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VAPORIZATION IN SUPERHEATED OLIGOMER AND POLYMER LIQUIDS

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UDC 536.423.1

The method of impulsive heating of a wire probe is used to measure the spontaneous boiling point of commercial synthetic isoprene rubber and its solutions in saturated hydrocarbons, polyethylene glycols, and polyethylsiloxanes with allowance for thermal degradation of the polymer. A formula is obtained to describe the dependence of the boiling point of the polymer solution on heating time.

The boiling of solutions of polymers is characterized by certain features which are reflective of their properties – high viscosity, the presence of stratified regions, and thermal degradation at high temperatures. In the present study, we will focus on the boiling of concentrated solutions undergoing rapid heating – when the polymer component undergoes thermal degradation. A survey of studies of the steady boiling of dilute polymer solutions was presented in [1], while data on the boiling of certain stratifying polymer solutions was reported in [2, 3].

Vaporizaton in pure liquid polymers cannot occur without their thermal degradation, since high-molecular-weight compounds are nearly incapable of being converted to the gaseous state. With an increase in the degree of polymerization, it also becomes increasingly difficult for a macromolecule to undergo conversion from the condensed phase to the gas phase; on the other hand, an increase in the length of the chain is generally accompanied by a decrease in the effective activation energy or thermal degradation [4]. Thus, there is a certain maximum molecular weight at which vaporization is still possible. This limit, of course, depends on the structure of the polymer. For polyethylene, for example, this limiting value is of the order of 540 [5]. Tests that we conducted with commercial polyethylsiloxanes [6] – for which boiling is the same as for low-molecular-weight liquids – showed that this limit is no lower than 1300-2000 for the oligomers we studied. It must be noted, however, that special methods make it possible to obtain molecules with a weight up to $6 \cdot 10^6$ in the gas phase [7].

As a result, if a liquid polymer is heated, it first undergoes thermal degradation. Then the products of this process dissolve in the liquid phase. Finally, bubbles filled with degradation products begin to appear. This pattern may be complicated by further decomposition of the liquid into several coexisting liquid phases and their subsequent boiling.

Let us suppose that at the initial moment of time a polymer solution has a concentration c_0 and temperature T_0 which is less than the temperature at which thermal degradation begins. Pressure in the solution then remains constant, while its temperature increases with

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1062-0125/92/6202-0200$12.50

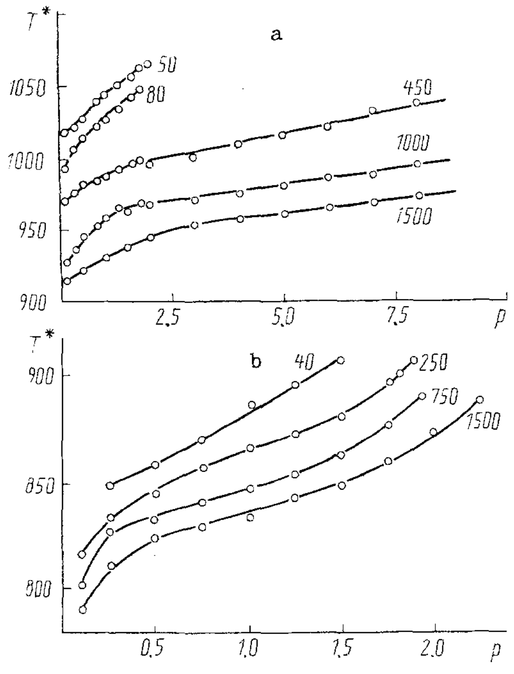

Fig. 1

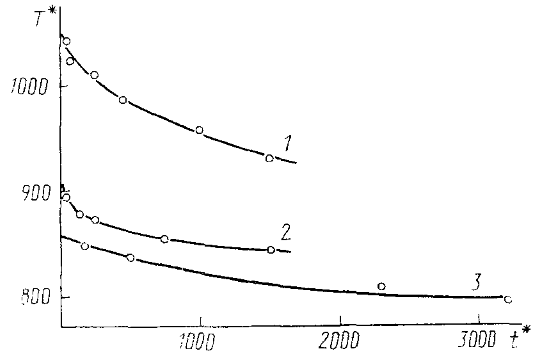

Fig. 2

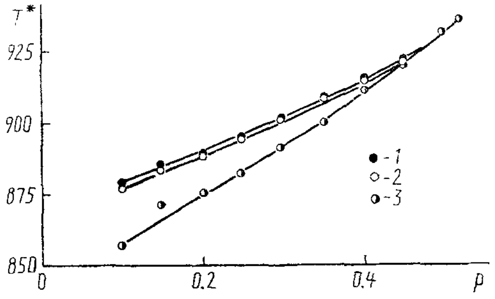

Fig. 3

Fig. 1. Dependence of the boiling point T* (K) of SPR rubber (a) and PEG-400 (b) on pressure p (MPa) and heating time t* (μsec).

Fig. 2. Dependence of boiling point T* (K) on heating time t* (μsec): 1) SPR, p = 1.0 MPa; 2) PEG-400, p = 1.5 MPa; 3) PEG-300, p = 1.98 MPa.

