Bubble Nucleation in Polymeric Liquids Under Shock Processes[1]

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ABSTRACT

The paper studies the phenomenon of spontaneous boiling-up of polymeric liquids on their heating at rates $\dot{T}$ up to 10^7 K/s. A model of thermal equation of state for (polymer + monomer) systems and a procedure of determination of spontaneous boiling-up temperature T^* for polymer liquids, taking into account its decomposition, are suggested. The experimental data on $T^*(\dot{T})$ for a number of polymer melts are compared with those calculated by the model.

KEY WORDS: liquid-vapor spinodal; spontaneous boiling-up; thermal decomposition; polymer melt.

1. INTRODUCTION

The problems of boiling of polymeric liquids have lately received much attention, mainly in connection with technical applications of this phenomenon [1]. We shall consider the limiting regime of boiling - spontaneous boiling-up in a limiting superheat of liquid with respect to the liquid-vapor equilibrium temperature. When specific requirements are fulfilled, this regime is observed for polymer-solvent systems experimentally by different methods [2-4]. It is convenient since the temperature of spontaneous boiling-up is not related with the details of heater design being determined by the properties of the liquid at a given pressure p. The values of $T^*(p)$ are close to the boundary of the liquid absolute instability and may serve as an evaluation from below for the liquid-vapor spinodal.

In experiments it has been found that at a relatively low weight fraction of a polymeric component ($c < 0.6$) the temperature of spontaneous boiling-up somewhat increases with increasing c. Such a result is in agreement with the prediction of the homogeneous nucleation theory for solutions with a nonvolatile component [5]. The situation becomes less predictable in the region of highly concentrated solutions ($c \to 1$). The temperature $T^*(c \to 1)$ rises abruptly going deeper into the region of thermal instability of a substance. The system composition acquires the character of a dynamic variable. As a result, there appears the dependence of T^* on the heating way. Our aim was to elucidate the peculiarities of rapid bubble nucleation in polymeric liquids, including polymer melts that do not boil without decomposition.

We used for this purpose the method of pulse heating of a substance on the surface of a wire probe [6]. A reproducible response of polymer melts similar to the signal of spontaneous boiling-up of a simple molecule liquid has been revealed at heating rates above $3 \cdot 10^5$ K/s [7,8]. The response temperature T^* depends on the pressure and the heating rate. A qualitative explanation of this experimental fact was

based on the assumption of boiling-up of thermodecomposition products forming in the process of heating. A detailed analysis of this phenomenon requires a knowledge of the thermal equation of state of a polymer. A model of such equation for polymers and polymer solutions in a monomer is given below. The liquid-vapor spinodal has been determined allowing for the decomposition of a polymeric liquid. The spinodal temperatures have been compared with the experimental data on T^*.

2. EQUATION OF SPINODAL

From the general principles of mechanics the equation for pressure may be written as follows:

$$p = 2K/3 + U/3 , \tag{1}$$

where K is the specific (per volume unit) kinetic energy of molecules, U is the virial of the system volume unit [9].

Let us consider a polymeric liquid as a system of n monomers. Part of them is connected into macromolecules forming long chains. We shall assume that the potential energy of interaction between monomers does not depend on whether they are connected into a chain or not. Polymerization decreases the degrees of freedom of a bound monomer with respect of the free one. Then the specific kinetic energy of a polymer system is written with the correction factor $(1-\varepsilon) < 1$: $K = (1-\varepsilon)3nkT/2$. We shall introduce the effective specific number of molecules N^* so that by definition

$$1-\varepsilon = N^*/n . \tag{2}$$

The virial of a system of monomers can be found from the equation of state. We shall use the van der Waals type equation of state. Then Eq. (1) may be transformed to the dimensionless form:

$$\pi = \frac{8\nu\tau}{3-\nu} - 3\nu^2 - \frac{8}{3}\varepsilon\nu\tau \ , \tag{3}$$

where $\tau = T/T_k^0$, $\pi = p/p_k^0$, $\nu = n/n_k^0$. Here $T_k^0 = 8a/27bk$, $p_k^0 = a/27b^2$, $n_k^0 = 1/3b$ are the coordinates of the thermodynamic critical point of a liquid of free ($\varepsilon = 0$) monomers. Using the condition for spinodal $(\partial\pi/\partial\nu)_\tau = 0$ we determine the position of the spinodal of a polymeric liquid in coordinates τ,π and π,υ:

$$\begin{aligned} 4\tau &= \frac{\nu(3-\nu)^2}{1-\varepsilon(1-\nu/3)^2}, \\ \frac{\pi}{\nu^2} &= 3 - \frac{2\nu}{1-\varepsilon(1-\nu/3)^2}. \end{aligned} \tag{4}$$

Here the density υ may be considered as a parameter covering the values from υ_k to 3. The melt density at the critical point υ_k is determined by the cubic equation:

$$1 = \nu_k + \varepsilon(1-\nu_k/3)^3 . \tag{5}$$

Solution of the system of Eq. (4), (5) shows that with decreasing N^* (and, consequently, $1 - \varepsilon$) the critical temperature of a polymeric liquid increases and the critical pressure, on the contrary, decreases. In the limiting case of an infinitely long chain ($\varepsilon = 1$) we have : $\tau_k = 3{,}375$, $\pi_k = 0$, $\nu_k = 0$. The spinodal of a pure polymer is located, except the vicinity of the critical point, in the region of negative pressures.

