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Size and confinement effects on the glass transition behavior of polystyrene/*o*-terphenyl polymer solutions

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Polystyrene (PS)/*o*-terphenyl (*o*TP) solutions confined to nanometer scale pores were studied by differential scanning calorimetry to investigate size and confinement effects on the glass transition. We observed two glass transitions T_g in all thermograms for materials confined in the controlled pore glasses. One was at a lower temperature than the bulk state T_g and the other was at a higher temperature. The lower transition temperature decreases with decreasing pore size, which is consistent with previous reports from this laboratory on small molecule glass formers and some other reports in similar systems. Although *o*TP and *o*TP/PS are not hydrogen bonding materials, we interpret the higher temperature transition as due to the existence of an interacting layer at the pore surface. A two-layer model in which there exists a ''core'' liquid in the center surrounded by the interacting layer at the pore surface is consistent with our observations.

INTRODUCTION

It is expected that the apparent thermodynamic response of a material may depend on the surrounding environment as well as on the nature of the material itself. In particular, if we consider size or constraint as environments, there has been much study of the effects of environment on both first and second order transitions. While the classic Gibbs-Thompson relation describes the effect of size and surface energy on the first order melting transition (see, e.g., Refs. 1–3), the impact of size and constraint on the glass transition, which is often treated as a second order transition, is still controversial.

Subsequent to Jackson and McKenna's report[4] of the first calorimetric study of the vitrification of glass forming liquids in controlled pore glasses (CPG's), a large number of studies have been performed of the glass transition behavior and the liquid dynamics of glass forming materials in confining geometries. Confinement has been studied by several approaches—both the methods of confinement and the methods used to probe confinement effects are diverse. Confinement has been obtained by imbibing liquids into CPG's or sol-gel pore glasses.[1,3–16] The current study falls into this class. In addition, constraints have been obtained by spin coating thin films onto substrates,[17–28] cross-linking polymer networks and swelling them with solvents or polymers,[2,11,29] creating microemulsions of glass forming materials,[30,31] taking the natural constraints arising in the amorphous region between crystalline lamellae in semicrystalline polymers,[29,32,33] or by mixing polymers with rigid nanometer size additives.[29] Block copolymers having nanometer sized domains have also been reported to show changes in the glass transition.[34–40] In the bulk of these studies it was concluded that the confining geometry or reduced size shifts the T_g by an amount ΔT_g with respect to the bulk value. Confusion in the understanding of constraint and size effects exists, however, because the sign and magnitude of the glass transition temperature change ΔT_g seems to be material, confinement and size specific. In addition, the studies also indicate that different measurements on similar systems might give different results. In some instances the changing T_g may also be affected by compositional variations.[34] The lack of a common theory to explain the glass transition itself makes it more difficult to explain size or confinement effects on it. For the thin film studies a recent review by Jones and Forrest[41] describes the current state of understanding. We also add that at a symposium held at the American Physical Society Centennial[42] meeting in Atlanta, GA, there were reports from most of the major groups working in this area. The reported results and discussions held outside of the meeting suggest a level of disagreement similar to that described in the above paragraphs. Our interpretation of the state of the field is that the different schools of thought do not fully agree on the observed phenomenology or its interpretation.

This article presents the first results from an ongoing study to use calorimetric methods to investigate the change of the glass transition behavior in confined geometries for polymer solutions having different concentrations. Here we report results related to the effect of size or confinement on the glass transition of *o*-terphenyl/polystyrene (*o*TP/PS) solutions by examining their behavior in controlled pore glasses. The results are compared with those for *o*TP alone. To our knowledge, there are no other reports of the calorimetric response of polymer solutions in CPG's, although the dynamical response above the glass transition has been examined using dielectric spectroscopy (DE).[11]

EXPERIMENTAL

Materials

The CPG's used in this study were supplied by Dr. Wolfgang Haller of the National Institute of Standards and Technology (NIST).[43,44] The CPG's come in the form of a white and free-flowing powder of 120/200 mesh size (0.15–0.17 mm). The mean diameter of the glass beads was obtained from optical microscopy. The mean pore diameter, the range

TABLE I. Controlled pore glass properties (Ref. 44).

	Pore diameter [nm]	Pore distr.[a] [%]	Pore vol. [cm^3/g]	Surface area[b] [m^2/g]	Beads diameter[c,d] [mm]
CPG1	11.6	8.6	0.78	155	0.175 ± 0.043
CPG2	25.5	3.7	0.96	95.5	0.170 ± 0.041
CPG3	47.9	4.3	1.26	59.5	0.151 ± 0.033

[a] 90% of the pore diameters are within this range.

[b] Determined by the nitrogen adsorption method (BET equation).

[c] Determined by optical spectroscopy.

[e] Mean of data ± one standard deviation.

of diameters that describes 90% of the pores, and the pore volume for each CPG were determined by mercury intrusion. The values as reported by Haller[44] for the glasses used here are given in Table I.

We derivatized the surfaces of the CPG's with hexamethyldisilazane to convert the surface hydroxyl groups to trimethylsilyl groups. The procedure followed has been described previously.[1] This treatment makes the glass surface more hydrophobic and promotes wetting by organic liquids. Each CPG was first cleaned with chloroform for 24 h. The chloroform was decanted off and the CPG was dried thoroughly in a vacuum oven at 100 °C. The hexamethyldisilazane was then added to cover the glass beads, stirred with a spatula to release trapped air bubbles, and heated at 55 °C for 24 h. Following this treatment, the reagent was decanted off and the CPG was rinsed well with chloroform and dried thoroughly in a vacuum oven. The CPG was stored in a desiccator when not in use.

The *o*-terphenyl (1,2-diphenylbenzene) (*o*TP) was obtained from Aldrich Chemical Co. (99% purity) and used without further purification. The polystyrene (PS) (manufacturer supplied values for $M_p = 100\,000\,\mathrm{g\,mol^{-1}}$ and PDI $= 1.05$) was obtained from PSS (Germany) and used without further purification. Each amount of PS was dissolved in *o*TP at 80 °C for 48 h. The concentration window was higher than the overlap concentration (c^*).[45] For the PS used here, c^* was calculated to be 0.0506 g/cm^3 (see Table II). The PS concentrations used in this study ranged from c^* to $4c^*$ and are given in Table II.

