Bubble Nucleation in Polymeric Liquids Under Shock Processes[1]

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This paper studies the phenomenon of spontaneous boiling-up of polymeric liquids on heating at rates ($\dot{T}$) up to 10^7 K · s^{-1}. A model of the thermal equation of state for (polymer + monomer) systems and a procedure for determination of the spontaneous boiling-up temperature T^* for polymeric liquids, taking decomposition into account, are proposed. The experimental data on $T^*(\dot{T})$ for a number of polymer melts are compared with results calculated from the model.

1. INTRODUCTION

The problems of boiling of polymeric liquids have received much attention lately, mainly in connection with technical applications of this phenomenon [1]. We 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 experimentally for polymer–solvent systems by different methods [2–4]. It is convenient since the temperature of spontaneous boiling-up is not associated with the details of heater design but is 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.

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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 increases somewhat 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, a dependence of T^* on the heating path appears. Our goal was to evaluate the peculiarities of rapid bubble nucleation in polymeric liquids, including polymer melts that do not boil without decomposition.

For this purpose we used 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 onset of spontaneous boiling-up of a simple molecular liquid has been revealed at heating rates above 3×10^5 K $\cdot$ s^{-1} [7, 8]. The response temperature T^* depends on the pressure and the heating rate. A qualitative explanation of this experimental result was based on the assumption of boiling-up of thermodecomposition products formed 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 an 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^*. A different approach to the problem based on the construction of a semiempirical model or wide-range equation of state for polymers has been presented elsewhere [9].

2. EQUATION OF SPINODAL

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

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

where K is the specific (per unit volume) kinetic energy of molecules and U is the virial of the system unit volume [10].

Let us consider a polymeric liquid as a system of n monomers. Some of them are connected into macromolecules to form long chains. We assume that the potential energy of interaction between monomers does not depend on whether or not they are connected into a chain. Polymerization decreases the degrees of freedom of a bound monomer with respect to

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 introduce the effective specific number of molecules N_e, so that, by definition,

$$1 - \varepsilon = N_e/n \tag{2}$$

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

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

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

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

Here, the density v may be considered as a parameter covering the values from v_k to 3. Using the condition for critical point, we find that the melt density at the critical point v_k is determined by the cubic equation:

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

Solution of the system of Eqs. (4) and (5) gives the spinodal surface for a polymeric liquid; see Fig. 1. With decreasing N_e (and, consequently, increasing ε), 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 $\tau_k = 3.375$, $\pi_k = 0$, and $v_k = 0$. The spinodal of a pure polymer is located, except in 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
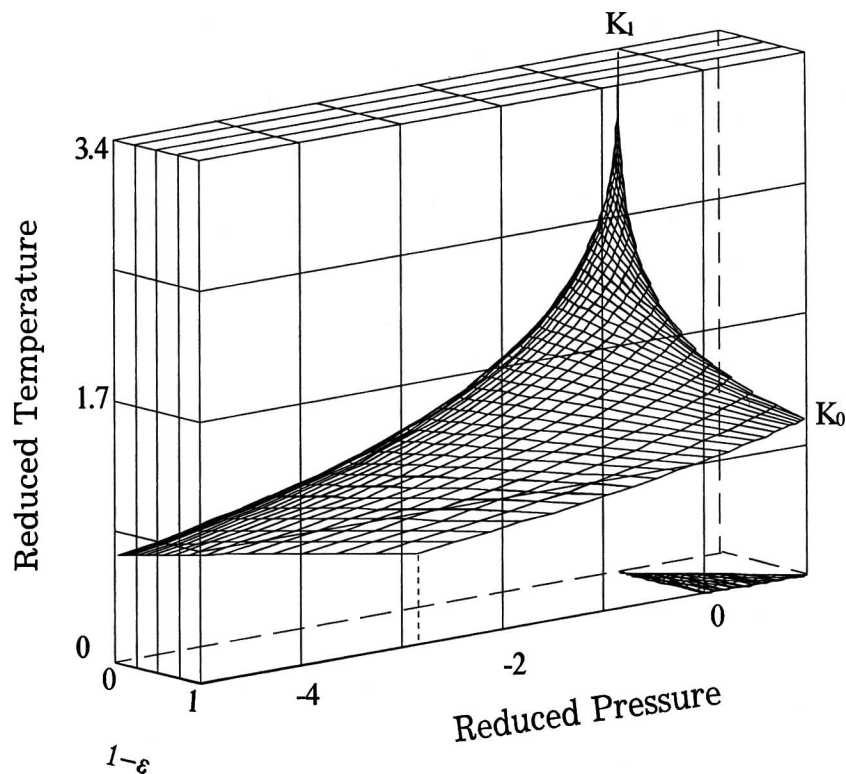
Fig. 1. Reduced temperature on the liquid- vapor spinodal for a polymeric liquid versus reduced pressure and fraction of broken bonds. $K_0\{1; 0; 1\}$ and $K_1\{0.001; 0.999; 3.19\}$ are the critical points of a monomer and polymer, respectively.