3. DETERMINATION OF THE SPONTANEOUS BOILING-UP TEMPERATURE.

To describe the pattern of boiling-up with decomposition of a polymeric liquid it is necessary to find the dependence of a number of broken bonds on the conditions of heating. Let us introduce the distribution of molecular sizes in the depolymerized system. We introduce the density of chain distribution by the number

of bonds in the chain ξ, so that the number of chains with sizes from ξ to $\xi + d\xi$ per volume unit is equal to $F(\xi)d\xi$. To calculate N^* we introduce the correlation length r along the molecule expressed in bond number. Parts of the long chain molecule separated by a distance exceeding r move independently and give a contribution to the kinetic energy as separate molecules. Then

$$N^* = \sum_{j=0}^{[s]-2} (j+1) \int_{jr}^{(j+1)r} F(\xi)d\xi + [s] \int_{([s]-1)r}^{\xi^*} F(\xi)d\xi \ , \tag{6}$$

where ξ^* is the maximum chain length, $s = \xi^*/r$, $[s]$ is the integer number closest from above to the ratio ξ^*/r.

Let us consider a homogeneous melt with a specific number of chain molecules N_0 of ξ^* bonds each. It is assumed that in the course of heating all bonds connecting monomeric elements have the same probability of being broken regardless of their position. Then using the solution of the problem on the random subdivision of intervals [10], we have obtained for the distribution function

$$F(\xi) = i(i+1)\frac{N_0}{\xi^*}\left(1 - \frac{\xi}{\xi^*}\right)^{i-1} . \tag{7}$$

where i is the number of cut points. After substituting (7) into (6) and (2) we find ε:

$$\varepsilon = 1 - \frac{1+i}{\xi^*}\sum_{j=0}^{[s]-1}(1 - j/s)^i \ . \tag{8}$$

The condition of applicability of the continuous approximation (7) is reduced to the requirement of small probability of finding two cut points to find themselves at a distance shorter then the bond length. For large values of i Eq. (8) is simplified: $\varepsilon = 1-\alpha$, where $\alpha \equiv (1+i)/\xi^*$ has the meaning of degree of depolymerization.

In the course of heating the degree of depolymerization increases owing to the thermal decomposition. The number of bonds in a volume unit will be denoted as $m = n - (1+i)\cdot N_0$, and the rate of cuts will be written as follows:

$$\frac{d}{dt} m = -m \cdot B \cdot \exp\left(-\frac{E}{kT}\right), \tag{9}$$

where E is the activation energy of bond break, B is the kinetic coefficient, t is the time. After integrating (9) we obtain for the linear regime of heating and with the initial value $i = 0$

$$\alpha = 1 - \left(1 - \frac{N_0}{n}\right) \cdot \exp\left[-\frac{B\,E}{k\,\dot{T}} \int_{W(0)}^{W(t)} \exp\left(-\frac{1}{x}\right) dx\right], \tag{10}$$

where $W(t) = kT(t)/E$, $\dot{T}$ is the heating rate.

Eq. (10) predicts an essentially nonlinear $\varepsilon(T)$ dependence at a given heating rate, see fig. 2. In the framework of the model the temperature and the moment of boiling-up of a polymeric liquid are determined by the point of intersection of the trajectory of the heating $T(t)$ with the spinodal of liquid for the current value of $\varepsilon(t)$. Figure 3 shows in the plane π-τ the boiling-up temperatures for decomposed polymer and for its solutions in a monomer obtained by solving the system of equations (4), (5), (8), (10). The model predicts a possibility of ordinary boiling-up of a polymer melt at negative pressures. The characteristic response signals observed in our experiments at the temperature $T^*(p > 0)$ apparently correspond to a certain degree of decomposition of macromolecules.

4. EXPERIMENTAL

Spontaneous boiling-up temperatures at different values of pressure and heating rate have been measured for a number of polymers (polyethylene, polystyrene, polyethylene oxide, polydimethyl siloxane) and their solutions in

solvents (diethylene glycol, ethylbenzene, toluene, carbon dioxide). We used the method of pulse heating of a thin wire probe, which ensures the controlled heating of a substance and real-time determination of its temperature. The pulse length in our experiments was from 0.01 to 1.0 ms. The time of thermal relaxation of the probe (d= 0.02 mm) is about 1 μs. The method has been recently described by us in detail [4], including this Symposium [8]. This fact enables us to come directly to the results.

