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The glass transition of organic liquids confined to small pores

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The glass-transition temperatures, T_g , of organic liquids confined to small pores were studied by differential scanning calorimetry (DSC). The T_g was measured as a function of pore size in controlled pore glasses (CPG) having pore diameters in the range of 40–730 Å. The surface of the glass was treated with hexamethyldisilazane to promote wetting by the organic liquids studied (*o*-terphenyl and benzyl alcohol). Glasses formed in the pores had a lower T_g than in the bulk and the reduction in T_g increased as the pore size decreased. For example, the depression of the glass transition temperature, ΔT_g , of benzyl alcohol in 40 Å and 85 Å pores was 7.2 K and 3.1 K, respectively. The magnitude of ΔT_g also depends on the material; e.g. for *o*-terphenyl in the 85 Å pores, ΔT_g was 8.8 K versus 3.1 K for benzyl alcohol. In general, it was noted that ΔT_g was considerably less than for the depression of the crystalline melting point, ΔT_m , studied in related work. For example, for benzyl alcohol in the 85 Å pores, ΔT_m was ~ 25 K and ΔT_g was ~ 3 K.

1. Introduction

While it is well known that restricted geometries and small size have a significant effect on first-order phase transitions such as crystalline melting [1–3], solid–solid [3], and superfluidity [4] transitions, there has been little work performed to characterize the influence of these parameters on second-order or kinetic transitions, namely the liquid to glass transition [5–7]. This is in spite of the fact that the study of the behavior of glass-forming substances in confined geometries is of fundamental importance for several reasons beyond the comparison with the first-order behavior mentioned above. For example, it is possible that such studies could be used to differentiate among theories of the glass transition. Do free volume models [8–11] or entropy models [12,13] better predict the influence of geometry and size on the magnitude of the glass transition? Are the kinetics [14] involved with glassy behavior altered due to size limitations? Can small size affect the molecular mobility of glasses [6,7,14–16]? Does the limitation of the ‘size’ of the liquid which forms the glass facilitate the glass-formation process and if so, why [5–7]?

In this paper we do not address all of these

questions. However, we examine the role of system size on the glass-transition temperature and the change in the heat capacity at the glass transition. To do this, we present results from a study of two glass-forming organic liquids (*ortho*-terphenyl and benzyl alcohol) in controlled pore glasses having pore diameters, d , ranging from 40 to 730 Å. We show that the glass-transition temperature decreases as pore size decreases, although not as much as does the melting point of the same materials. The ΔC_p at T_g is independent of pore size, unlike the apparent heat of fusion at the melting point [2]. The results are discussed in terms of current ideas of the glass-transition event.

Table 1
Controlled pore glass (CPG) properties

Mean pore diameter (Å)	$\pm \%$ ^{a)}	Pore volume ^{b)} (cm ³ /g)
39.5	12.8	0.13
85	13.5	0.59
156	5.7	0.90
255	3.7	0.96
729	8.6	0.98

^{a)} 90% of the pore diameters are within this range.

^{b)} determined by mercury intrusion method.

2. Experimental

The controlled pore glasses (CPG) used in this study were supplied by Dr Wolfgang Haller of the National Institute of Standards and Technology [17]. The CPG is a white, free-flowing powder of 120/200 mesh size. The mean pore diameter, the percentage of pores that are within 90% of this size, and the pore volume (in cm^3 of liquid per g of glass) for each CPG were determined by mercury intrusion and are given in table 1. The surface of the CPG was derivatized with hexamethyldisilazane to convert the surface hydroxyl groups to trimethylsilyl groups. This treatment makes the glass more hydrophobic and promotes wetting by organic liquids. The derivatization procedure is described elsewhere [2].

A Perkin-Elmer* differential scanning calorimeter (DSC-2C) was used, and the lowest achievable starting temperature was 140 K [2]. The DSC sample pans were large volume, stainless-steel pans (Perkin-Elmer* No. 0319-0218) sealed with an o-ring to prevent liquid loss. The CPG and organic material were weighed separately into the pre-weighed sample pan so that quantitative measurements could be made. The procedures for sample preparation and instrument calibration have been described elsewhere [2].

For o-terphenyl (1,2-diphenylbenzene), the quenched glass was prepared by heating well above the melting point ($= 329.3$ K) to 350 K for 15 min and then cooling at 10 K/min to 190 K. The T_g s were then measured in heating scans at 10 K/min. For the benzyl alcohol, which is a liquid at room temperature (melting point $= 257.9$ K) the glass was prepared by cooling at 5 K/min to 140–150K and then reheating at the same rate to obtain the T_g . ΔT_g is defined as the difference between the bulk T_g and the T_g at a given pore diameter measured at the midpoint of the transition range. Values of ΔC_p were also determined as a function of pore size for each material. For benzyl alcohol, ΔT_m values were also determined as outlined elsewhere [2].

