Spontaneous Boiling Up as a Specific Relaxation Process in Polymer–Solvent Systems

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SYNOPSIS

The phenomenon of spontaneous bubble nucleation in extremely supersaturated (superheated) polymer–solvent systems has been studied experimentally. Spontaneous boiling-up temperatures T^* for polystyrene and poly(ethylene glycol) solutions in a number of solvents have been measured at different values of pressure p and weight fraction of polymer c by the pulse heating method. The heating rate $\dot{T}$ varied from 10^5 to 10^7 K/s. For all systems studied, the values of T^* have been found to increase with increasing p and c. The $T^*(p, c)$ dependence is discussed with the use of the data on the degree of compatibility of components. The peculiarities of polymeric solutions manifest themselves in the region $c \rightarrow 1$, as follows: (i) an abrupt increase (by 1–2 orders of magnitude) in the slope of the $T^*(c)$ dependence, and (ii) the appearance of the dependence of T^* values on the heating rate. Our approach to the interpretation of this result assumes a change in the initial composition of a solution in the course of heating due to polymer decomposition. An example of the extended phase diagram of a polymer–solvent system including the kinetic surface of $T^*(p, c)$ is given. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The type of phase diagram and the mechanism of phase separation essentially determine the properties of a polymer–solvent system under changes of temperature, pressure, and concentration. The analysis of phase diagrams of such systems usually includes the liquid, crystalline, and liquid crystalline types of equilibria. The condensed state–vapor equilibrium is typically beyond the scope of the discussion; this type of equilibrium plays an important role in the thermodynamics of two component low-molecular-weight liquids. It is also not forbidden for systems with a polymeric component. The latter statement is based on the similarity of approaches to the description of heterogeneous equilibria in low-molecular-weight and polymeric systems.[1] The boiling-up of polymeric liquids is often observed in practice, for instance, in connection with the processes of removing volatile impurities, evaporating a solvent from a solution, and producing foamed materials.[2,3] Therefore, it is of interest to extend the traditional phase diagram into the region of elevated temperatures and include into it the equilibrium with a vapor phase.

There are few pieces of evidence that the equilibrium vapor pressure of a polymeric solution is close to that of a pure solvent up to high polymer concentrations.[2,4] Of greater interest is the phenomenon of spontaneous bubble nucleation in a superheated phase. The system relaxation in this case proceeds via the avalanche-like formation of vapor nuclei and their subsequent growth. The location of the kinetic line (or the surface) of spontaneous boiling up (SBU) in the phase diagram of a small molecular liquid can be determined reliably enough.[5,6] The features characteristic of the spontaneous mechanism have also been observed in the boiling-up of some polymer–solvent systems.[3] In this paper we discuss the conditions of manifestation of such a relaxation mechanism in polymeric liquids. In experiments on the pulse heating of microquantities of a substance, it has been found that the value of SBU temperature $T^*(p, c)$ for a polymeric solution is reproduced in a stable way, and is a convenient indicator of its concentration (c) and pressure (p).[7] This paper presents

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the results of studies of the SBU boundary of polymer–solvent systems versus pressure, heating rate, composition, and molecular parameters of the components. As an example, Figure 1 shows the "extended" phase diagram of a polystyrene–acetone system. The values of $T^*(p, c)$ have been measured by the pulse heating method. The pulse length was $t^* = 100$ μs. The characteristic time of spontaneous nucleation is of the order of 10^{-6} s,[5] which is essentially shorter than the relaxation time of the system via the phase separation mechanism.[8] The values of T^* for the miscibility gap ($p < 0.5$ MPa, $c \sim 0.1$–0.2) were obtained immediately after the drop in the homogeneous solution pressure to the chosen value.