Some results are presented in fig. 4. The analysis of the whole set of experimental data on $T^*(p, \dot{T})$ [7,8,11,12] shows the characteristic features of boiling-up of polymer melts: a decrease in $\dot{T}$ leads to a decrease in the values of T^*, dT^*/dp, $1/p_k$ and has proved to be equivalent to the introduction of additional volatile componenet into the system (see Fig. 8 in [8]). This experimental fact is explained by the thermal decomposition of a polymer and is in accordance with the presented model. Boiling-up, in essence, is an indicator of a certain content of volatile products of a chemical reaction. Evaluations show that this content in the course of pulse heating does not exceed 1 wt.% [7].

5. COMPARISON OF THE MODEL WITH EXPERIMENTAL DATA

It is also important to check the quantitative agreement between the model and our experimental results. It has proved to be possible if the critical temperature of a polymer is known. We evaluated this temperature on the basis of $T^*(p, \dot{T})$ data by the method described in [11]. Then, knowing the average length of a molecular chain, we found the initial value of ε and the critical temperature of monomeric fluid. These data are sufficient to determine the temperature on the spinodal $T_{sp}(\varepsilon)$ and compare it with the data on $T^*(\dot{T})$[1]. Figure 5 shows the results of calculation of $\tau(1/\dot{T}, \pi = 0)$ at different values of E in combination with experimental data

[1] When correlating the results of calculation and experiment, i.e. $T_{sp}(\varepsilon)$ and $T^*(\dot{T})$ we take into account, on the one hand, the difference in definition of these temperatures, and on the other hand, the proximity of their values on the liquid-vapor phase diagram [$T^*(1/\dot{T} \to 0) \to T_{sp}$].

extrapolated to zero pressure. In these calculations the molecular-weight distribution in the initial polymer was neglected. By selecting the average value of E (in the general case being unknown due to its dependence on T and the sample supermolecular structure) one can describe the experimental data on the boiling-up kinetics of polymers rather well. Evidently, this is facilitated by using in calculations the values of T_k obtained from the same experiment. But we do not know yet any other reliable procedure of evaluation of the critical parameters of polymers.

6. CONCLUSION

The presented model makes it possible to predict the values of spontaneous boiling-up temperatures of polymers in shock processes from the equation of spinodal and evaluate the effective macrokinetic characteristics of thermal decomposition from the best agreement between ~~in~~ the results of calculation and experiments. The binodal of a polymer melt is hardly measurable due to the long time of establishment of liquid-vapor equilibrium. Nevertheless it exists and determines the size of the vapor critical nucleus. Owing to its microscopic size the unstable equilibrium with the surrounding liquid is established relatively fast.

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FIGURE CAPTIONS

Fig. 1. Reduced temperature on the liquid-vapor spinodal for polymeric liquid versus reduced pressure and fraction of broken bonds. $K_0\{1;\ 0;\ 1\}$ and $K_1\{0.001;\ 0.999;\ 3.156\}$ are the critical points of monomer and polymer, respectively.

Fig. 2. Parameter ε versus reduced temperature and heating rate for low density polyethylene. $E = 200$ kJ/mol, $B = 4\cdot10^{11}$ s^{-1}, $\xi^* = 2200$, $s = 1$, $T_k = 1175$ [11].

Fig. 3. Reduced temperature on the liquid-vapor spinodal for polymer + monomer system versus reduced pressure. $N_0/n = 0.001$ (1); 0.1 (2); 0.5 (3); 1.0 (4). $\dot{T} = 10^7$ K/s. The remaining data are identical to those in fig. 2.

Fig. 4. Spontaneous boiling-up temperature for low-density polyethylene (LDPE, 1), poly (ethylene oxide) (PEO, 2), polydimethyl siloxane (PDMS, curves 3) versus pressure at $\dot{T} = 2\cdot10^7$ K/s (open circles) and $8\cdot10^5$ K/s (solid circles). The number-average molecular weight of the samples was $31\cdot10^3$, $17\cdot10^3$, and $562\cdot10^3$, respectively.

Fig. 5. Comparison of the calculated temperatures $\tau_{sp}[\varepsilon(1/\dot{T})]$ (curves) with the experimental data on $\tau^*(10^8/\dot{T})$ (circles). Numbers on curves show the selected values of E [kJ/mol]. $p = 0$; $B = 4\cdot10^{11}$ s^{-1}. **5a** : LDPE, $\xi^* = 2200$, $s = 1$, $N_0/n = 4{,}5\cdot10^{-4}$, $T_k^0 = 361$ K; **5b** : PEO, $\xi^* = 400$, $s = 1$, $N_0/n = 2{,}5\cdot10^{-3}$, $T_k^0 = 368$ K.