Considerations of solvent quality and diffusion into the pores

We could not find quantitative data for the solution properties of PS in *o*TP, although a few studies report *o*TP to be a good solvent for PS. These studies[46,47] provide no quantitative estimate, however, of the solvent quality. We chose *o*TP as the solvent for PS because it was used in the prior study by Jackson and McKenna,[4] its glass transition temperature is within the range of our experimental apparatus and it has an appropriate solubility parameter as a good solvent for the PS $[\delta_{OTP} = 18.08 \times 10^3\ (\mathrm{J/m^3})^{0.5}]$.[48] This value allowed us to estimate the basic properties of PS in *o*TP.[49] The estimated solution properties from the solubility parameter are listed in Table III. For the parameters in the Mark-Houwink-Sakurada (MHS) equation α is 0.703. This indicates that *o*TP is a good solvent for PS.

In establishing the experimental procedures, it was thought to be necessary to determine the time required to ''soak'' the CPG's in the polymer solutions for long enough that they equilibrate in the pores, i.e., for the PS chains to fully diffuse into the CPG's. First, the diffusivity as a function of molecular weight was estimated for the dilute solution limit. It is, then, straightforward to get the diffusivity for the PS chain in the semi-dilute regime. To estimate the diffusivity into the pores in the semidilute regime, we followed the work of Karasz and co-workers.[50,51] Taking the concentration dependence of the diffusivity of PS in 2-fluorotoluene for each molecular weight and the pore diameter dependence of diffusivity of the semidilute solution in the pore (D_1) we

TABLE II. Diffusion properties of *o*TP/PS solutions in each size CPG.

	Concentration of PS (mass fraction)	c [g/cm^3]	c/c^{*a}	$D_1[\times 10^{12}\ \mathrm{m^2\,s}](t_{\mathrm{ul}}[h])$		
				CPG1	CPG2	CPG3
*o*TP/PS1	0.0468	0.0506	1.0	2.203 (0.95)	2.287 (0.87)	3.043 (0.35)
*o*TP/PS2	0.0923	0.1012	2.0	2.920 (0.71)	3.032 (0.66)	4.033 (0.27)
*o*TP/PS3	0.1282	0.1518	3.0	3.443 (0.61)	3.575 (0.56)	4.755 (0.27)
*o*TP/PS4	0.1640	0.2024	4.0	3.871 (0.54)	4.018 (0.50)	5.344 (0.20)

[a] $c^* = M_p/[N_A(2^{1/2}R_G)^3] = 0.0506\,\mathrm{g/cm^3}$ (Ref. 45), where M_p: Peak of molecular weight distribution, N_A: Avogadro's number, R_G: Radius of gyration.

TABLE III. Solution properties of *o*TP/PS solution.

Solution property	Equation
Intrinsic Viscosity [cm^3/g]	$[\eta]=0.0126\,M^{0.703}$
Radius of Gyration [nm]	$R_g=0.0151\,M^{0.5677}$
Diffusion Coefficient at $c\to 0$ [cm^2/s]	$D_0=0.2631\times 10^{-4}\,M^{-0.5677}$

estimated the ultimate time t_{ul} for the polymer solutions to enter into the pores from Eq. (1).[45] After the ultimate time, the average concentration in the pore diameter is expected to be constant. The parameter d in Eq. (1) is the diameter of the CPG particles.

$$\frac{\overline{c_I}(0)}{c_{I,\mathrm{eq}}}=1+2A\sum_{n=1}^{\infty}(-1)^n S_n \exp\left[-\left(\frac{n\pi}{d}\right)^2 D_I t\right],$$

where

$$S_n\equiv\int_0^{nx}\frac{\sin x}{x}\,dx. \tag{1}$$

The in-pore diffusivity and ultimate time for each solution are given in Table II. In our preparation of samples, the CPG's were soaked in the solutions for times much greater than t_{ul}. However, we note that in actual practice the *o*TP and the *o*TP/PS solutions seemed to be drawn into the pores through capillary action rather than by simple diffusion.

Calorimetry

The Perkin-Elmer DSC7 used in this study was equipped with an intercooler system to operate from −60 °C. The instrument was calibrated using an indium standard at a heating rate of 10 °C. The oven in the instrument was purged with helium gas and the exterior enclosure of the machine was purged with dried air. The sample pans used in this study were large volume, stainless-steel pans (Perkin-Elmer No. 0319-9128). We did not use an *o*-ring for sealing the pans because it caused a spurious signal in the temperature range of interest here. Preparation of samples proceeded by first adding to each sample pan approximately 10 mg of CPG and an amount of the *o*TP/PS mixture comparable with the pore volume of the CPG. All CPG/solution mixtures contained in the sample pans were stored in an oven at 80 °C ±0.2 °C to let them have a sufficient time to diffuse the solution into the inside of the CPG pore (see previous section). [The *o*TP/PS mixture had been rapidly quenched into dry ice and retained a solid form at room temperature such that we could break the material into a powder form. This was easier to work with than the material in the form of a solution. When the material was heated to 80 °C it was a liquid and could diffuse into (or be pulled into) the CPG.] We ran DSC scans for each silanized CPG alone to assure that the pore glasses themselves did not have an appreciable thermal signal within the temperature range of our experiments.

To measure the glass transition response, samples were maintained at 90 °C for 30 min to erase any prior thermal history. Samples were then quenched to −60 °C at a nominal 200 °C/min cooling rate. And they were kept at −60 °C for 5 min to stabilize the machine and heated to 90 °C with 10 °C/min heating rate. The heating programs used for the DSC study and the heat treatment are illustrated in Fig. 1. Before and after the DSC experiments the samples were reweighed to ensure that the pans were sealed properly. No weight-loss was detected.