BACKGROUND

A superheated liquid, as a particular case of a supersaturated state, is observed when the system crosses the line of liquid–vapor equilibrium $T_s(p)$ without undergoing a phase transition. The value of superheat $\Delta T = T - T_s$ that precedes the boiling up determines its intensity. Typical experimental ΔT values are of the order of 1–10 K, depending on both the conditions of heat supply and the initiating action of different factors. At a sufficiently small value of the product Vt, where V is the volume of a superheated phase and t is the lifetime of a superheated state, one can achieve the limiting values of $\Delta T(p)$ starting the mechanism of SBU. For example, for water at atmospheric pressure we have $T^* - T_s$ = 210 K.[10,11] It is a typical activation process, which proceeds via the formation of a critical size bubble that is in an unstable equilibrium with a superheated liquid. The temperature at the beginning of SBU T^* has been called "the temperature of attainable superheat" of a liquid. The values of T^* for simple liquids and solutions, measured by different methods, agree with the calculation in the framework of the homogeneous nucleation theory with the work of critical bubble formation written in a thermodynamic approximation[11,12]: $W_* \sim \sigma^3/(p_v - p)^2$, where σ is the surface tension and p_v is the pressure in the critical bubble. The kinetic characteristic of the process is the nucleation rate of viable bubbles, defined as $J = J_0\exp(-W_*/k_BT)$. The changing part of the quantity J is determined mainly by the exponential term. The SB is characterized by a high slope of the $J(T)$ dependence, being approximately 3 or 4 orders of J magnitude per 1 K. Thus, the isokinetic surfaces of $T^*(p, c)$ appear to be nearly insensitive to the value of J and may be regarded as boundary surfaces in phase diagrams.
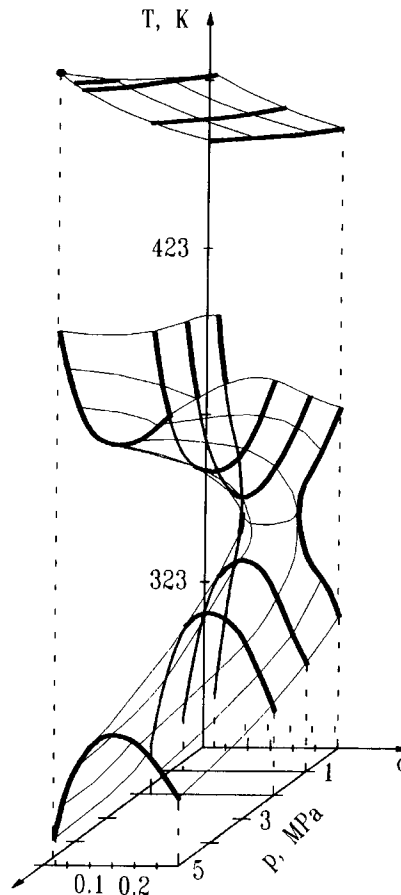

Figure 1 Phase diagram for polystyrene (PS)–acetone solution showing the cloud-point surface ("hourglass," data of Zeman and Patterson[9]) and SBU surface (upper). $\bar{M}_w = 2 \cdot 10^4$.

As an example, Figure 2 shows the lines of liquid–vapor stable and unstable equilibrium for CO_2 solution in hexadecane. As this figure shows, the region of superheated states is extended considerably with the addition of a volatile component. This feature is common for binary systems and will be used by us in the subsequent discussion. The increase of the supersaturation scale related to the introduction of a second component poses additional problems. First, requirements for the methods of measurements and for the device recording the initial stage of boiling up by a certain sign become more rigid. Second, deviation of the pressure, the surface tension, and the critical-size bubble composition from the corresponding values on the saturation line, used in calculation by the homogeneous nucleation theory, increase.