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 unit volume is equal to $F(\xi)\,d\xi$. To calculate N_c, 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

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

where ξ_x is the maximum chain length, $s = \xi_x/r$, and $[s]$ is a higher integer number closest to the ratio ξ_x/r.

Let us consider a homogeneous melt with a specific number of chain molecules N_0 of ξ_x 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 [11], we have obtained for the distribution function,

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

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

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

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

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

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

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

$$\frac{i+1}{\xi_x} = 1 - \left(1 - \frac{N_0}{n}\right)\exp\left[-\frac{BE}{k\dot{T}}\int_{W(0)}^{W(t)}\exp\left(-\frac{1}{x}\right)dx\right] \equiv \alpha \tag{10}$$

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

Equation (10) predicts an essentially nonlinear $\varepsilon(T)$ dependence at a given heating rate. The actual value of degree of polymerization for a

linearly heated polymer is presented in 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 $\pi-\tau$ plane the boiling-up temperatures for a decomposed polymer and for its solutions in a monomer obtained by solving the system of Eqs. (4), (5), (8), and (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.
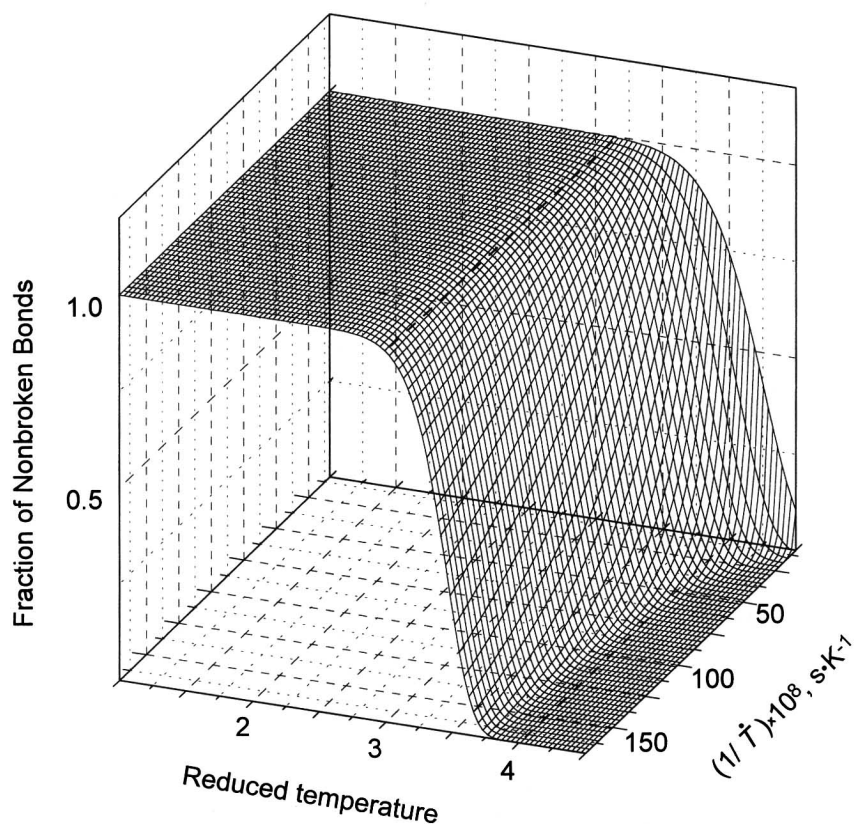