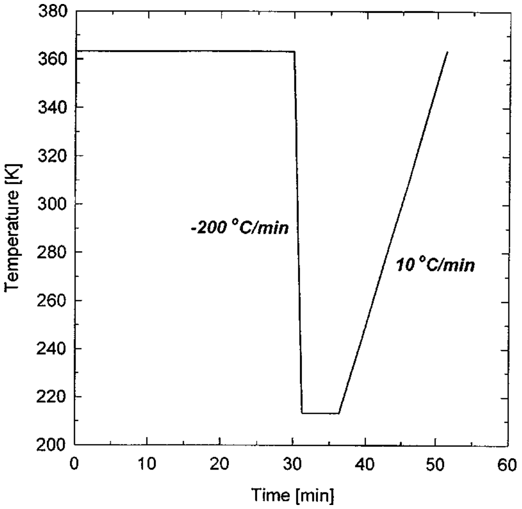

FIG. 1. Diagram of the thermal program followed in DSC measurements of the samples.

We remark that during slow cooling of the solvent without the presence of the CPG there was a crystallization trace that could have an effect on the glassy properties. There was no crystallization trace in the 200 °C/min quenched *o*TP. The results reported here are for experiments conducted by heating at 10 °C/min following the 200 °C/min quench. (The cooling rate in these experiments was chosen to be 200 °C/min, which is significantly faster than the rate used in the Jackson and McKenna[3,4] studies. This is because the pure *o*TP used here crystallized in the slow cooling experiments. In a set of studies with the polymer solutions and with material in the pores where crystallization did not occur, we found that the effect of cooling rate was small and did not dramatically impact the results reported here.) We used the fictive temperature T_f as the T_g in all measurements.[52] T_f was calculated using the integration method to obtain the enthalpy as a function of temperature.[52] We used T_f as the T_g because it provides a consistent estimate of the relevant glassy state formed upon cooling that is relatively insensitive to the enthalpy relaxation process that occurs during the heating step. The reader is referred to Refs. 53 and 54 for discussion of the errors involved in DSC measurements of the glass transition temperature and the fictive temperature.

RESULTS

Figure 2 shows the DSC thermograms for *o*TP and *o*TP/PS solutions in the bulk state. The glass transition can be seen to shift weakly to higher temperatures with increasing concentration of PS. Figure 3 shows the change of glass transition temperature of the *o*TP/PS solutions as a function of PS concentration. The increase in T_g is less than expected from the Gordon equation for the composition dependence of the glass transition temperature in polymer-diluent systems.[55] (This weak dependence of T_g on the concentration

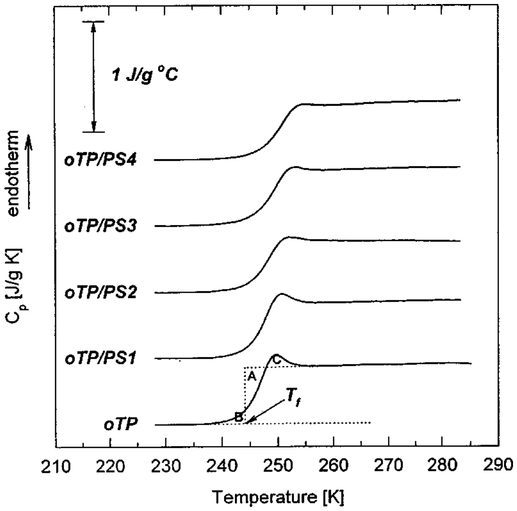

FIG. 2. DSC thermograms of *o*TP and *o*TP/PS solutions in the bulk state during 10 °C/min heating ramp following a 200 °C/min quench. The fictive temperature, T_f, was determined as a temperature at which the area of A is same as the sum of B and C.

of PS in this concentration range makes the *o*TP/PS system a good one for the current study because it decreases errors induced by possible uncertainties in the concentration of the solution within the CPG). The previous work of Jackson and McKenna[4] indicated that crystallizing liquids form plugs rather than wetting the interior surface of the CPG. The formation of a plug minimizes the contact of the liquid with the glass surface, suggesting poor wetting characteristics, a high contact angle of the liquid with the interior pore surface and relatively flat menisci for the liquid-vapor interfaces. The DSC thermograms for *o*TP/PS1 (0.046 mass fraction) solution in the CPG1 ($d = 11.6$ nm) at pore fillings of 0.45, 1.00, and 4.14 (ratio of total solution volume to pore volume in the DSC pan) are shown in Fig. 4. The behavior of the bulk solution is shown at the bottom of the figure for reference. The expected pore volume for CPG1 is 0.78 cm^3/g (Table I). The T_g in the pore is found to be independent of the degree of pore filling, indicating that the solution forms plugs rather than wetting the interior surfaces of the CPG. This is consistent with the prior results of Jackson and McKenna.[1,4] In the case of the solution overfilled to 4.14 times the pore volume, the T_g of the bulk solution becomes apparent as well. Interestingly, the DSC thermograms for the *o*TP or *o*TP/PS solutions confined in the pore show what appear to be two glass transitions. One is at a higher temperature than the bulk state T_g and the other is at a lower temperature. These are discussed in detail subsequently.

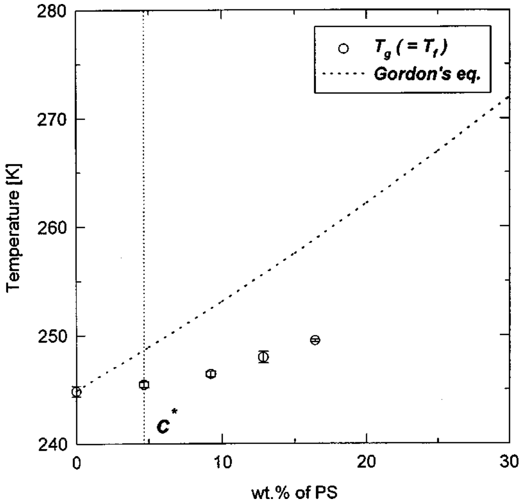

FIG. 3. Concentration effect on the glass transition T_g (Fictive temperature T_f), of *o*TP/PS solutions ($c^* =$ overlap concentration).