Experiments on the superheat of a substance require the real-time determination of temperature (or pressure, depending on the means of penetration
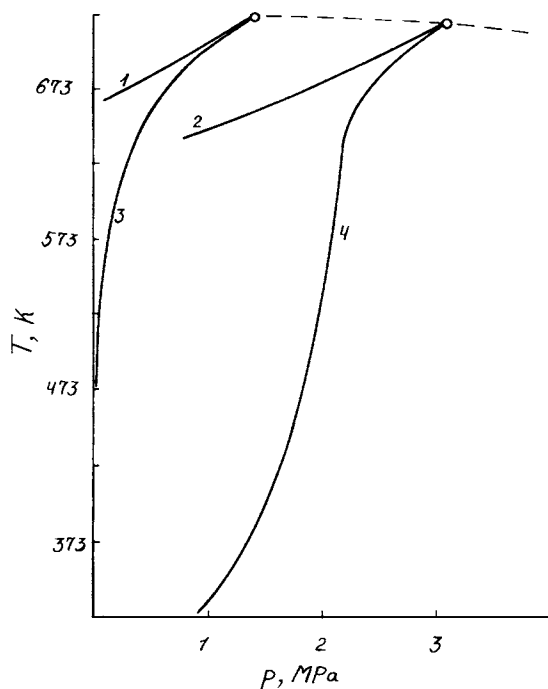
Figure 2 The attainable superheat lines (1, 2), vapor-liquid binodals (3, 4), and critical points (open circles) for hexadecane and CO_2 solution (0.10 mol. fraction) in hexadecane, respectively. The smoothed line 4 is plotted according to the data of Tremper and Prausnitz[13] and Sebastian and colleagues.[14] The critical curve (dashed line) is based on the data of Nikitin and coworkers.[15]

into the metastable region). The action should be applied rapidly enough and on a small quantity of a substance. The experience of working with superheated liquids has shown that one can break through the background of heterogeneous nucleation only at characteristic values of the product Vt of the order of $Vt \lesssim 10$ mm^3 s. The acceptable value of Vt in each particular case depends on a number of hardly controllable factors. The strong $J(T)$ dependence mentioned above results in the explosive boiling of an extremely supersaturated liquid. This circumstance creates prerequisites for unambiguous registration of the SB moment by a certain sign; for instance, a characteristic "splash" on the time dependence of the pressure, light scattering intensity, or the temperature of a quick-response probe. Details of the experimental methods can be found in books[11,17] and reviews.[5,6]

The first experiments on the superheat of polymer-solvent systems were carried out by well-known methods. The method of a droplet rising in a host liquid with a fixed temperature gradient was used to measure the temperature T^* of PS solutions in cyclohexane[18] and benzene[19] at ambient

pressure. The method of pulse heating of a wire probe was used to study the $T^*(p)$ dependence for poly(ethylene glycol) solutions in water[20] and in carbon dioxide.[21] It has been found that: (i) T^* tends to increase with increasing polymer content; and (ii) the value of $\Delta T^*(c) = [T^*(c) - T^* (c = 0)]$ in the range of $c \lesssim 0.6$ is small, $\Delta T^*(c)/[T^* (c = 0) - T_s (c = 0)] \ll 1$ at $p/p_c \ll 1$, p_c being the critical pressure of a solvent.

Alternatively, experiments on the pulse heating of plasticized and gas-saturated polymer melts have shown that in the region $c \to 1$, the slope of the $T^*(c)$ dependence increases up to 10^2 K per wt % and the average level of T^* values at $c = 1$ is about 1,000 K.[20] For this reason, the method of a rising droplet based on thermostating of the measuring cell at $T = T^*$ has proved to be unsuitable for studying the complete $T^*(p, c)$ surface. For these purposes we have used the method of pulse heating.[16,17]

EXPERIMENTAL

The method of pulse heating of a wire probe immersed into a medium under investigation has been recently described by us in detail as applied to monitoring the kinetics of curing and the kinetics of dissolution of gas component.[7] Here we shall only point out the essence of the method.

The main element of the measuring circuit is a wire probe connected to the bridge circuit. The probe diameter is 20 μm, the length is 1–2 cm, and the material is platinum. The probe is heated by rectangular voltage pulses. The idea of the method is based on the sensitivity of the probe heating rate to conditions of heat transfer to a liquid. The change in the temperature of the probe is determined by measuring its electric resistance. The temperature of the probe surface at the moment of spontaneous boiling up is taken for T^* of a liquid. This moment is marked by characteristic peculiarities in the oscillogram and in the synchronized photographs of the probe.[7,16]

The method makes it possible to perform measurements in a wide range of variables: p, c, and t^*, where t^* is the heating time of a liquid from the initial to the SBU temperature. In our experiments the values of t^* varied from 20 μs to 3 $\times 10^3$ μs. The pressure varied from 10^{-2} MPa to a certain limiting value $p_l(t^*)$, at which the response signal was no longer resolved. The design of measuring cells and experimental procedures have been described by Skripov and colleagues[7] and Nikitin and coworkers.[15]