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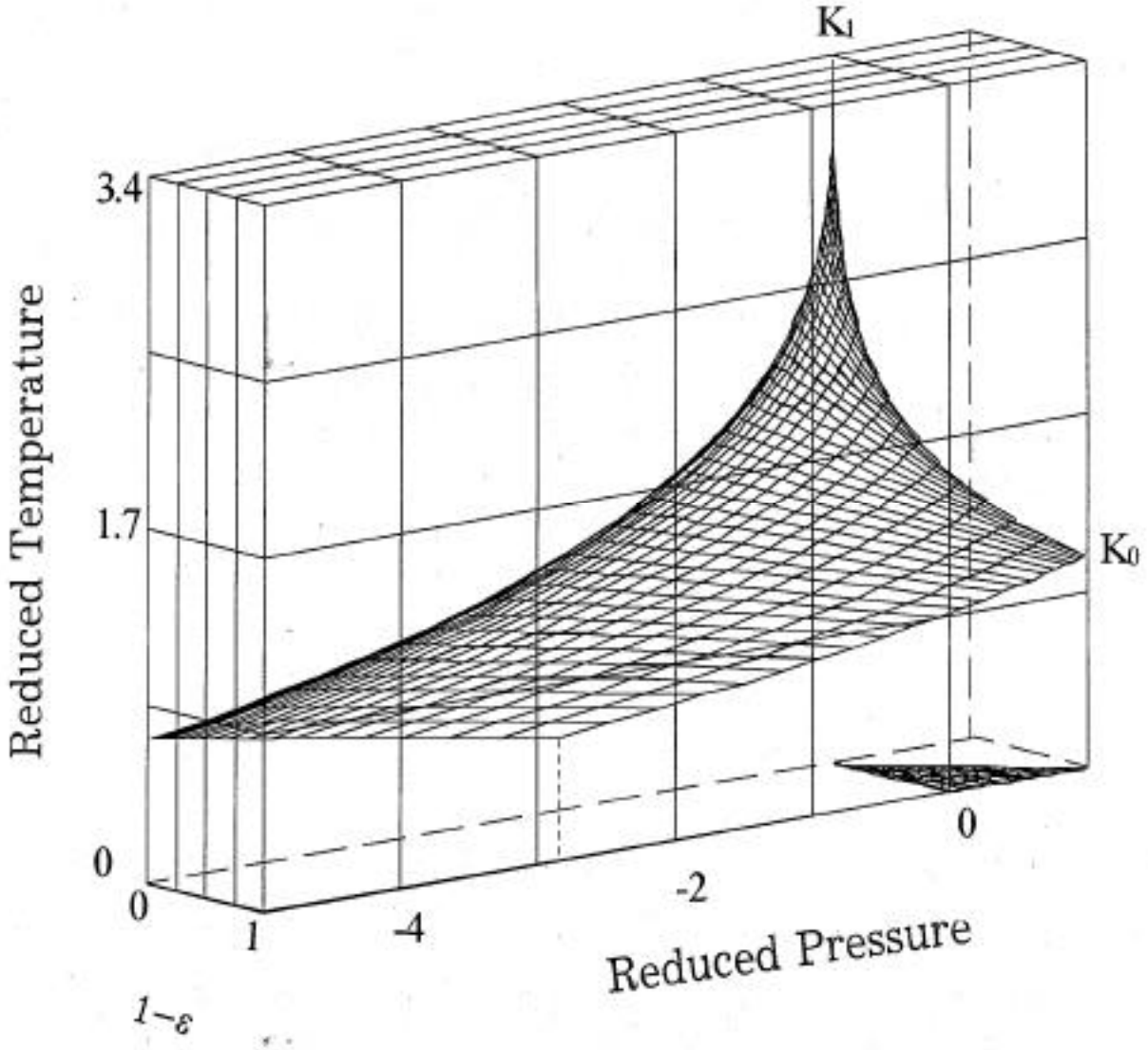
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K0
Reduced Temperature
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