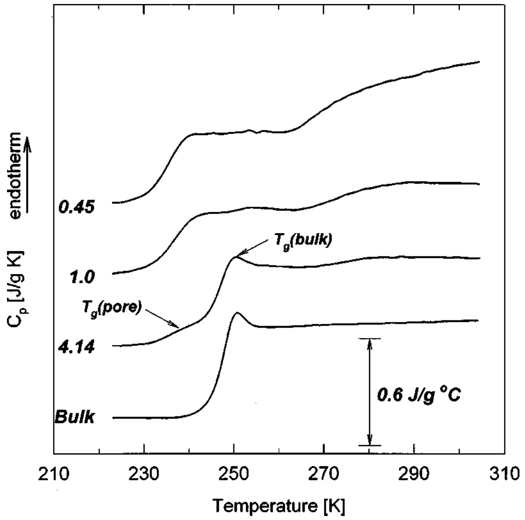

FIG. 4. DSC thermograms for the *o*TP/PS1 solution in CPG1 (11.6 nm pore diameter) at various degrees of pore filling (ratio of total solution volume to pore volume in the DSC pan) during 10 °C/min heating ramp following a 200 °C/min quench. DSC thermogram for *o*TP/PS1 solution in the bulk state is shown at the bottom of the figure for reference.

The DSC thermograms for the pure *o*TP and the *o*TP/PS solutions in each of the three pore sizes are compared with those in the bulk materials in Fig. 5. All thermograms for the materials in the pore have an additional transition at a temperature higher than the T_g of the bulk material. Figure 5(a) depicts the fictive temperature construction used to estimate the values for the upper and lower transition temperatures from the thermograms. We also note that some of the thermograms exhibit a hump between the two major transitions and we ascribe this to an excess of material that is outside of the pores and, therefore, exhibits bulk behavior.

In earlier work, it was noted[3] that from Kauzmann's notation,[5,6] the ratio of T_g and T_m is often near $\frac{2}{3}$ for many glass-forming liquids. This suggests that the glass and melting transitions reflect a common tendency toward order, even if the transitions do not belong to the same class, and that the transition temperatures might vary similarly. The Gibbs-Thomson equation predicts that the melting point depression in confined geometries varies as the inverse of the pore diameter. This suggests that it is reasonable to plot the observed transition temperatures against inverse pore diameter and we present our data in this fashion.

The effect of pore size on the values T_{lo} and T_{hi} for *o*TP and *o*TP/PS solutions is shown in Figs. 6 and 7. As seen in Fig. 6, the ΔT_{lo} (as $[T_g(1/d) - T_g(\infty)]/T_g(\infty)$) of *o*TP and the *o*TP/PS solutions decreases with decreasing pore diameter (increasing $1/d$). [$T_g(\infty)$ is the T_g of the bulk-state material.] The shift of T_{lo} in the CPG from the bulk state increases as the PS concentration increases. We also note that