Three poly(ethylene glycol) (PEG) samples with nominal molecular weights of 1,000, 20,000 and 40,000 were obtained from MERCK-Schuchardt (Munich, Germany). Molecular weight distributions were 1.02, 1.15, and 1.19, respectively (gel permeation chromatography). Two samples of polystyrene (PS), $\bar{M}_w$ = 2 × 10⁴ and 1.64 × 10⁵, were kindly supplied to us by colleagues from Moscow State Academy of Fine Chemical Technology. Spectroscopic-grade acetone and cyclohexane and commercial-grade esters of phthalic acid (from dibutyl phthalate to dioctyl phthalate), styrene, diethylene glycol, and carbon dioxide, with a stated minimum mole purity of 99%, were used for solution preparations.

RESULTS AND DISCUSSION

The main results are given in Figures 1–6. For the convenience of their discussion the same figures show typical data for solutions of small molecules.

By gradually decreasing solvent content in a polymer–solvent system, we have revealed that the signal–response similar to that of spontaneous boiling is resolved in the entire range of compositions (the case c = 1 will be discussed below). With increasing c the response retains confinement in time and reproducibility with respect to temperature, i.e., the inherent features of SBU. Its amplitude–frequency characteristics, as well as the $T^*(c)$ dependence, do not show any singularities typical of changes in the response regime. This circumstance allows one to treat SBU as a specific relaxation process in a highly supersaturated polymeric system. For small molecule solvents, the bubble nucleation and subsequent growth is the basic relaxation mechanism in a superheated phase. The situation for polymeric liquids is not so unambiguous. These liquids may be metastable and not in equilibrium with respect to a number of parameters. In different regions of the p–c–T diagram, the relaxation of a system is expected to "switch on" the mechanisms of conformational transitions, thermal decomposition, and phase separation with a chain of intermediate structures. These processes do not rule out (or replace) SBU, which is a relatively quick-response thermal outflow regulator. But their interaction may influence the conditions of SBU manifestation. On the other hand, the results of $T^*(p, c,)$ measurements at different heating rates give indirect information on the character of relaxation of a rapidly heated polymeric system. The stable re-
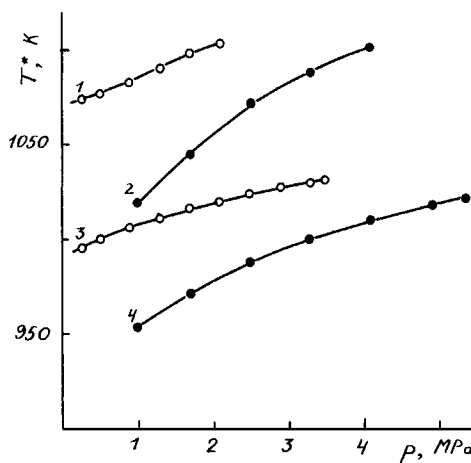

Figure 3 Pressure dependences of T^* for PEG–40,000 (1, 3); CO₂ solution (0.5 wt. %) in PEG (2, 4) at $\dot{T}$ = 5 × 10⁶ K/s (1, 2) and 5 × 10⁵ K/s (3, 4).

producibility of T^* values implies the reproducibility of relaxation processes preceding SBU.

Let us now discuss these results. For all systems investigated the values of T^* have been found to increase with increasing p and c. The $T^*(p, c)$ surface is asymmetric and has the largest value of the ordinate at the point (p_l; c = 1). As in the case of small molecule solutions, the $T^*(p)$ dependence is of a simple form (close to the linear one); see Figures 1–3. The peculiarity introduced by a polymeric component manifests itself in the essentially nonlinear character of the $T^*(c)$ dependence; see Figure 4. In the region c < 0.6–0.8, the effect of a polymeric component is insignificant on the scale of $T^*(c)$ variation. The values of T^* within this interval range from T^* (c = 0) to 1.1 × T^* (c = 0) and do not exceed the solvent gas–liquid critical temperature. The ordinary SBU of a mixture with a nonvolatile component is observed. At c > 0.8 the $T^*(c)$ curve rises abruptly, going deeper into the region of thermal instability[†] of a polymer. This circumstance principally limits the possibilities of predicting T^* values in this range of c. In the course of heating, the initial solution transforms into a system of variable composition, the phase diagram of which can hardly be defined. Dispersed thermodecomposition products become potential nucleation sites. The dependence of T^* on the heating rate $\dot{T}$ becomes important (see Fig. 3). The decrease in $\dot{T}$ has proved to be equivalent to the introduction of a low-molec-