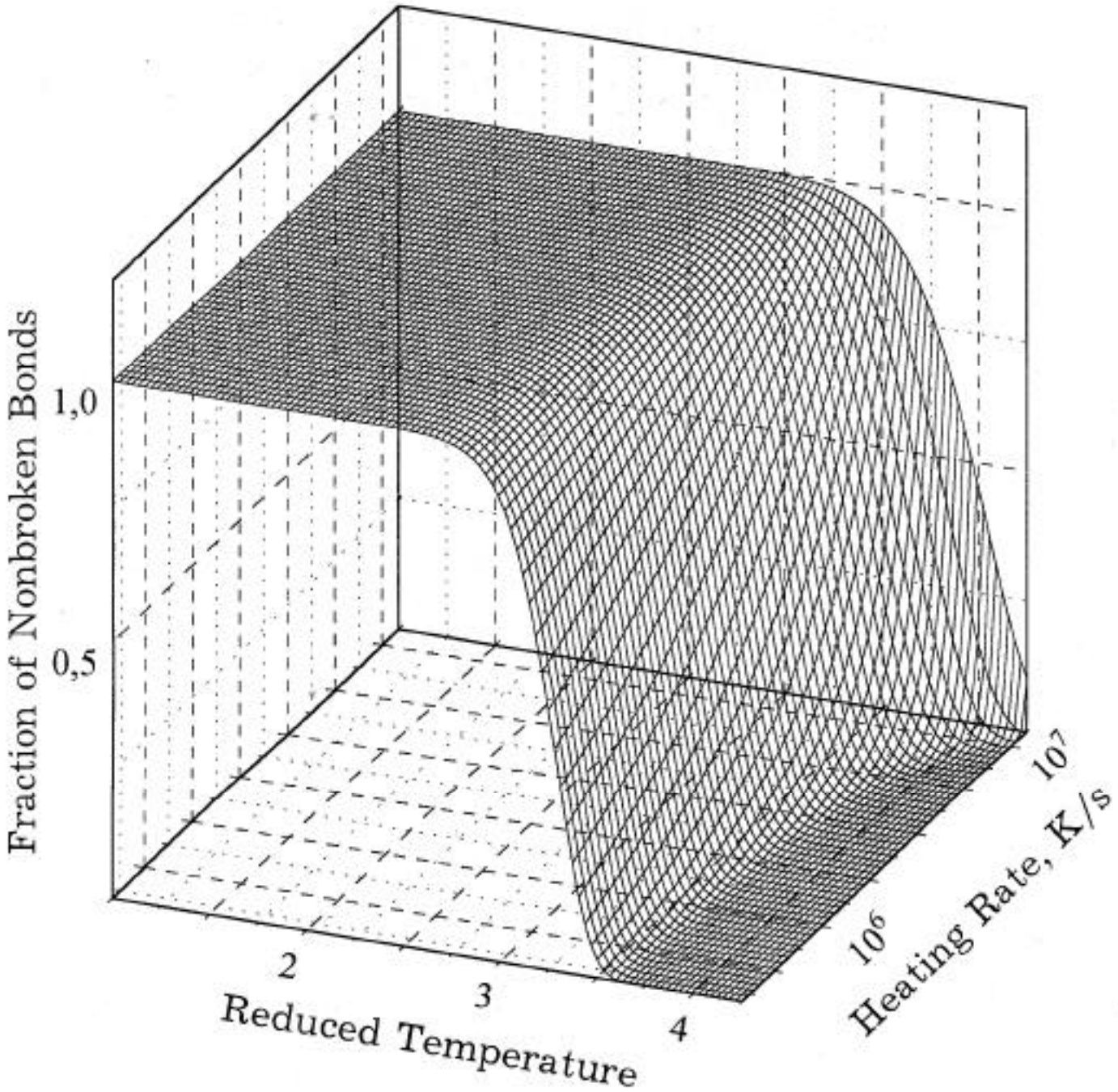
1
-4
-2
0
Reduced Pressure
1−ε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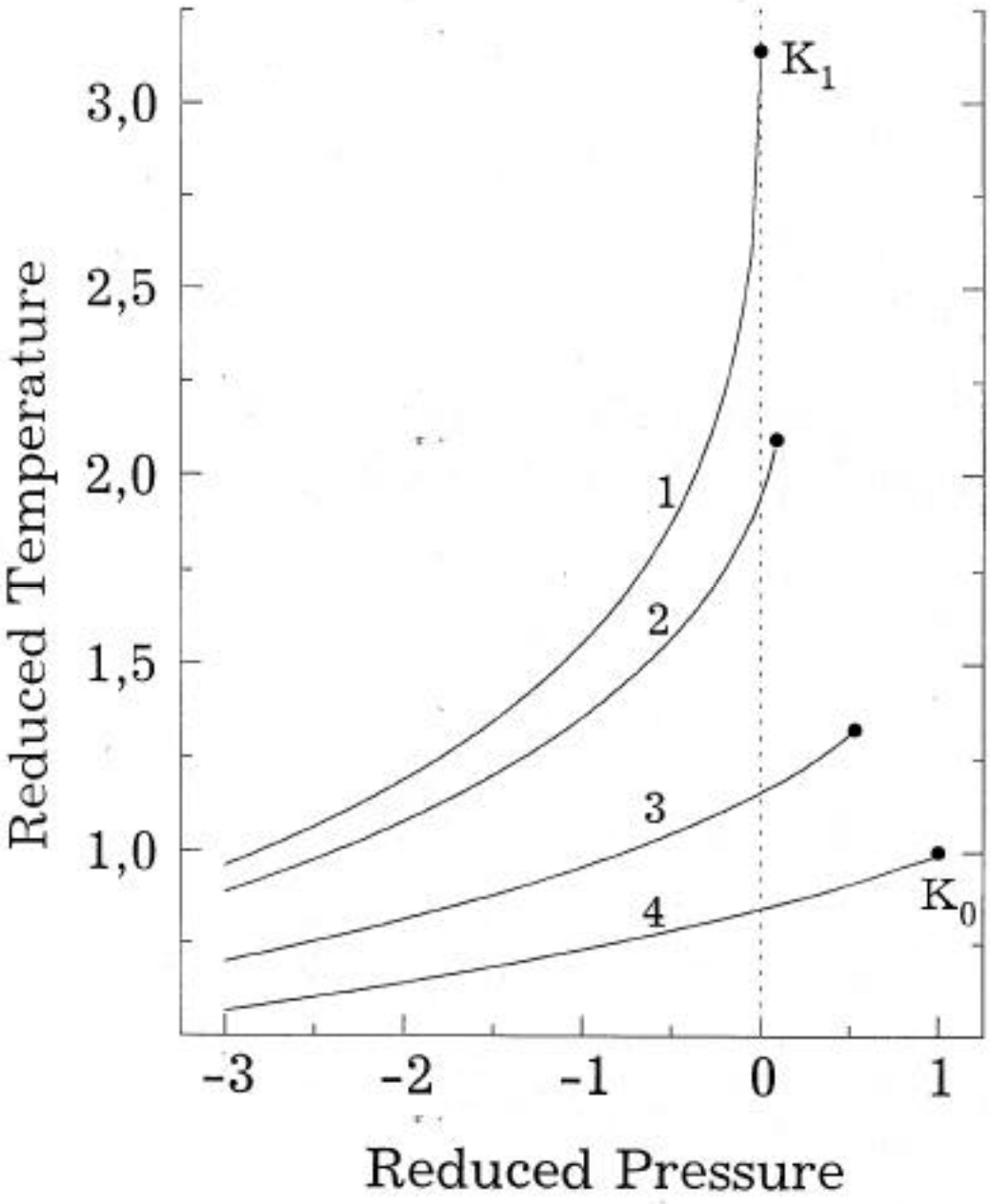
0,5
2
3
4
Reduced Temperature
10^6
10^7
Heating Rate, K/s