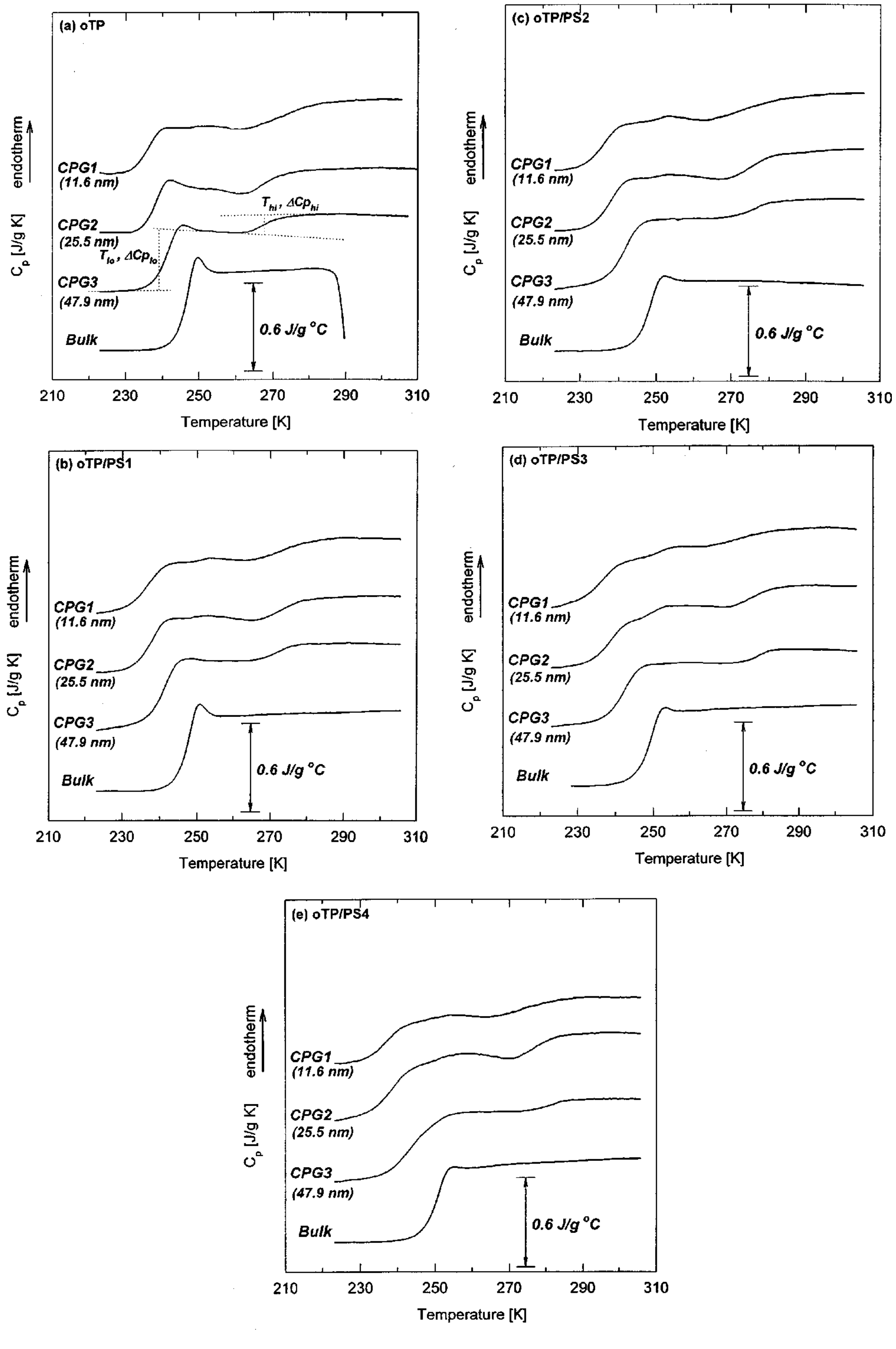

FIG. 5. DSC thermograms for (a) *o*TP, (b) *o*TP/PS1, (c) *o*TP/PS2, (d) *o*TP/PS3, and (e) *o*TP/PS4 during 10 °C/min heating ramp following a 200 °C/min quench.

the change in T_{lo} is dramatic when one goes from the bulk to the largest pore ($d = 47.9$ nm; $1/d = 0.021\,\mathrm{nm}^{-1}$). Then the rate of change of T_{lo} vs $1/d$ begins to slow. The differences between the two smallest pore sizes are only of the order of 1.5 °C or less (see Table IV).

The change of T_{hi} vs $1/d$ for the *o*TP and low concentration solutions shows a different behavior from that of the highly concentrated solutions. For the pure *o*TP there is a monotonic increase in T_{hi} as $1/d$ increases and the low concentration solutions show a maximum in T_{hi} at $1/d \approx 0.04$. The more highly concentrated solutions show monotonic decreases in T_{hi} as $1/d$ increases.

Finally, if one examines the thermograms [Figs. 5(a)–5(e)], it can be seen that the values for the total change in the heat capacity ΔC_p are approximately the same as for the bulk material (0.52 J/gK). This allows the decomposition of the heat capacity change into contributions from the T_{hi} and T_{lo} transitions. This is considered in the Discussion section.

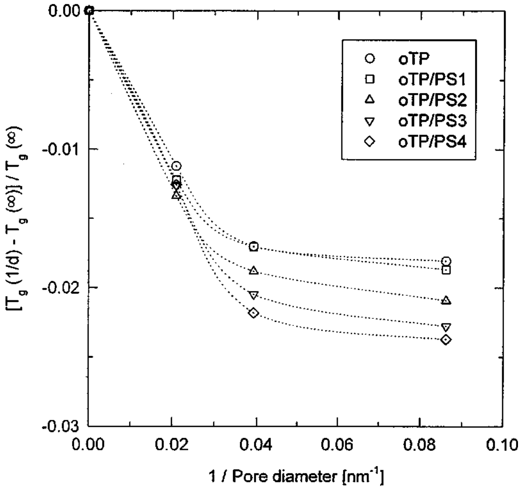

FIG. 6. $[T_g(1/d) - T_g(\infty)]/T_g(\infty)$ versus $1/d$ for oTP and oTP/PS solutions for the lower glass transition. [$1/d$ refers to the material in the pore and ∞ refers to the bulk material].

DISCUSSION

In the above we have described the calorimetric behavior of ortho-terphenyl/polystyrene solutions in nanometer scale pores. The major event seen is the downward shift of a lower glass transition with decreasing pore size and the existence of an additional glass transition at temperatures higher than the bulk T_g in both oTP in the absence of PS and all of the oTP/PS solutions investigated. The results are summarized in Table IV. The reduction of the glass transition of the oTP relative to the bulk material is consistent with what was observed previously using DSC by Jackson and McKenna[3,4] for oTP and benzyl alcohol and by Jonas and co-workers[5,6] for a series of small molecule glass formers. The presence of a second transition at a higher temperature, however, was not reported in those studies and the reasons for this are currently unclear. One possibility is the use of a different calorimeter in this study and another is that the oTP used in this study is 99% pure and not the high purity material used by Jackson and McKenna. This, however, would not explain the lack of a second transition in the other solvent systems. Upon reexamination of the original Jackson and McKenna notebooks we found that there was evidence of a second transition of only slightly lower magnitude than that reported here. However, in some experiments the transition did not appear and in others it may have been present, but obscured by the onset of crystallization. We also note that in prior studies,[3,4] the reported values of ΔC_p, while nearly invariant with pore diameter, and showing a relatively large uncertainty, were somewhat lower than the value for bulk oTP. This would be consistent with the observations here—except that the other transition was not always observed. Also, we obtained some of the original samples and, in the current experimental apparatus, found behavior similar to that reported here. However, the upper transition was observed, in the 8.5 nm pores, to be at only 260 K, which is lower than an extrapolation of our results could explain. Why this would be, is unclear at this time. The sample being 10 years old or an extreme sensitivity of the higher transition to the details of the surface treatment are possible reasons. Hence, we do not think that the results here contradict the prior work, but build on it with the observation of the second transition not obvious in the prior work for unknown reasons.

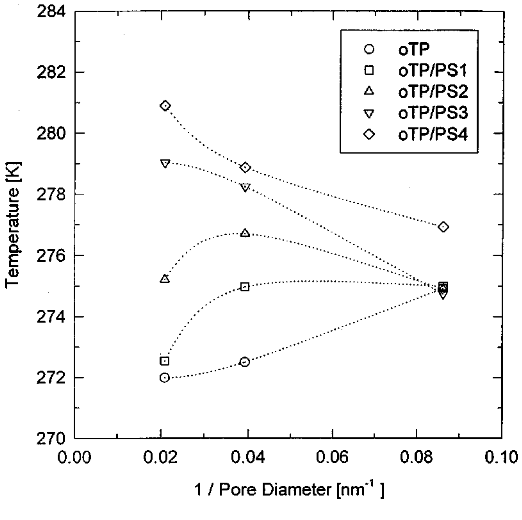

FIG. 7. Higher glass transition temperature $T_{\rm hi}$, versus inverse pore diameter for oTP and oTP/PS solutions in the CPG.

