Homogeneous Nucleation of Vapor from Polymer Solutions

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ABSTRACT: The limit of superheat is measured for solutions of polystyrene in cyclohexane at atmospheric pressure. The presence of polymer leads to increases in superheat of the order of 10 °C, to an extent that depends upon both molecular weight and concentration.

Introduction

If a liquid is carefully isolated from surfaces that might provide sources of heterogeneous nucleation of vapor, i.e., normal boiling, then it is possible to raise the temperature of the liquid well above its normal boiling point without the occurrence of a vapor phase. For pure liquids, classical nucleation theory[1] predicts that the limit of superheat is about 88–91% of the critical temperature, and experimental data for a variety of liquids confirm this.[2]

We are interested in the effect on the limit of superheat of adding soluble polymer to a pure liquid. As we shall demonstrate, the addition of high molecular weight polymer increases the limit of superheat to a degree that varies with molecular weight and concentration.

Classical nucleation theory is presented and discussed in a number of sources. For example, Blander and Katz[3] present an expression of the nucleation rate J (number of bubbles formed per cm^3 per second) in the form

$$J = 3.73 \times 10^{35}\left(\frac{d^2\sigma}{M^3B}\right)^{1/2} \exp\left[\frac{-1.182 \times 10^5\sigma^3}{T(P_V - P_L)^2}\right] \quad (1)$$

Symbols are defined in the Nomenclature section, but we point out here that the numerical coefficients given in eq 1 require use of the units presented with these symbols. In writing eq 1 we have adopted the common approximation that, at atmospheric pressure, the Poynting correction is unity.

As others have pointed out, the exponential term dominates the variation of J with parameters, and over a very narrow temperature range J increases from a small number (corresponding to unlikely observation of nucleation) to a very large number. Because the temperature range is narrow one defines a single nucleation temperature, or *limiting superheat* T_s, and observations of nucleation (as mentioned above) consistently suggest that $T_s = 0.89T_c$. If physical property data are available one may calculate the value of J at T_s and find values in the range 10^4–10^6 bubbles cm^{-3} s^{-1}. Further, the value of J changes by about 3 orders of magnitude per degree Celsius in the neighborhood of T_s.

As Reid has pointed out,[10] no kinetic theory is available to treat nonideal liquid mixtures, of which polymer solutions are certainly an example. A stability theory may also be developed with thermodynamic arguments and has been successfully applied and tested for pure liquids and ideal mixtures. No such extension to polymer solutions has been carried out. Hence there is no theoretical basis upon which our results can be compared or discussed.

Measurements

The limit of superheat is measured by the standard rising-drop method.[4] A small drop of the test liquid is introduced through a syringe at the bottom of a column filled with a denser immiscible liquid. The drop rises through the column under the influence of buoyancy. The column is transparent glass and is wrapped helically along its length with resistance wire. By controlling the pitch of the helix and the current through the wire, one may impose a temperature profile, increasing upward, in the host liquid in the column. By choosing a relatively viscous host liquid, one may suppress convection and thermal mixing due to drop motion. When proper care is taken one may observe a drop that rises, and in doing so heats up, until the drop reaches the limiting superheat T_s. At this point the drop explodes and creates a vapor bubble. One repeats such experiments until a thermocouple can be positioned in the host liquid at the level where nucleation is consistently observed.

Experiments were performed first with pure organic solvents and their mixtures, in order to check the data against literature values. Then solutions of polystyrene in cyclohexane were prepared. In all cases, glycerol served as the host liquid.

Polysciences polystyrene was used. Four monodisperse samples were studied, at molecular weights of 2 × 10^3, 4 × 10^3, 50 × 10^3, and 100 × 10^3. Dilute solutions were prepared with Mallinckrodt AR grade cyclohexane. These solutions were then filtered through a 0.2-μm Fluoropore filter made by Millipore Corp. From this stock, concentrated solutions were prepared by evaporating solvent by passing filtered air over the dilute solutions.

Solutions were introduced through a septum at the bottom of the column with a Hamilton microsyringe. Drop volumes of 0.1, 0.2, and 0.4 μL were studied. The limit of superheat was found to be independent of drop size in this range, an indication that no appreciable diffusion of solvent into the host phase was occurring.

Results

Figure 1 shows data obtained with mixtures of pentane and cyclohexane. The observed limiting superheat is plotted against mass fraction. *Mole* fraction is more commonly used in presenting data for liquid mixtures. However, since molecular weight of some polymers may be uncertain, or since many polymers are not available in monodisperse samples, we choose to present these results using *mass* fraction. Our data differ slightly from those of Holden and Katz[4] for the pure solvents; we are 2 °C low for pure pentane and 3 °C high for pure cyclohexane. On the other hand, our data are within 1 °C of the values presented by Blander.[2]

Figure 2 shows data for low molecular weight polystyrenes in cyclohexane. Also shown is a line connecting the values of limiting superheat for cyclohexane and pure styrene, which we may regard as the lowest molecular weight polystyrene. A single data point obtained for a 5.5% styrene/cyclohexane solution is in good agreement with this curve. Out to 30% polymer the variation of T_s with polymer concentration is linear when plotted in this form.

