation increases. The duration of this stage decreases with an increase in the temperature of the medium and the initial content of TAT. The signal-response recorded in the test was due to the beginning of boiling of the viscous fluid. The course of the process on the second, shallower section is determined to a significant extent by the reaction temperature. At T_0 = 80-90°C, the rate of increase T_* is decreased by one order. We believe that the reason for such an abrupt slowing of the reaction is suppression of curing by the glass transition when a certain degree of conversion is reached. The vitrification temperature of the polymer found by a thermomechanical method lies within the interval 90-110°C.

At T_0 = 130-140°C, the amplitude of the response-signal (reflecting the intensity of the boiling process) decreases monotonically from values on the order of 2 V to the noise level, i.e., 0.1 V. This occurs by roughly the thirtieth minute and is evidence of the difficulty of the formation and growth of fluctuation bubbles in a highly viscous cross-linked substance. This conclusion was supported by visual observations of the surface of reserve heaters connected during this stage of the process. At the same time, another signal with an amplitude of 2-3 V also appears — but at a higher temperature. The jump T_* separating the two sections of the curve is accompanied by a jump in signal amplitude, which indicates a shift in the nature of the response. The highly elastic properties of the polymerizing system become dominant around the jump. The response generated as a result of an abrupt decrease in the heat-transfer coefficient is connected with disturbance of the contact between the heater and the substance during heating. An increase in frequency and the effective stiffness of the polymer network is accompanied by a monotonic increase in T_* — which in the given case is the maximum temperature at which the integrity of the contact is preserved. As a result of irreversible destruction of the boundary at $t \geq 3$ h, the regime in which one heater was used several times — which was allowable for the first stage of the reaction and part of the second stage — was replaced by a single-use regime. Due to low thermal stability, products of thermal degradation accumulate in the hot layer. This circumstance places a limitation on the frequency of repetition of the heating pulses and complicates detailed study of the neighborhood of the jump T_*.

The present study has yielded empirical data on the least-studied type of metastable state — the superheated state of polymer systems. The character of the relations found to express the dependence of maximum superheat on pressure, heating rate, and molecular weight is typical of relaxational transformations to the polymer state. It was found that T_* is highly sensitive to low-molecular-weight additions. We followed the dynamics of the change in T_* during polymerization of a monomer and curing of an oligomer. The results

have been analyzed mainly on the basis of indirect proofs, in view of the lack of an established method of interpretation. A more detailed discussion of the findings will require the use of additional empirical techniques and broadening of the range of systems subjected to investigation.

NOTATION

T, temperature; T_*, temperature corresponding to the attainable superheating; T_S, equilibrium boiling point; T_0, temperature of environment; p, pressure; p_ℓ, limiting pressure; p_c, critical pressure; M, molecular weight; τ, time for substance to heat from T_0 to T_*; c, concentration of dissolved substance; J, nucleation frequency; Φ, degree of conversion; t, actual time; t_*, moment at which vapor begins to form.

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