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[†] As the region of thermal instability of a substance, we shall denote the region of $\{T, c\}$ variation in which the thermal decomposition of a polymer or solvent starts to shift the values of T^* (for the time scale $t^* \lesssim 10^{-3}$ s) of an initially stable solution.
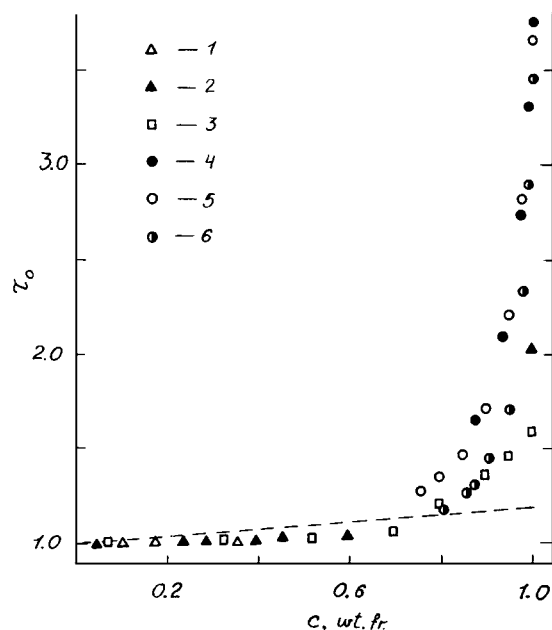
Figure 4 Reduced temperature $\tau_0 = T^*(c)/T^*$ $(c = 0)$ versus polymer weight fraction for polymer–solvent systems. 1: PS $(M = 50,000)$–cyclohexane,[18] T^* $(c = 0) = 493$ K at $p = 0.1$ MPa. 2: PS $(M = 100,000)$–benzene,[19] 499 K, 0.1 MPa, $c = 1$, our data. 3: PEG $(M = 20,000)$–diethylene glycol, 685 K, 0.5 MPa. 4: PEG $(1,000)$–CO_2, 277 K, 1.0 MPa. 5: trifunctional oligopropylene oxide $(M = 5,000)$–CO_2,[23] 277 K, 1.0 MPa. 6: polydimethyl siloxane $(M = 562,000)$–CO_2,[23] 274 K, 0.2 MPa. The dashed line corresponds to styrene–cyclohexane solution.

ular-weight substance into the system. Such an analogy makes it possible to simulate the $T^*(\dot{T})$ dependence of a polymer by introducing into it a certain quantity of a low-molecular-weight substance imitating thermodecomposition products.

In a general case, a polymer forms various products of thermal decomposition. Simplifying the situation, let us assume that we have a single product, for instance CO_2. Knowing the solubility of CO_2 in the polymer melt $x(p_s, T_s)$, one can determine the dependence of $T^*(x)$ at a chosen value of t^*. Such a dependence for a PEG–CO_2 system is shown in Figure 5. The dependence of $T^*(t^*)$ for PEG was determined in the parallel experiment. Then, by comparing the values of x and the values of t^* causing the same decrease in T^*, one can evaluate the degree of polymer decomposition expressed in terms of the "generalized" value of x (see Fig. 5). Here one can also see the liquid–vapor equilibrium curve for this system. (The procedure for its determination is given in the Appendix.) Hence we are able to relate the characteristics of SB of a polymer melt to an ordinary phase diagram of a superheated liquid. The

essential feature typical of polymeric liquids is a high level of T^* values and, therefore, a deep penetration into the region of thermal instability. Nevertheless, the degree of polymer decomposition obtained by such an approach is small. At $t < 3$ ms we have $x \sim 10^{-1}$ wt %.