Fig. 2. Parameter ε versus reduced temperature and reciprocal heating rate for low-density polyethylene. $E = 200$ kJ · mol^{-1}, $B = 4 \times 10^{11}$ s^{-1}, $\xi_v = 2200$, $s = 1$, $T_k = 1175$ K [12]. The dashed line shows the track of intersection of this surface and the polymer spinodal at $p = 0$.
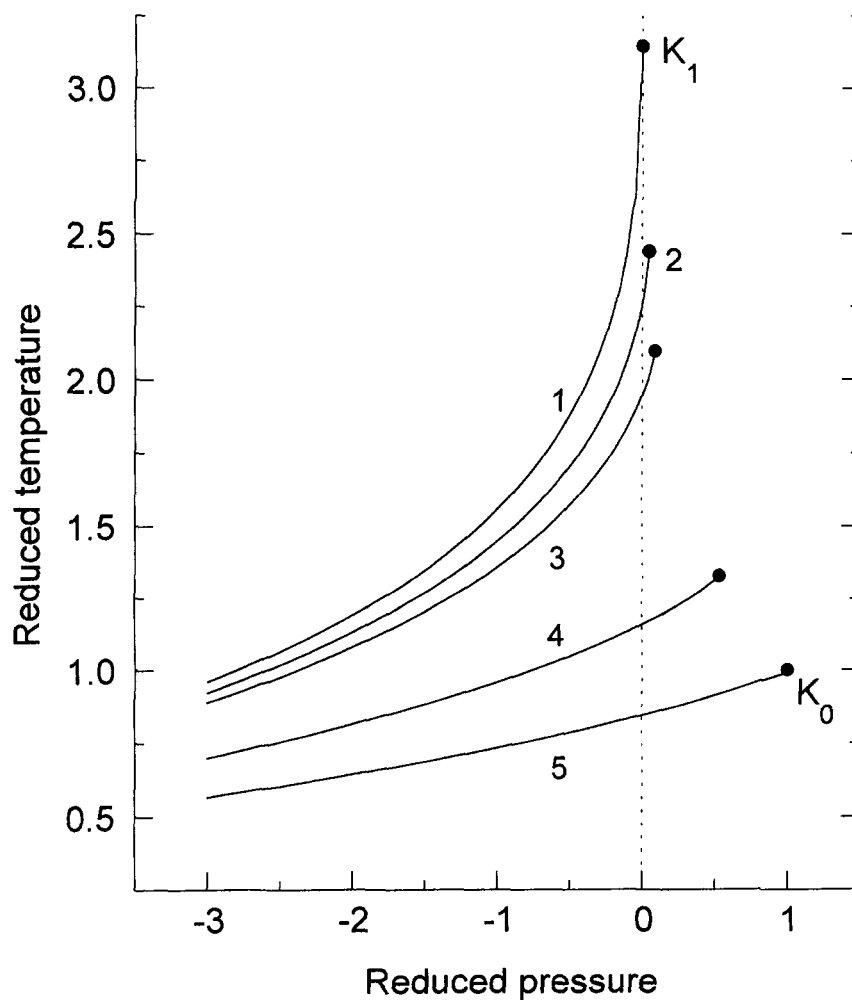
Fig. 3. Reduced temperature on the liquid-vapor spinodal for a polymer + monomer system versus reduced pressure. $N_0/n = 0.001$ (curve 1), 0.05 (curve 2), 0.1 (curve 3), 0.5 (curve 4), and 1.0 (curve 5). $\dot{T} = 10^7$ K · s^{-1}. The remaining data are identical to those in Fig. 2.