Fig. 3. Boiling point T* (K) of PES-5 in relation to pressure p (MPa) and heating time t* (μsec): 1) t* = 60 μsec; 2) 250; 3) 1000.

time in accordance with the linear law $T = T_0 + \dot{T}t$. The polymer decomposes during heating, the degradation process being described by the Arrhenius equation with certain effective kinetic parameters,

$$\frac{dc}{dt} = -c^n A \exp\left(-\frac{E}{RT}\right). \tag{1}$$

We will assume that boiling of the solution begins as a result of the method of homogeneous nucleation at a certain temperature T* – the spontaneous boiling point [8]. We will expand this into a series and limit ourselves to the linear term

$$T^*(c) \simeq T^*(c_0) + \beta(c - c_0). \tag{2}$$

Integrating (1) with the condition $E/RT_0 \gg E/RT \gg 1$ and inserting it into (2), we obtain the dependence of the spontaneous boiling point of the polymer solution on heating time:

$$T^*(t^*) = T^*(c_0) - \beta c_0 \left\{1 - \exp\left[-\frac{RT^*}{E} A t^* \exp\left(-\frac{E}{RT^*}\right)\right]\right\},\ n = 1,$$

$$T^*(t^*) = T^*(c_0) - \beta\left\{c_0 - \left[c_0^{1-n} - (1-n)\frac{RT^*}{E} A t^* \exp\left(-\frac{E}{RT^*}\right)\right]^{\frac{1}{1-n}}\right\},\ n \neq 1. \tag{3}$$

We measured the boiling points of commercial synthetic isoprene rubber SPR and its solutions in saturated hydrocarbons (n-heptane, n-dodecane, n-nonadecane), polyethylene glycols (PEG), and commercial polyethylsiloxanes (PES-1-PES-5).

We used the method of impulsive heating of a wire probe immersed in the test liquid [6, 8, 9]. The probe – a platinum wire 20 μm in diameter and 1-2 cm in length – was heated by a current pulse lasting 30-3200 μsec. This corresponds to a heating rate $\dot{T} = 10^5$-10^7 K/sec. At the moment boiling begins, a change in the regime of heat transfer between the probe and the liquid results in a sharp change in the rate of heating of the probe. This leads to the generation of an electric signal (boiling signal). In our tests, this signal was isolated by a low-frequency filter and recorded by an oscillograph. The mean temperature of the probe at the beginning of boiling was determined from its resistance. When boiling begins, vapor nuclei are formed in a boundary layer of the thickness 10^{-8}-10^{-9} m. We took the temperature of this layer to be equal to the temperature of the middle of the probe surface. The latter was calculated from the mean temperature of the probe, with allowance for a correction for two factors: heat transfer at the probe junctions with current leads; the radial temperature distribution inside the probe. The error of measure of boiling point T^* (K) was 0.7%. Pressure in the liquid was measured with class-0.4 manometers.

Figure 1a shows results of measurement of the boiling point of SPR rubber. Seventy-five percent of this rubber consists of 1,4-cis units. The molecular weight is (120-160) × 10^3. Figure 1b shows the test results for the polyethylene glycols. We studied polyglycols with weights of 300 and 400 produced by the "Merk Schuchardt" company. When rapidly heated, the boiling point of polyethylene glycols is considerably greater than the temperature at which their thermal degradation begins – which, according to [10], is 570 K. It is evident from Fig. 1 that the rubber and the polyglycols behave similarly with respect to boiling. With an increase in heating time, boiling point decreases and there is a substantial increase in the pressure to which the boiling signal can be tracked. Both of these phenomena can be attributed to degradation of the liquid and its saturation with low-boiling degradation products. In fact, the preliminary saturation of PEG-300 with carbon dioxide also leads to a decrease in boiling point and an increase in the thermodynamic critical pressure [11].

Figure 2 shows the dependence of the boiling point of the test substances on heating time. The curves in Fig. 2 were constructed on the basis of results calculated from Eq. (3) with the following parameter values:

	SPR	PEG-300	PEG-400
n	1	1	1
E, kJ/mole	50	100	160
A, sec^{-1}	$1.71\cdot10^6$	$3.84\cdot10^9$	$1.86\cdot10^{14}$
$T^*(c_0)$, K	1050	858	905
β, K	300	300	80

It can be seen that the proposed formula describes the measurements quite well. The values we obtained for the effective activation energy for thermal degradation of polyethylene glycols is consistent with the data of other researchers [10, 12]. For example, the authors of [12] state that effective activation energy depends on the degree of degradation and ranges from 79 (the beginning of degradation) to 305 kJ/mole; within a sizeable interval, E = 238 kJ/mole. In our experiments, the degree of degradation reached by the moment boiling began was small. We should point out the low activation energy for the thermal degradation of SPR rubber. According to [10], for natural rubber E = 234-263 kJ/mole at T = 564-584 K. The decrease in activation energy in our tests may be connected with catalytic action by the probe surface.

TABLE 1. Boiling Point T* (K) of Solutions of SPR Rubber (atmospheric pressure, heating time 50 μsec)

Solvent	Concentration of polymer, mass %				
	0	25	50	75	100
n-heptane	492	492	492	585	1020
n-dodecane	598	602	608	693	1020
n-nonadecane	690	693	705	790	1020

In contrast to rubber and polyethylene glycols, the dependence of the spontaneous boiling point of polyethylenesiloxanes on pressure and heating time (Fig. 3) is the same as for low-molecular-weight liquids. With an increase in pressure, the curves T*(p) obtained for different t* converge to a single point that can be identified with the thermodynamic critical point. This suggests that although the boiling point of polyethylenesiloxanes is considerably higher than the temperature at which thermal degradation begins (510-540 K [13]), the concentration of degradation products is negligible at the moment boiling begins and the vapor bubbles are filled with molecules of the initial substance.

Let us briefly discuss the boiling of solutions of SPR rubber in saturated hydrocarbons (see Table 1). It was found that the dependence of boiling point on composition is essentially nonlinear. Even a small addition of a hydrocarbon may cause a sharp decrease in boiling point; on the other hand, the presence of a polymer in the solution up to concentrations of 50 mass % has little effect on boiling. The same type of concentration dependence of boiling point is seen for other systems composed of a polymer and a low-molecular-weight substance [14, 15], which is an indication of the nonideal nature of such solutions.

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