Experimental evidence against the existence of an ideal glass transition

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A B S T R A C T

The absolute liquid heat capacity of poly(α-methyl styrene) was determined at temperatures far below T_g and T_K in previous work by use of pentamer/polymer athermal mixtures. Here the data is compared to data compiled by Wunderlich and coworkers from 0 K to above T_g in order to obtain the absolute entropy for the polymer in its equilibrium state at temperatures as much as 180 K below the glass temperature or 130 K below the Kauzmann temperature. The results provide no evidence of a second-order transition or of a smeared transition in the entropy. In addition, we find no evidence that the entropy would become negative at a finite temperature.

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1. Introduction

The glass transition has been said to the most important unresolved problem in condensed matter physics [1]. For the last 50 years, an important framework for the glass transition has been the postulated existence of an ideal thermodynamic glass transition below the experimentally accessible transition [2,3]. The ideal glass transition was invoked by Gibbs and DiMarzio in part to resolve the Kauzmann paradox [4], the observation that the entropy of glass-forming liquids often extrapolates to zero at a finite temperature. However, several recent works suggest that, in fact, there is no need to invoke an ideal glass transition to resolve the Kauzmann paradox [5–11], including modeling of the equilibrium heat capacity of amorphous polyethylene by Pyda and Wunderlich [7,8], Monte Carlo simulations by Binder and coworkers [9,10], and work by Stillinger and coworkers [11].

A major obstacle to resolving whether or not there is an ideal glass transition is the lack of suitable experimental methods to determine the equilibrium liquid response of a glass-forming material below its glass temperature (T_g). The difficulty lies in the inordinately long times required to achieve equilibrium density as temperature is reduced below T_g. For example, although the nominal T_g is often taken to be the value corresponding to a relaxation time of approximately 100 s, the time required to reach equilibrium only 10 K below T_g increases by four orders of magni-

tude for the typical glass former, polystyrene [12]. In fact, the logarithmic increase in the relaxation times as one approaches and goes below T_g has been well-known for decades [13,14]. Consequently, it is, practically, impossible to obtain equilibrium properties in the vicinity of the Vogel (T_∞) or Kauzmann (T_K) temperatures – even though it has been demonstrated [15–17] that relaxation times do not diverge at these temperatures and it has been argued recently that the general body of literature does not support the divergence of timescales in glass-forming liquids [18,19]. However, although it is not possible to reach equilibrium density and directly measure liquid properties far below T_g, we have recently developed a novel experimental approach [20] that exploits the properties of athermal polymer/oligomer blends and makes possible the determination of the equilibrium liquid heat capacity of a polymer at temperatures far below T_g.

Blends of a polymer with its own oligomer are unique because chemically, the two components are identical except for molecular weight differences and except for potential differences caused by the end groups on the oligomer that depend on the synthesis method. An exceptional blend system is poly(α-methyl styrene) and its pentamer because the oligomer can by synthesized without chemically different initiator groups at the ends of the molecules. Consequently the only difference between the poly(α-methyl styrene) and its specially synthesized oligomer is molecular weight, and since the chemical structure is identical, it is expected that these blends are athermal. Furthermore, based on work on both poly(α-methyl styrene) and a homologous alkane series [20,21], we have shown that if the oligomer has ten atoms in its backbone

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(i.e., its degree of polymerization is five), the heat capacity is constant per mole repeat unit, and because the oligomer acts as a plasticizer, this allows us to directly measure the equilibrium liquid heat capacity of the polymer at temperatures far below T_g.

Here we describe our previous experimental results [20] demonstrating that the poly(α-methyl styrene)/oligomer system does form an ideal blend in which the heat capacity is not a function of composition. We then extend our previous analysis by comparing our heat capacity data with that compiled by Gaur and coworkers [22] from 0 K to above T_g. Matching their data with ours, we are able to obtain the equilibrium liquid entropy and enthalpy (relative to the glass values at 0 K) for the polymer at temperatures far below T_K. The results show not only that there is no evidence of a second-order transition or a smeared transition in either the entropy or enthalpy, but also that there is no evidence that the entropy becomes negative at a finite temperature. We note that since poly(α-methyl styrene) does not crystallize, we cannot determine whether the liquid entropy crosses the crystalline entropy value at a finite temperature.

2. Experimental

Poly(α-methyl styrene) and its pentamer were obtained from Polymer Source Inc. (Dorval, Canada). The oligomers were synthesized by anionic polymerization such that the chain ends do not have a different chemical structure from the repeat unit. The polymer has a molecular weight of $M_n = 1.08 \times 10^5$ and $M_n/M_w = 1.04$; T_g for the polymer is 444 K as measured on heating after cooling at 40 K/min using the step-scan procedure outlined in our previous study [20]. The molecular weight of the pentamer is $M_n = 656$ with $M_w/M_n = 1.40$. Mixtures of poly(α-methyl styrene) and its pentamer were prepared at concentrations varying from 2 to 98 wt% pentamer.