In addition, we sent samples of our material and the original samples to Simon[57] who kindly ran experiments on an apparatus similar to that used here. Her results were the same as those we obtained for the entire set of samples. We also note that Donth[58] has observed the two transitions with a different type of DSC apparatus and for a different small molecule organic compound.

We also note that experiments using dielectric spectroscopy have reported shifts of the T_g in porous glasses both downwards[8,10–16] and upwards[7,9,13,15] relative to the bulk material. In addition, some of the dielectric work has reported[11–14] two relaxation processes in the liquid state in the porous glasses which is consistent with the observation here of a lower and higher T_g.

In our view, it is appropriate to assign $T_{\rm lo}$ as the glass transition temperature of a ''core'' liquid in the pore and $T_{\rm hi}$ as the glass transition temperature of an interacting ''surface'' layer. Here we are assuming that we have concentration homogeneity across the pores. Such a contention is supported by the observation that the pure oTP exhibits both transitions. We note also that the $T_{\rm hi}$ values are generally 30 to 40 °C higher than $T_{\rm lo}$ and approximately 30 °C above the bulk glass transition temperature for all of the systems studied. In the concentration range in which we are working this would imply a concentration difference of, perhaps 30%, between the core liquid and that constrained at the surface based on the Gordon[55] equation discussed above (see also Fig. 3). For the actual oTP/PS solution studied here, the differences would need to be even greater. However, we have no other direct evidence that there is not a partitioning of the polymer and solvent between the surface layer and the core liquid.

From a theoretical view, the two classical approaches to the glass transition event,[59] the configurational entropy model of Gibbs and DiMarzio[60] and the general class of free volume models, might cause one to look for alternate explanations for the behavior in the confined liquid. If only the entropy theory is considered, the decreases in entropy due to the confinement can be expected to result in an increase in

TABLE IV. Parameters for upper and lower glass transition for PS/*o*TP and PS/*o*TP solutions in CPG's.

Pore diameter [nm]	Mass fraction of PS	$T_{\mathrm{lo}}\,[K]$a,b	$T_{\mathrm{hi}}\,[K]^{\mathrm{a,b}}$	$\Delta C_{p,\mathrm{lo}}$ [J/g K]	$\Delta C_{p,\mathrm{hi}}$ [J/g K]	Thickness of interacitng layer $[\mathrm{nm}]^{\mathrm{b,c}}$	Volume fraction of upper T_g material
11.6 (CPG1)	0 (*o*TP)	235.48 ± 0.67	274.92 ± 1.46	0.400 ± 0.067	0.223 ± 0.050	1.15 ± 0.14	0.357 ± 0.040
	0.047 (*o*TP/PS1)	235.75 ± 0.11	275.00 ± 0.62	0.378 ± 0.043	0.174 ± 0.050	0.99 ± 0.21	0.312 ± 0.070
	0.092 (*o*TP/PS2)	235.54 ± 0.13	274.91 ± 1.34	0.413 ± 0.067	0.182 ± 0.050	0.96 ± 0.14	0.303 ± 0.040
	0.128 (*o*TP/PS3)	236.10 ± 0.43	274.75 ± 1.89	0.355 ± 0.120	0.120 ± 0.679	0.76 ± 0.33	0.242 ± 0.099
	0.164 (*o*TP/PS4)	237.10 ± 0.22	276.93 ± 1.36	0.316 ± 0.069	0.141 ± 0.050	0.96 ± 0.18	0.302 ± 0.051
25.5 (CPG2)	0 (*o*TP)	236.00 ± 0.67	272.50 ± 0.78	0.421 ± 0.071	0.238 ± 0.042	2.58 ± 0.42	0.362 ± 0.052
	0.047 (*o*TP/PS1)	236.59 ± 0.45	274.96 ± 0.92	0.424 ± 0.051	0.193 ± 0.031	2.18 ± 0.20	0.312 ± 0.026
	0.092 (*o*TP/PS2)	236.63 ± 0.23	276.69 ± 1.19	0.421 ± 0.047	0.195 ± 0.023	2.21 ± 0.18	0.317 ± 0.023
	0.128 (*o*TP/PS3)	237.29 ± 0.72	278.23 ± 0.81	0.369 ± 0.082	0.152 ± 0.034	2.03 ± 0.22	0.292 ± 0.029
	0.164 (*o*TP/PS4)	238.10 ± 0.37	278.87 ± 0.80	0.430 ± 0.108	0.169 ± 0.044	1.95 ± 0.11	0.282 ± 0.015
47.9 (CPG3)	0 (*o*TP)	239.03 ± 0.32	271.98 ± 1.72	0.414 ± 0.060	0.162 ± 0.052	3.59 ± 0.69	0.277 ± 0.048
	0.047 (*o*TP/PS1)	239.10 ± 0.21	272.54 ± 1.06	0.465 ± 0.032	0.113 ± 0.022	2.45 ± 0.30	0.194 ± 0.022
	0.092 (*o*TP/PS2)	239.46 ± 0.41	275.21 ± 1.09	0.466 ± 0.061	0.103 ± 0.035	2.17 ± 0.45	0.173 ± 0.034
	0.128 (*o*TP/PS3)	241.41 ± 0.23	279.03 ± 1.49	0.433 ± 0.046	0.096 ± 0.022	2.26 ± 0.28	0.180 ± 0.021
	0.164 (*o*TP/PS4)	242.93 ± 0.30	280.90 ± 1.11	0.486 ± 0.085	0.083 ± 0.031	1.77 ± 0.32	0.142 ± 0.025
∞ (bulk)	0 (*o*TP)	244.83 ± 0.49		0.524 ± 0.025			
	0.047 (*o*TP/PS1)	245.44 ± 0.27		0.502 ± 0.007			
	0.092 (*o*TP/PS2)	246.41 ± 0.27		0.472 ± 0.033			
	0.128 (*o*TP/PS3)	247.96 ± 0.53		0.481 ± 0.021			
	0.164 (*o*TP/PS4)	249.49 ± 0.12		0.463 ± 0.021			

[a] Fictive temperature.

[b] Mean of data ±one standard deviation.