* Certain commercial companies are named in order to specify adequately the experimental procedure. This in no way implies endorsement or recommendation by NIST.

3. Results

The glass-transition temperature, T_g , was observed to shift to lower temperatures when the system size was reduced by confining the liquid to small pores. A composite of the experimental data obtained for DSC scans for o-terphenyl confined in the pores of CPG with various pore diameters is shown in fig. 1, with reference to the behavior of bulk, pure o-terphenyl. In the scans shown for the 85 Å, 255 Å and 730 Å pore diameters, the pores are filled to roughly the expected maximum pore volume for a given size (table 1), and only one T_g is observed. For the o-terphenyl in the 40 Å pores shown in fig. 1, the very large shift in T_g of 18–19 K allows a clear resolution of bulk T_g and the T_g of the pore liquid since in this case, excess liquid is included to illustrate ΔT_g directly. For all the pore diameters studied, the change in C_p from the glass to the melt is smeared out or broadened for the pore liquid relative to the bulk. This is especially

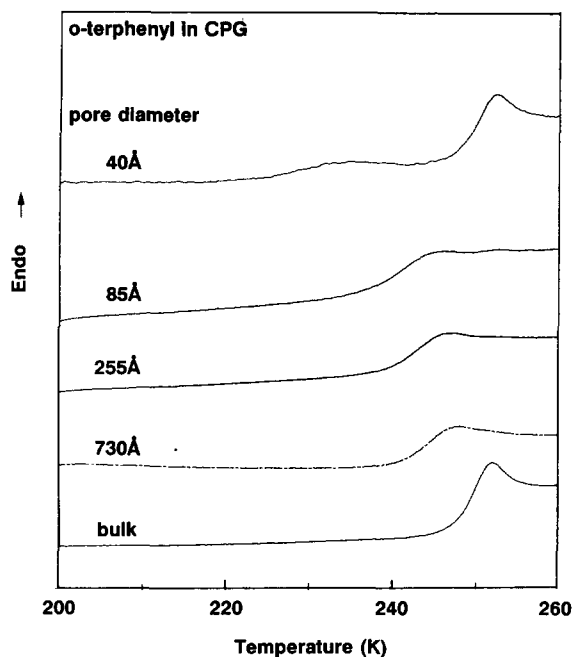


Fig. 1. Data showing the reduction in the glass-to-liquid transition temperature, T_g , of o-terphenyl confined in controlled pore glasses of pore diameters of 40, 85, 255 and 730 Å, with comparison to bulk, pure o-terphenyl shown in the bottom scan.

Table 2
 T_g , ΔT_g , ΔC_p and ΔT_m as a function of pore size

Substance	Diameter (Å)	T_g (K)	ΔT_g (K)	ΔC_p (cal/g deg)	ΔT_m (K)
o-terphenyl	40	229.9	18.2	0.09	n.d. ^{a)}
	85	239.3 ± 0.5 ^{b)}	8.8	0.13 ± 0.022 ^{b)}	
	156	241.9	6.2	0.10	
	255	242.3	5.8	0.10	
	730	243.7 ± 0.6 ^{b)}	4.4	0.11 ± 0.021 ^{b)}	
	bulk	248.1 ± 0.5 ^{b)}	–	0.13 ± 0.021 ^{b)}	
Benzyl alcohol	40	161.5	7.2	0.14	– ^{c)}
	85	165.6	3.1	0.11	25.3
	156	166.7	2.0	0.13	12.6
	730	166.0	2.2	0.15	~ 4
	bulk	168.7	–	~ 0.12 ^{d)}	–

a) n.d. = not determined for o-terphenyl, see text.

b) Mean of data ± one standard deviation.

c) No melting peak was observed for benzyl alcohol in the 40 Å pores.

d) Value is approximate due to difficulty in preparing a quenched glass in pure benzyl alcohol.

true for the 40 Å pore diameter CPG, which also has low pore volume (0.13 cm³/g), resulting in the magnitude of the transition being small compared to the other pore diameters studied.

The midpoint of the transition region of the curve was interpreted as T_g and the values of T_g , ΔT_g and ΔC_p are given in table 2 for both o-terphenyl and benzyl alcohol. Measured values for ΔT_m are also included in table 2 for benzyl alcohol

so that a comparison can be made in the magnitude of the shifts in the crystalline melting transition and the glass transition. For o-terphenyl, crystallization is more difficult and often requires long annealing periods [18]; thus the ΔT_m for o-terphenyl was not studied in this work.