Figure 3 shows data obtained with high molecular weight polymers. At a molecular weight of 50 000 the data are similar to those for lower molecular weight samples, although it does not appear that the dependence is linear at low concentrations.

The highest molecular weight studied, 100 000, shows the most interesting behavior. It appears that the limiting

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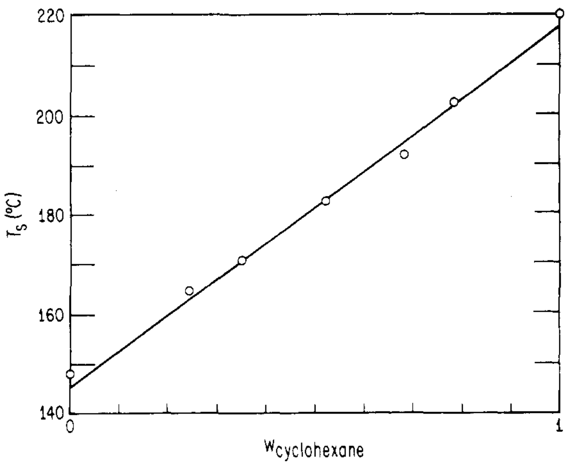

Figure 1. Data on limiting superheat for binary solutions of cyclohexane and pentane. Composition is mass fraction.

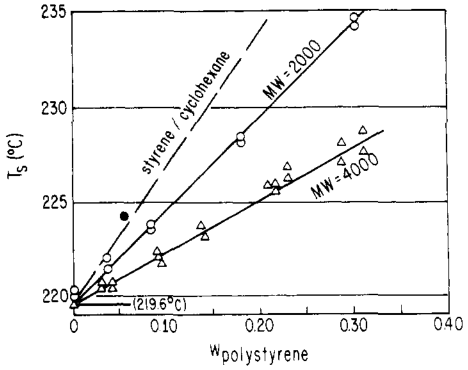

Figure 2. Data on limiting superheat for low molecular weight polystyrene in cyclohexane. T_s for pure cyclohexane is taken as 219.6 °C.

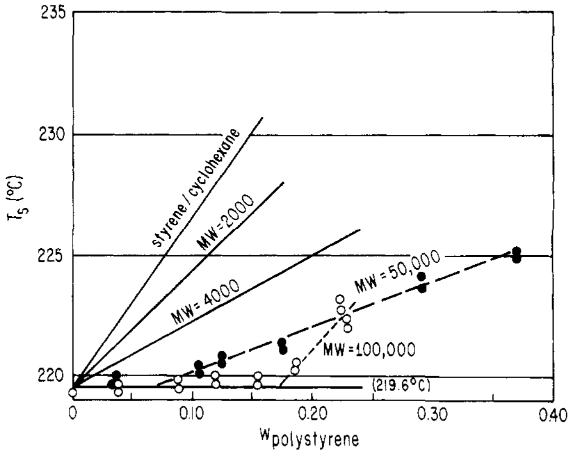

Figure 3. Data on limiting superheat for high molecular weight polystyrene in cyclohexane.

superheat is that of the solvent, all the way out to about 15% polymer. There is some indication that T_s rises above the solvent value, beyond 15% polymer.

Interpretation of Results

The presence of polymer brings about several changes in solution properties, all of which have the potential to alter the homogeneous nucleation temperature. Especially in the case of the high molecular weight samples, the polymer solutions are considerably more viscous, by several orders of magnitude, than the solvent. Viscous effects have the capacity to retard the rate of nucleation, a phenomenon treated quantitatively by Kagan[5] and discussed by Attar.[6] However, our observations show that the increase in superheat, relative to the solvent, becomes smaller as molecular weight increases. Since the viscosity is a strong increasing function of molecular weight, it does not appear that our data reflect viscosity control of nucleation.

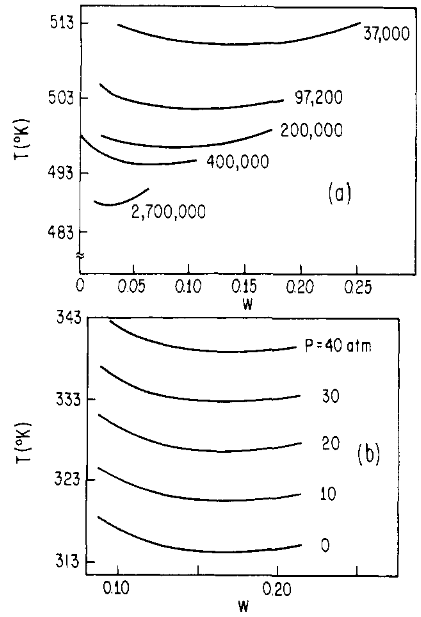

Figure 4. (a) LCST curves for polystyrene/cyclohexane (after Saeki et al.[8]). T_s = 493 K for solvent. (b) Pressure dependence of LCST for polystyrene/diethyl ether at MW = 20 400 (after Saeki et al.[9]). T_s = 420 K for solvent.