Reduced Temperature
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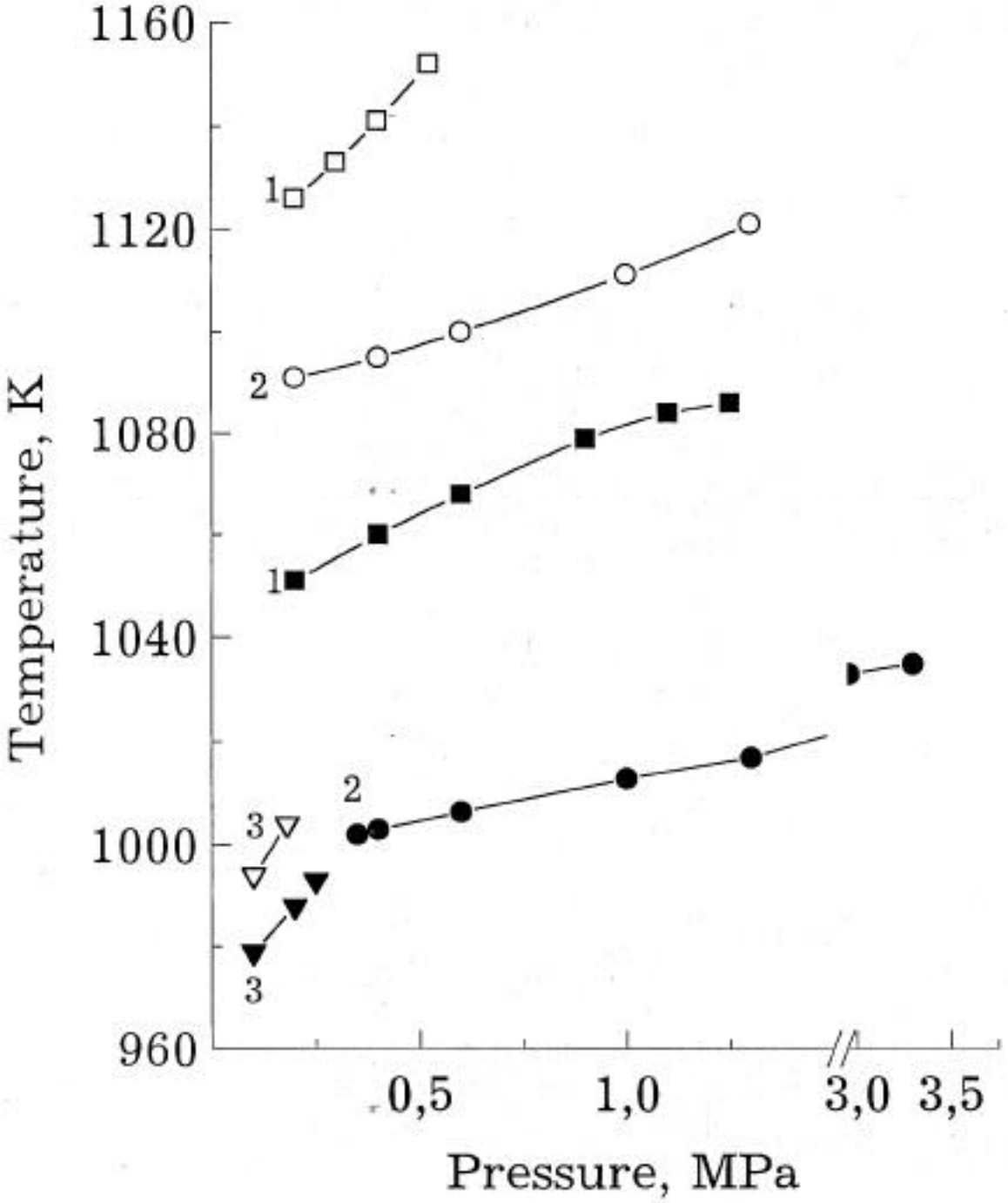
2,5
2,0
1,5
1,0
K1
K0
1
2
3
4
-3
-2
-1
0
1
Reduced Pressure