Macromolecules play a passive but presumably important role in the process of boiling up. Jennings and Middleman[18] have revealed that the value of T^* for PS–cyclohexane solutions at $c = const$ depends on molecular weight of PS (see Fig. 6). We have found similar dependence for solutions of two fractions of PS in toluene. It should be noted that the sign of this dependence is opposite to that of the corresponding dependence for small molecule solutions (see curve 2 on Fig. 6). We ascribe such a result to the decrease in the degree of compatibility in a single-phase solution with increasing molecular weight of a polymer.[24] In this case one may expect the increase in the probability of existence of free solvent clusters in the solution volume comparable with a critical bubble size, $2r_* \sim 10^{-9}$ m. (The values of $r_*(J, p)$ for a set of solvents are presented in Skripov and colleagues.[11]) Such clusters are likely to be nucleation sites. Then the larger the cluster size, the smaller the value of $\Delta T^*(c)$. In order to
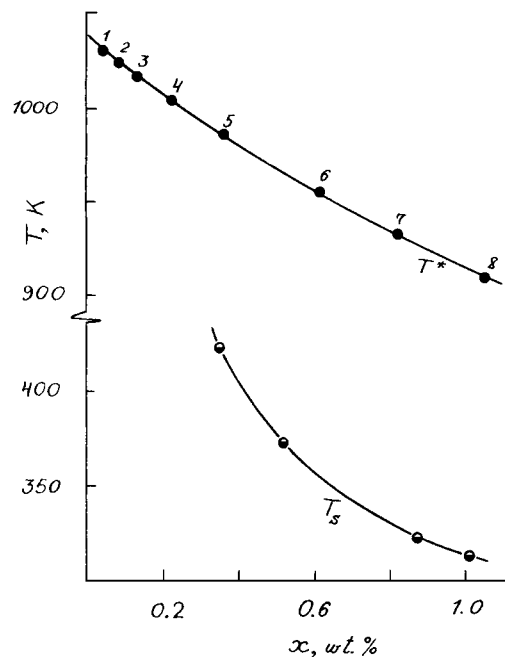

Figure 5 Interpretation of the $T^*(t^*)$ results for PEG $(1,000)$ based on the dependence of T^* on CO_2 content in PEG. The t^* values are as follows, in μs: 1: 20; 2: 40; 3: 80; 4: 200; 5: 460; 6: 1,100; 7: 1,800; 8: 2,900. $T_s(x)$ is the vapor–liquid equilibrium curve for this system. $p = 0.4$ MPa.
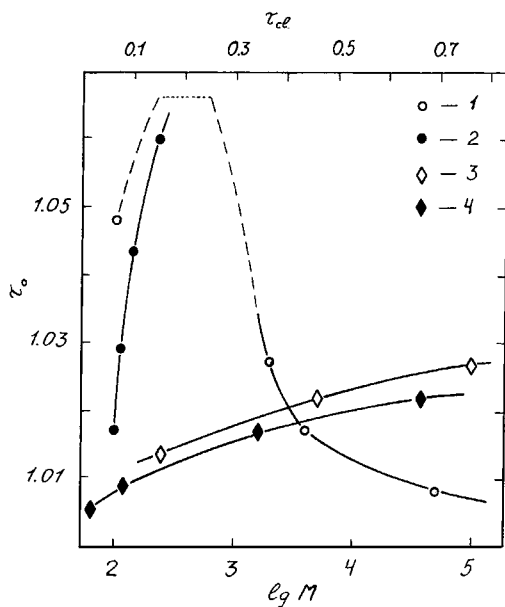
Figure 6 Reduced temperature τ_0 versus molecular weight of the dissolved substance (1, 2) and versus deviation from the cloud-point curve (UCST) $\tau_{ol} = (T_O - T_{ol})/T_{ol}$ for the following systems: 1: PS (30 wt %)–cyclohexane[18] in combination with our data for styrene-cyclohexane solution; 2: 30 wt % solutions of n-alkanes (heptane, octane, decane, and hexadecane) in hexane; 3, 4: 40 wt % solutions of PS ($M = 164{,}000$) in dibutyl phthalate (3) and dioctyl phthalate (4).

check this hypothesis we have carried out somewhat different experiments, investigating PS solutions in phthalates. The degree of compatibility was varied by means of varying the initial temperature T_o of a solution. The values of T_o were chosen on both sides of the crossover separating the regions of theta solvent and good solvent.[25] With increasing deviation from the cloud-point curve (UCST) the values of T^* also increased (see Fig. 6). The cloud-point curve locations are taken from Suvorova and colleagues.[26] Such a result supports our hypothesis on the correlation between the degree of compatibility of components and the values of T^* for a solution.