A Perkin Elmer Pyris 1 DSC with a Freon intercooler system was used in step-scan mode to obtain absolute heat capacities from approximately $T_g - 50$ K to $T_g + 50$ K for each blend and for the pentamer. Measurements for the neat polymer, however, covered the entire temperature range from 222 to 482 K. All measurements were made in a nitrogen atmosphere. The DSC temperature was calibrated by a two-point method with indium and mercury, the heat flow was calibrated with indium, and the heat capacity was calibrated in step-scan mode using a sapphire standard. The measured heat capacity of the sapphire was reproducible to within ±0.15%. The measured heat capacity of the polymer samples is reproducible to better than ±2% [20].

3. Results and discussion

The heat capacities of poly(α-methyl styrene) and its mixtures with pentamer are shown in Fig. 1. The heat capacities of all of the mixtures, as well as those of the pure polymer and pentamer, fall on the same liquid and glass lines. The fact that the equilibrium heat capacity (per gram), levels off at low degrees of polymerization supports Wunderlich's hypothesis [23,7] that polymerization suppresses the rotational and translational contributions to the heat capacity and that only the vibrational, conformational and external contributions to the heat capacity are important as chain length increases above 10 atoms. More importantly, although the values of the liquid ($C_{p\ liq}$) and glassy ($C_{p\ glass}$) heat capacities depend on the temperature, they do not depend on pentamer concentration, indicating that the blends are athermal:

$$C_{p\ liq} = 0.5541 + 0.003692T, \tag{1}$$

$$C_{p\ glass} = -0.3300 + 0.006425T - 0.000003072T^2, \tag{2}$$

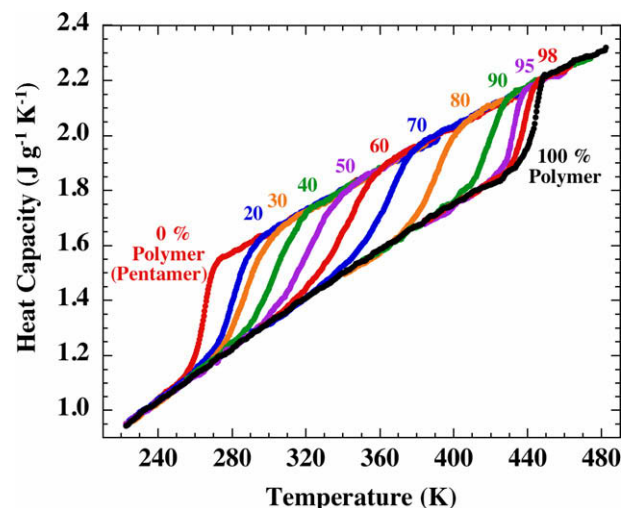where the units of C_p are J g^{-1} K^{-1} and the unit of T is Kelvin.

Fig. 1. Heat capacity vs. temperatures for mixtures of poly(α-methyl styrene) and its pentamer ranging from 0% polymer (100% pentamer) on the far left to 100% polymer on the far right. After Ref. [20]. (For best clarity, the reader is referred to the web version of this article.)

Fig. 2 compares our data with the recommended values published by Gaur et al. [22] based on three independent studies [24–26] performed in several temperature ranges and their own unpublished data. The uncertainty claimed in these prior studies ranges from 0.5% to 2%, but the uncertainty in the recommended values is not reported; furthermore the data by Lebedev and Rabinovich [24] with the lowest uncertainty did not agree with the results of Gaur and Wunderlich above 200 K and were not used. Our data is considered to be accurate to ±2%, and in the glassy state agrees well within this error with the recommended values. It should be remembered that our glassy state data is that for the pentamer, blends of polymer and pentamer, and neat polymer, the latter over the entire temperature range. The fact that our blend and pentamer data in their glassy states agrees with our polymer data from 222 K to the T_g of the neat polymer and is consistent with the data of Gaur et al. [22], supports our assertion that the heat capacity for our polymer/pentamer blends is not a function of blend composition.
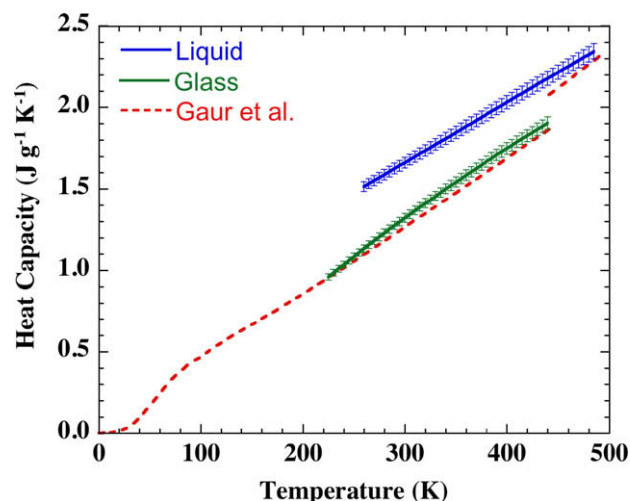

Fig. 2. Temperature dependence of the liquid and glassy heat capacities for poly(α-methyl styrene) and its blends based on the measurements shown in Fig. 1. Also shown is the data for poly(α-methyl styrene) recommended by Gaur et al. [22]. (For best clarity, the reader is referred to the web version of this article.)