In fig. 2, the T_g is plotted versus $1/d$. Several observations are apparent from these data which we present but cannot fully explain at this time. For example, at equivalent pore diameters, the shifts in T_g for o-terphenyl are greater than those observed for benzyl alcohol. Also, in the case of benzyl alcohol, the shifts in T_g appear to more closely approach zero at large pore size (~ 2 K at the 730 Å size) than for o-terphenyl (~ 4 K at the 730 Å size). A similar feature for the two sets of data is that the ΔC_p of the transition is not affected by the system size but is comparable to that measured for the bulk liquid.

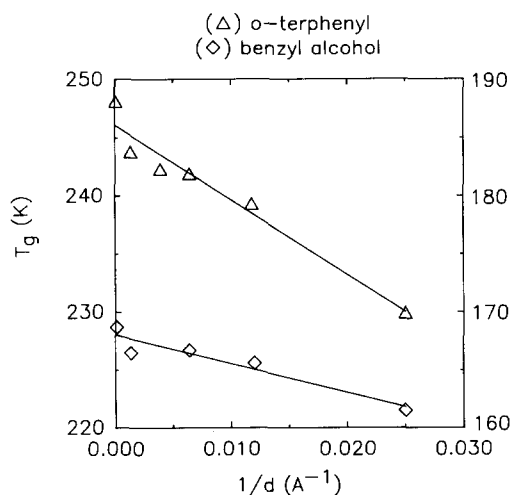


Fig. 2. T_g versus $1/d$ for o-terphenyl and benzyl alcohol confined in controlled pore glasses with diameters from 40–730 Å. The bulk T_g is given on the far left axis ($d \rightarrow \infty$) for reference.

4. Discussion

The reduction in the glass-transition temperature observed for liquids confined in restricted geometries is similar in direction, but smaller in magnitude, than the reduction of the first-order crystalline melting point, reported in detail in related work [2]. For example, benzyl alcohol in

the 85 Å pores gave a ΔT_m of ~ 25 K, while ΔT_g was only 3 K (Table 2).

The shifts in T_g observed for liquids vitrified in small pores were compared with those obtained by the microemulsion method of Angell and co-workers [5–7], and found to be very different. In their method, a similar size scale is formed during the vitrification of simple liquids dispersed in glass-forming microemulsions, with domain sizes estimated to be ~ 20 – 60 Å (from transmission electron microscopy studies) [5]. However, the very broad transition range of the vitrified liquid in the microemulsion is shifted only slightly (2 K) and is above the bulk T_g . Thus, size effects do not appear to be significant [5], within the experimental error (due to the broadness of the transition). We do not know the reason for the different results in these two systems, but suggest that the fixed nature of the controlled pore-glass geometry is a more ideal system with which to study the effect of size on T_g . As shown previously in fig. 1, the transitions observed for the pore liquid confined in CPGs are well-defined and unambiguous.

Why does a small system size so strongly influence the glass-transition temperature of o-terphenyl and benzyl alcohol? Some possible theoretical and experimental explanations for the observed reduction in T_g are now presented. Entropy models [12,13] of the glass transition would predict the entropy of a liquid in a small pore to be decreased [19], thus shifting the T_g to higher temperatures, in opposition to the experimental behavior described above. To predict the observed shift in T_g to lower temperatures, the entropy at any given temperature must increase. Similarly, based on free volume concepts of the glass transition [8–11], one would expect that free volume should increase to produce the observed shift. Either an increase in entropy or in free volume could be explained if the bulk density of the liquid in the pores is reduced, perhaps as a result of difficulty in packing the molecules. This effect would be more significant for very large molecules like o-terphenyl, and may explain why the observed shifts in T_g for o-terphenyl are larger than for benzyl alcohol. A reduction in bulk density might also occur if the glass is formed under a negative pressure [20]. For o-terphenyl, the pres-

sure dependence of T_g has been measured at positive pressures and T_g is found to increase by 20 K per kilobar [20,21]. Thus, very large negative pressure would be required to explain the magnitude of the shifts in T_g observed in this work. This appears unlikely since the cavitation pressure for o-terphenyl is -70 bar [20]. The suggestion [17] that T_g may be reduced due to plasticization of the organic glass by the trimethylsilyl groups on the surface of the CPG was discarded based on data showing similar shifts in T_g for benzyl alcohol in the untreated CPG samples.

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