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, 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 duration 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 in detail [4, 8].

Some results are presented in Fig. 4. The analysis of the complete set of experimental data for $T^*(p, \dot{T})$ [7, 8, 12, 13] 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, and $1/p_k$ and has proved to be equivalent to the introduction of an additional volatile component into the system (see Fig. 8 in Ref. 8). This experimental result 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. Analyses 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 Ref. 12. Then, knowing the average length of a molecular chain, we found the initial value of ε and the critical temperature of a monomeric fluid. These data are sufficient to determine the temperature on the spinodal $T_{sp}(\varepsilon)$ and compare it with the data on $T^*(\dot{T})$.[4] Figure 5 shows the results of calculations of $\tau_{sp}(1/\dot{T}, \pi = 0)$ at different values of E in combination with experimental data 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 unknown due to its dependence on the temperature 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 the values of T_k obtained from the same experiment in the calculations. But we do not yet know any other reliable procedure of evaluation of the critical parameters of polymers.

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[4] 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 [$T^*(1/\dot{T} \to 0)$ $\to T_{sp}$].
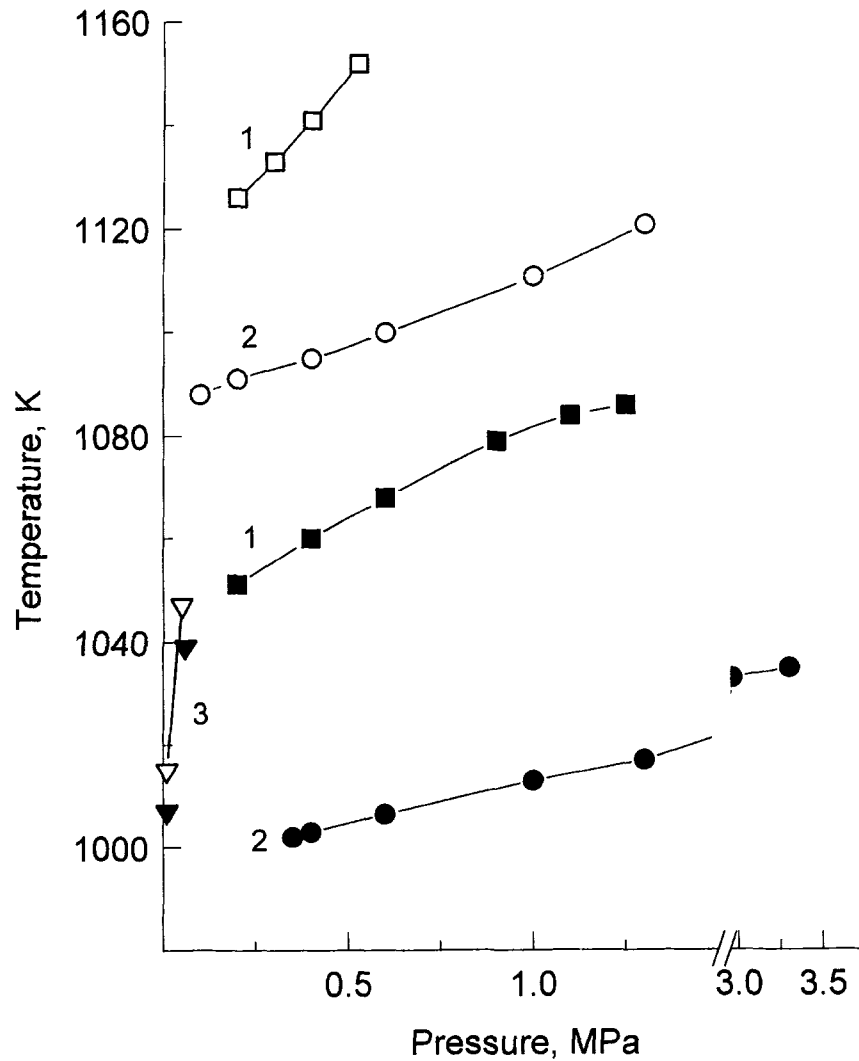
Fig. 4. Spontaneous boiling-up temperature for low-density polyethylene (LDPE; curve 1; commercial grade), poly(ethylene oxide) (PEO; curve 2; Merck Schuchardt), polydimethyl siloxane (PDMS; curve 3; Aldrich Chemical Co.) versus pressure at $\dot{T} = 2 \times 10^7$ K·s^{-1} (open circles) and 8×10^5 K·s^{-1} (solid circles). The number-average molecular weight of the samples was 31×10^3, 17×10^3, and 190×10^3, respectively.
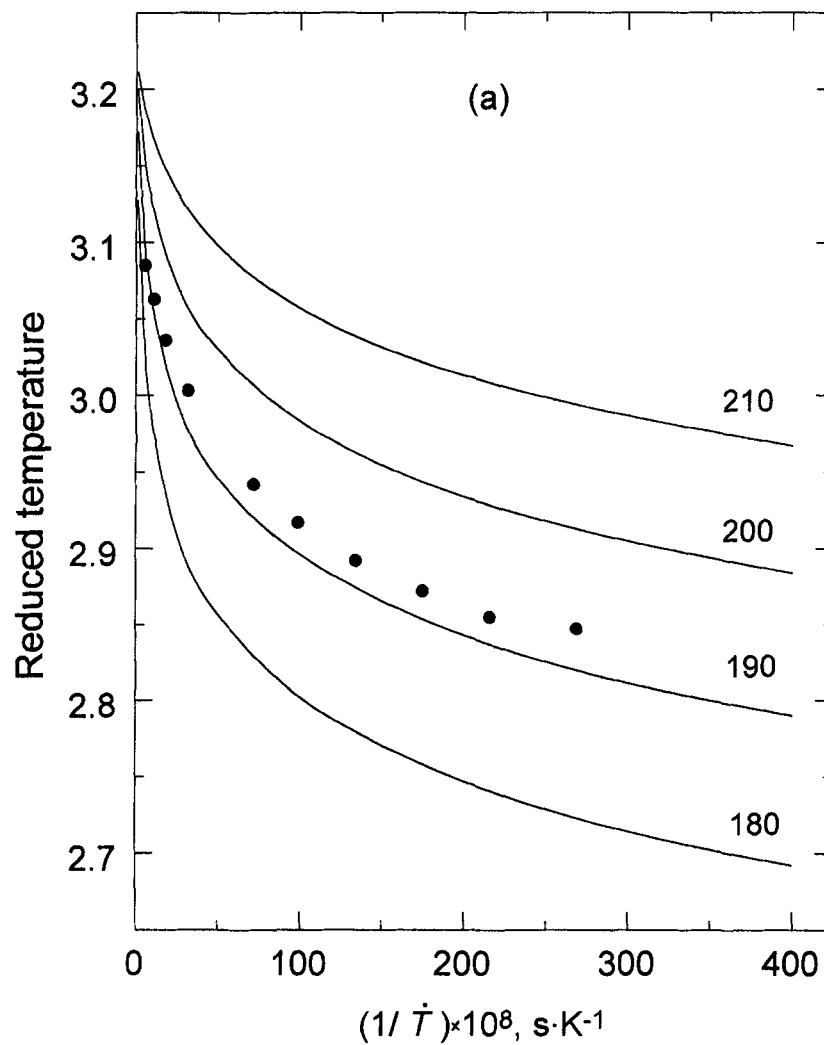