1160
1120
1080
1040
1000
960
Temperature, K
0,5
1,0
3,0
3,5
Pressure, MPa
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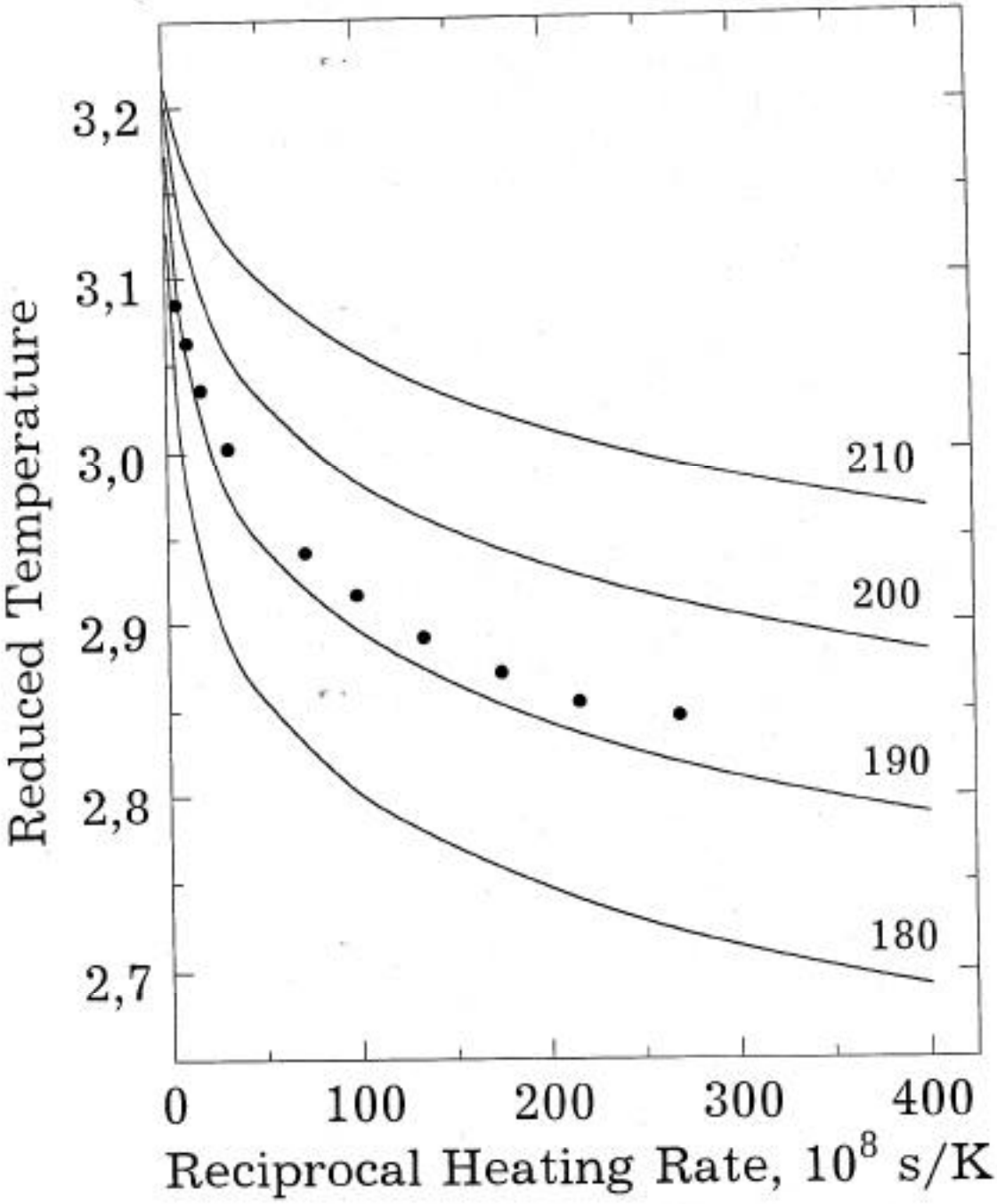
2
1
2
3
3