We believe that an explanation of these observations may lie in consideration of another aspect of phase behavior of polymer solutions. It is known that at elevated temperatures a polymer solution will separate into two liquid phases—one polymer rich and the other polymer poor. This transition occurs at the so-called lower critical solution temperature (LCST), and a brief review of the thermodynamics of the LCST is given by Somcynsky.[7]

Figure 4a shows data of Saeki et al.[8] for the LCST of polystyrene/cyclohexane solutions. Two points are to be noted here. Curves are displaced toward lower temperatures as molecular weight increases. For high enough molecular weights, in this case above about MW = 500 000, the LCST falls below the limit of superheat for the solvent.

It is important, as well, to recognize that the data of Figure 4 are obtained under such conditions that the solution is always subject to its vapor pressure, which is generally quite a bit higher, at these temperatures, than the atmospheric pressure at which we have measured the limit of superheat. Data on the pressure dependence of the LCST are available for polystyrene in several solvents, but not in cyclohexane. These data show significant reductions in the LCST as atmospheric pressure is approached. Figure 4b, for example, shows data of Saeki et al.[9] for polystyrene in diethyl ether. Data are well below the limiting superheat of 420 K for the solvent.

From these observations, the following speculative proposal may be offered. Figure 5 shows, qualitatively, two curves of the LCST, at atmospheric pressure. If a *low* molecular weight polymer, whose LCST lies entirely above T_s for the solvent, were studied at a concentration x_A, then the point A2, at T_s for the solvent, might not initiate nucleation since the presence of the polymer, in a *homogeneous solution*, could lead to an elevation of the limiting superheat for the solution. However, when the point A3 is reached on the LCST curve a solvent-rich phase appears and nucleation occurs in the solvent-rich phase, which

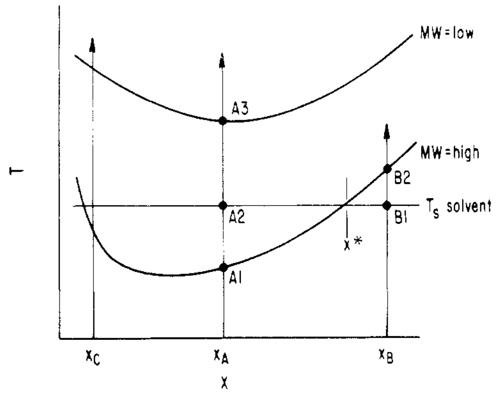

Figure 5. Qualitative sketch of LCST for two molecular weight polymers in solvent.

might be, at that point, well above its limit of superheat.

On the other hand, for a high molecular weight polymer solution of concentration x_A, the LCST is crossed *below* T_s for the solvent, and the solvent-rich phase does not nucleate until T_s is crossed. For this particular molecular weight, this would be true for all concentrations below x^*.

However, if $x_B > x^*$, then the situation is similar to that of the low molecular weight polymer solution and nucleation does not occur until point B2 on the LCST curve. Thus one would find, for high enough molecular weights, that the T_s curve would follow the solvent T_s until the temperature at which the LCST crosses the solvent T_s, beyond which point the T_s curve would rise along the LCST curve.

We note that there is an element of inconsistency in this speculation. It is assumed that a metastable state exists when the liquid is heated above its normal boiling point, and the observation is that this state exists over a wide temperature range. However, the description just presented above assumes that when the LCST is crossed, there is no metastability, and the two liquid phases are formed. There could be metastability with respect to the liquid–liquid transition as well. If so, then we have the unusual situation of two coexisting metastable states, i.e., a metastable state that could lead to two different instabilities—one liquid–liquid phase separation, and the other a vapor–liquid transition (bubble nucleation). What conditions determine which state prevails?

In order to clarify such a spectulative picture it is necessary to obtain data on the LCST, *at atmospheric pressure*, and on the limiting superheat, in the same solutions. Unfortunately, measurement of the LCST by currently known methods involves a relatively large sample volume confined by a solid interface. Such conditions make it unlikely that an LCST above the normal boiling point could be observed, since the sample would be exposed to sites that promote heterogeneous nucleation. Finally, one may hold out some hope for a theoretical (thermodynamic) approach to this problem, perhaps along the lines of the work of Sanchez.[11] It is interesting to note that phase separation in flowing polymer solutions, but with regard to the precipitation temperature, or cloud point, has been recently treated with success by Wolf[12] and by Rangel-Nafaile et al.[13]

Nomenclature

B	coefficient in eq 1
d	liquid density (g cm^{-3})
J	number of bubbles per unit volume per unit time which grow beyond critical size (cm^{-3} s^{-1})
M	molecular weight (g mol^{-1})
P_L	pressure on external liquid phase (atm)
P_V	vapor pressure (atm)
T	temperature (K)
σ	surface tension at liquid–water interface (erg cm^{-2})

Registry No. Polystyrene (homopolymer), 9003-53-6; cyclohexane, 110-82-7.

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