Thus, experimental data obtained by various methods for different systems show the sensitivity of T^* values to the microphase state of a solution. In the course of T^* measurements, variations of the degree of compatibility and of the heating rate have proved to be equivalent to the variation of the solvent concentration. This conclusion sets certain limitations on the application of the classical homogeneous nucleation theory for predicting the boiling-up temperature of polymeric systems. A more appropriate model for these purposes seems to be the model of spontaneous boiling up of an in-

homogeneously metastable liquid.[16] The homogeneous nucleation temperature itself serves as a convenient reference point for discussing the results of experiments and also for verification of the experimental technique on pure solvents.

CONCLUSION

By means of the pulse-heating method it has been revealed that under certain conditions (for instance, at a sufficiently high heating rate) the relaxation of a highly supersaturated polymer–solvent system can include the process of spontaneous boiling up. Clusters of a low-molecular-weight substance, i.e., solvent and/or thermodecomposition products with the shortest relaxation times, are the source of the vapor phase. Therefore, the values of $T^*(c, p)$ depend on the type of the phase diagram and on the kinetics of relaxation. The stable reproducibility of these results gives evidence for reproducibility of precursors of a macroscopic liquid–vapor phase transition.

A peculiar feature of polymeric solutions is the steep rise of T^* values at $c \to 1$ caused by difficulties in the formation of nucleation sites. The most controversial case is that corresponding to $c = 1$. The model of the generalized decomposition product allows us to describe this case in ordinary terms of superheat and boiling up of a binary system, and to explain the dependence of T^* on $\dot{T}$. As a further step in this investigation, we plan to study the SB conditions for polymer melts saturated with the most probable decomposition products.

APPENDIX

The solubility of CO_2 in PEG (1,000) at $T_s = 323$ K is known.[27] The preparation of polymer–gas solutions is described elsewhere.[7] $T^*(p)$ dependences for a number of fixed concentrations x of PEG–CO_2 solution at a chosen heating time t^* were determined experimentally. These data were used to plot the T^* ($x; p = const$) curves. For instance, such a curve at $p = 0.4$ MPa is shown in Figure 5. The values of T^* for the solution versus the temperature of a substance T_s under the pressure of CO_2 $p_s = 0.4$ MPa were measured in the next series of experiments. T_s values varied from 423 to 313 K. With decreasing T_s the solubility of CO_2 increased and, consequently, the values of T^* decreased. Both dependences were plotted on the same graph (see Fig. 7). By comparing them we found the approximation for the curve $T_s(x)$ at a chosen value of p. The process of CO_2
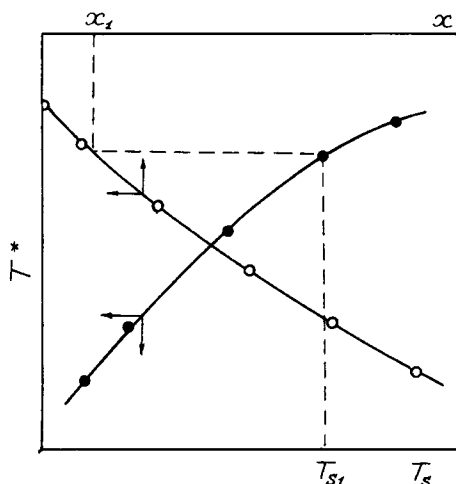
Figure 7 Schematic illustration of the procedure of liquid–vapor equilibrium data $T_s(x)$ determination.

dissolution with variation of T_s or p_s was monitored by repeated T^* measurements. The termination of changes in T^* with respect to current time and the height of the liquid column indicated the establishment of the equilibrium composition.

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