[c] Thickness$=d[1-(1-\Delta C_{p,\mathrm{hi}}/\Delta C_{p,\mathrm{tot}})^{1/2}]/2$, where $d=$pore diameter.

T_g. On the other hand, both the entropy theory and the free volume models suggest that a decrease in density, due to a hydrostatic tension, could cause the decrease in T_g. Zhang *et al.*[5] suggested that a negative hydrostatic pressure induced by the surface tension in a small cylindrical pore could be responsible for the observed downward shift in T_g in a confined geometry. In this case the negative hydrostatic pressure for a liquid in a cylindrical pore would be

$$\Delta P=-\Delta\sigma/R, \tag{2}$$

where $\Delta\sigma$ is the surface tension of the liquid and R is the pore radius. In *o*TP the surface tension[61] is 20 mN/m and $dT_g/dP=0.26\,^{\circ}\mathrm{C/MPa}$.[62] Then for the smallest pore diameter of 11.6 nm used in this study, the estimated decrease in T_g would be approximately 1.8 °C—which is obviously significantly smaller than the 9.3 °C decrease seen here (see Table IV). In addition, Jackson and McKenna[4] argued that the fact that the materials seem to form plugs in the pores implies that Eq. (2) is not correct for liquids in the CPG's. The other possible cause of a large hydrostatic tension would be the differences in coefficient of thermal expansion between the CPG's glass matrix and the *o*TP. An estimate[4] of the magnitude of the negative pressure change due to the coefficient of thermal expansion mismatch between *o*TP and the CPG suggests that it is too small to account for the observed depression. We do note, however, that the T_g depression observed sometimes in block copolymers has been attributed[35,38] to a negative hydrostatic tension. Clearly, the effect of confinement or size on the T_g is not readily explained from current theories of the glass transition. In addition, the multiple effects seen here and in other experiments seem to make simple explanations difficult.

The upper transition temperature was not reported in the prior[3,4,5] calorimetric experiments on glass-forming materials in CPG's. In the dynamic experiments (DE or NMR), however, two relaxations have been observed in the confined liquid above T_g.[6–14,16] The higher temperature glass transition observed in this DSC study may correspond to the additional dielectric loss peak (ε'') observed at lower frequencies[7–14,16] or an additional slower reorientational correlation time in ^{2}H-NMR relaxation experiments.[6] Most of the results have been explained as interactions at the liquid-solid interface, such as hydrogen bonding at the pore surface. The CPG's originally have polar -OH groups on the glass surface and these cause some H bonds with the imbibed molecules. However, the existence of the additional loss peak at lower frequencies when the pore surfaces are treated, as in this study, suggests a simple interaction between the imbibed solvent and the pore surface. In addition to the CPG systems, the effects of confinement and interface effects have been examined in thin polymer films using various tools such as elipsometry,[17,18,25] x-ray reflectivity,[19,20] surface force measurements,[21–23] positron annihilation,[26–28] etc., although there seems not to be full agreement on the direction in which the T_g changes. Some of these results also suggest an additional glass transition due to an interacting layer. For example, DeMaggio *et al.*[28] suggested a three-layer model consisting of an interface layer contacting the solid substrate (solidlike), a surface layer contacting either air or vacuum (liquidlike), and bulk layer between both surface layers. The thickness of each layer would vary according to the strength of the interaction at the interface layer.

In addition, the glass transition behavior of the amorphous phase in semicrystalline polymers under various crystallization conditions seems to indicate that confinement between crystalline lamellae[29,32,33] increases the T_g. Similar effects have been seen in nanocomposites reinforced with exfoliated clays.[29] Finally, in block copolymers the glass transition has been reported to both decrease and increase. The depression has been attributed to both compositional effects[34] as well as to a negative hydrostatic pressure[35,38] induced by the coefficient of thermal expansion mismatch between the blocks.

For the results reported in this study, we suggest that a two-layer model may provide some explanation of the additional, higher temperature, glass transition that we observed. We postulate the existence of two layers: a ''core'' solution and a ''surface'' or interface layer that is constrained. Recalling Fig. 6, T_{hi} of pure *o*TP increased with decreasing pore size (increasing $1/d$). This is similar to the behavior of the additional loss peak in the H-bonded glass forming material in a CPG. The result was explained as an H-bonding interaction within the pore. The probability of an interaction would be proportional to the pore surface/pore volume ratio. Forrest *et al.*[25] have discussed the existence of a restricted layer, which they expected to be equal to the end-to-end distance of the polymer even in the hard neutral wall of a pore. We believe that there is some restriction by the silanized CPG pore surface, although it should be weaker than the H-bonding interaction.

The T_{hi} of the more highly concentrated *o*TP/PS solution decreased with decreasing pore size. In this case it may be that the PS chains in the ''core'' solution affect the motion of the *o*TP/PS solution constrained by the pore surface. The PS chain in the ''core'' solution is unconstrained and can move easily. As a result, it can change the relaxation behavior of the *o*TP/PS solution on the pore surface because the PS molecule is large enough to span the two layers. The spanning PS chains cause the *o*TP/PS solution on the pore surface to move more easily (plasticize the surface layer). Therefore, the pore size dependence of the *o*TP/PS solution of the interface layer becomes closer to that of the ''core'' solution. This phenomenon was not seen in the pure *o*TP because its molecular size is too small to span the two layers. Further work using other molecular weight solutions may help elucidate this point.