3,2
3,1
3,0
2,9
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Reduced Temperature
210
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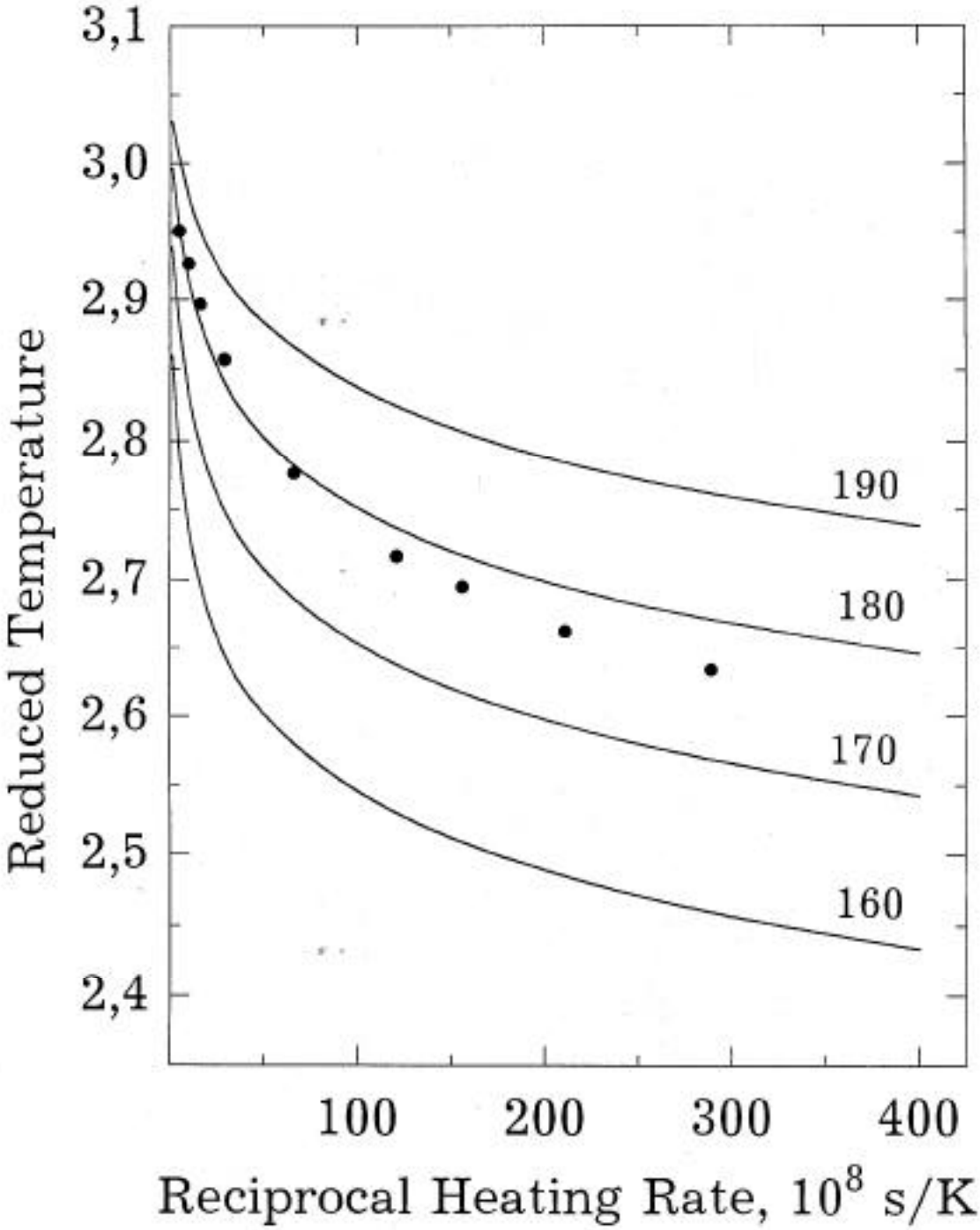
190
180
0
100
200
300
400
Reciprocal Heating Rate, 10^8 s/K


3,1
3,0
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2,5
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Reduced Temperature
190
180
170
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100
200
300
400
Reciprocal Heating Rate, 10^8 s/K