Fig. 5. Comparison of the calculated temperatures τ_{sp} (curves) with the experimental data on τ^* (circles) versus the reciprocal heating rate. Numbers on curves show the selected values of E [kJ · mol^{-1}]. $p = 0$; $s = 1$, $B = 4 \times 10^{11}$ s^{-1}. (a) LDPE, $\xi_x = 2200$, $N_0/n = 4.5 \times 10^{-4}$, $T_k^0 = 361$ K; (b) PEO, $\xi_x = 400$, $N_0/n = 2.5 \times 10^{-3}$, $T_k^0 = 368$ K.
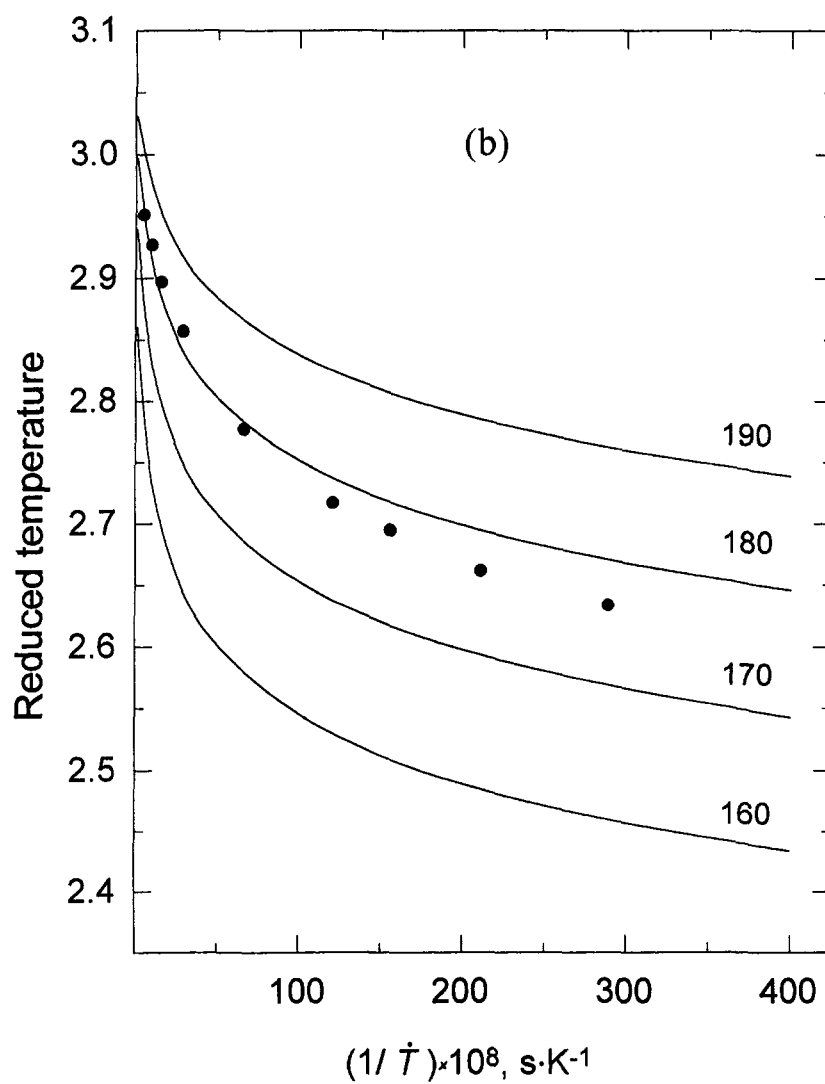
Fig. 5.   *(Continued)*

6. CONCLUSION

The model presented makes it possible to predict the values of spontaneous boiling-up temperatures of polymers in shock processes from the equation of the spinodal and to evaluate the effective macrokinetic characteristics of thermal decomposition from the best agreement between the

results of calculations 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. Because of its microscopic size, the unstable equilibrium with the surrounding liquid is established relatively fast.

ACKNOWLEDGMENTS

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