As part of our consideration of the two-layer model, we estimated the thickness of the interacting layer in the pore in a way similar to that of Gorbatchow *et al.*[13] who estimated it from the dielectric strength of the two relaxation modes. We assumed that the heat capacity changes at the glass transition of each phase were proportional to the number of molecules participating in the relevant transition process. Assuming a cylindrical pore shape the thickness of the interacting layer on the pore surface r_s could be estimated from the ratio of the ΔC_p's for the low-temperature and high-temperature transitions. [The method to estimate the values of ΔC_p for each is illustrated in Fig. 5(a)]. In Table IV the surface or interacting layer thicknesses for each system are tabulated. The thickness of the surface layer is compared with the pore radius for the different CPG's and PS concentrations in Fig. 8. There are several things to notice from these data. First, for each pore diameter the thickest layer is for the pure *o*TP. Second, the layer thickness declines as the concentration increases except for the smallest pore diameter in which the solution layer thicknesses seem essentially constant. Third, for the solutions the interacting layers seem to have approximately the same thickness in the 47.9 and 25.5 nm pores (2–2.5 nm), while in the smallest pores, the surface layers seem to be much thinner (≈1 nm). It is unclear why the surface layers would exhibit such behavior. In addition, based on the observation in the above paragraphs where it was argued that the PS chains ought to be able to span the layers, why the smallest pores would have the thinnest layers becomes surprising. Obviously further study is required to fully understand the behaviors described here.

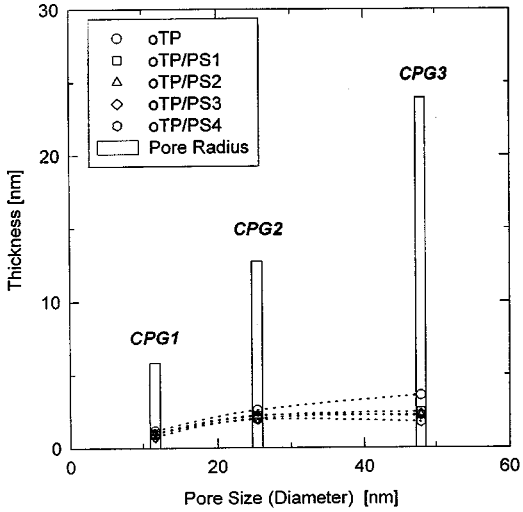

FIG. 8. Comparison of the interacting-layer thickness with pore radius for each CPG and for the various *o*TP/PS solutions.

As an additional note, we point out that computer simulations of polymer melts suggest[63,64] that the material at the surface aligns with the surface and that the diffusion coefficients parallel and perpendicular to the wall differ. Whether these results are general or limited to polymers remains to be investigated.

As another consideration, we have calculated the volume fraction (actually thermal signal fraction) of the two types of material (that corresponding to the upper transition and that corresponding to the lower transition) and the results for the upper T_g material are also depicted in Table IV. As seen, the volume fraction is approximately constant at about 0.3 for the two smaller pore sizes and much smaller for the largest pore size. Also, from this perspective, the *o*TP alone has a volume fraction in each layer that is relatively independent of the pore diameter. Here one need only recognize the existence of two types of material without regard to where they are located. A sort of phase-separated heterogeneity seems possible, but that would make little sense in light of the fact that the *o*TP alone also shows both transitions. From our view, the two-layer model seems reasonable.

Finally, we consider one other aspect of the confinement problem. It is well known that the glass transition temperature is path dependent.[59,65,66] Therefore, one might ask what is the path being followed in the CPG and how does it compare with the path of glass formation in other experiments, such as thin films. In some experiments that are relevant to this discussion, Colucci *et al.*[67] showed the behavior of a polymeric glass forming material in both isobaric glass formation conditions and in isochoric (constant volume) glass formation conditions. While the glass formation points were the same in pressure, volume, temperature space for the same cooling rates, the isochorically formed glasses had higher densities than the isobarically formed glasses with the same formation points. The CPG formed glasses might be isochoric glasses. What happens as one heats the glass towards the liquid state, which becomes a one atmosphere liquid, is unclear. A hint of the possible ‘‘anomalous’’ sort of behavior one might see is provided by the work of Angell and Qing[68] in which *o*TP was studied in nearly isochoric conditions to obtain cavitation. There, the apparent volume-temperature behavior upon reheating would suggest that the coefficients of thermal expansion for the glass formed under a negative hydrostatic pressure was dramatically less than that obtained for the glass formed at one atmosphere. (The reader is referred to Ref. 68 for details.) Yet, the Colucci *et al.*[67] work showed that the coefficient of thermal expansion, upon cooling, the isochoric glass was significantly greater than for the isobaric glass. Furthermore, in thin films, the path for vitrification is very complicated because the materials are spin coated and go through the glass transition as the concentration of the solution changes—a change that may involve several percent in volume. If one looks at Ferry[69] the concentration dependence of T_g of polystyrene in toluene would result in the T_g being near room temperature (where much spin coating occurs) at approximately 15% by mass of toluene. Because the films are constrained during glass formation, these large volume changes become anisotropic (confined to the film thickness) or give rise to residual stresses that may be built into the system. The path to devitrification may be very difficult to understand in such materials and subtle differences in preparation and annealing methods between laboratories may explain differences in some of the observations.

SUMMARY AND CONCLUSIONS

The behavior of the glass forming liquids *ortho*-terphenyl and *ortho*-terphenyl/polystyrene solutions in nanometer scale pores has been investigated using differential scanning calorimetry. The results from this investigation are calorimetric evidence for two glass transitions in the CPG geometry and measurements on polymer solutions. The lower transition temperature T_{lo} decreased as pore size decreased, which was consistent with previous results. The higher transition temperature T_{hi} for the more highly concentrated *o*TP/PS solutions decreased with decreasing pore size, whereas it increased for the pure *o*TP and went through a maximum for the less concentrated solutions. Based on the observation of the two glass transitions, we have proposed a two-layer model having a ‘‘core’’ liquid in the center of the pore surrounded by an interacting layer at the pore surface. The interacting layer seems to exist even in the non-H-bonding material studied here. Examination of the results within the two-layer model suggests that the PS chains in the ‘‘core’’ solution change the behavior of *o*TP/PS solution at the pore surface by spanning the two layers. In the pure *o*TP, it appears that the molecule is too small to span both layers. We have also estimated the surface layer thickness, r_s, from the ratio of heat capacity changes at T_{lo} and T_{hi}. The thinnest layers seemed to occur in the smallest pore diameter (11.6 nm). It is unclear why such behavior would occur.

Finally, without fuller theoretical models of the glass transition, the body of results described here and those obtained by other researchers in nanoscale and confined geometries remain a challenge to full understanding.

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