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Polymer 47 (2006) 3520–3527

polymer

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Polystyrene freeze-dried from dilute solution: T_g depression and residual solvent effects

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Received 18 December 2005; received in revised form 7 March 2006; accepted 8 March 2006
Available online 3 April 2006

Abstract

The calorimetric glass transition temperature, T_g, was measured for both linear and cyclic polystyrenes freeze-dried from dilute solutions of 0.10, 0.05, and 0.02% of polymer by weight in benzene. Upon freeze-drying, T_g was found to be depressed by 4–15 K depending on the sample, solvent concentration, and freezing conditions. Annealing under vacuum at moderate temperatures, from 40 to 140 °C and 0.05 Torr, resulted in the shift of T_g back towards its bulk value and was accompanied by a decrease in sample weight. The data is consistent with the observed weight loss being due to residual solvent. The amount of residual solvent is a strong function of the annealing temperature and the initial freeze-drying solution concentration; exposure to vacuum at temperatures far below T_g is generally insufficient for residual solvent removal.

Keywords: Glass transition temperature; Freeze-drying; Polystyrene

1. Introduction

The glass transition of amorphous materials has been extensively studied by a number of research groups but it has not yet been fully understood. Materials confined at the nanoscale, such as in polymer thin films or confined in the nanopores of controlled pore or sol–gel glasses, show behavior that differs from the bulk. [1] Amorphous polymers freeze-dried from dilute solutions have also been reported to show changes in the glass transition temperature, T_g [2–14]. It was originally speculated that depressions in T_g in polymer thin films and in freeze-dried polymers from dilute solutions were related [4,5]. However, in the present work, which is aimed at understanding the origin of the T_g depression in freeze-dried materials, we show that this is not the case. Rather, we present evidence that the T_g depression in polymers freeze-dried from dilute solution is simply due to the presence of residual solvent causing the well-known plasticization effect. The result has important implications for the majority of the work on polymers freeze-dried from dilute solutions since freeze-drying is generally accomplished at low temperatures and removal of residual solvent is attempted, if at all, at temperatures far below T_g where we show that complete solvent removal does not occur.

The paper is organized as follows. We first briefly review the background literature, we then report our experimental methodology and our results. This is followed by a discussion and a conclusion.

2. Background

The magnitude of the change in T_g upon freeze-drying from dilute solution depends on the details of sample preparation and the sample itself [2–9]. For example, very large T_g depressions, 40–64 K, are reported for polystyrene freeze-dried from dilute cyclohexane solutions [2,3], whereas depressions of between 2 and 15 K have been reported for various polystyrenes freeze-dried from dilute benzene solutions. [4–6] In related work, rapid vaporization of solvent from dilute polymer solutions has also resulted in the depression of T_g for various polymers. [10,11] It is found that no depression in T_g occurs for polymer concentrations greater than a critical value (ca. 1×10^{-3} g/ml for polystyrene) and that depressions increase as the polymer concentration decreases [6,9–11]; for example, in the early work of Braun and Kovacs, no T_g depression is reported for polystyrene freeze-dried from a 1% solution in benzene [15]. Although a depression in T_g upon freeze-drying from dilute solution is the general result, an increase in T_g upon freeze-drying from dilute solution is observed [12,13] for polyacrylamide, which has strong hydrogen bonding.

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doi:10.1016/j.polymer.2006.03.035

The cause of the change in T_g from the bulk value upon freeze-drying, or other rapid drying techniques, from dilute solution has not been understood although many explanations have been proposed, such as the high surface to volume ratio or lower density [2,14], a change in specific structure or chain conformation during preparation [3,6], and stresses incurred due to freeze-drying [4]. A reduction of entanglements is also thought to result from freeze-drying from dilute solution [4,16,17] although there is contradictory evidence that significant chain interpenetration exists [18,19]; in any case, evidence suggests that reduction of entanglements is not the cause of the T_g depression in either freeze-dried materials [4,5] or in thin films [20–22], in spite of recent works, which make claims to the contrary [6,8,13].

Ideally, the freeze-drying process should consist of rapid solidification [18] such that entanglement density and chain interpenetration are similar to the dilute solution state, and the process should result in complete solvent sublimation. In reality, the former is difficult to accomplish [18], and we suggest here that complete solvent removal is also difficult to achieve. As part of our continuing work on the T_g depression in freeze-dried polystyrene, we were interested in obtaining larger T_g depressions than those obtained in our prior work [4,5] where we freeze-dried polystyrene from dilute benzene solutions; to this end, we attempted to prepare polystyrene freeze-dried from dilute hexane solutions following the work of Xue and co-workers [2,3]. However, we were unable to prepare such materials without observing a melting peak for hexane in the DSC scans. This led us to question the role of residual solvent in our initial work [4,5]. Although care was taken in that work to ensure that no residual solvent was present by performing thermogravimetric analysis (TGA), we show here that performing TGA at high temperatures above T_g does not ensure complete removal of solvent since the diffusion length scales increase dramatically upon compaction due to flow above T_g of the initially powdery freeze-dried sample. Therefore, the purpose of this work is (i) to investigate the effect of residual solvent on the glass transition of freeze-dried material by measuring the glass transition temperature as a function of the weight loss incurred during annealing under vacuum at temperatures both above and below the T_g of the bulk material and (ii) to examine the effects of temperature on residual solvent removal under vacuum. We performed these experiments as a function of the freeze-drying solution concentration.

3. Experimental

3.1. Materials

A high molecular weight linear polystyrene (PS), Dylene 8 from Arco Polymers, a low molecular weight linear polystyrene (PS-3680) from Aldrich Chem. Co., and a cyclic polystyrene (c-PS), c-PS 2590 [5], synthesized at the Institute Charles Sadron (ICS) and refractionated in the laboratories of Plazek at the University of Pittsburgh were studied. The properties of the materials are tabulated in Table 1. For freeze-dried samples, dilute solutions of 0.10, 0.05, and 0.02% polymer by weight in benzene (99.9+% purity, HPLC grade, from Aldrich Chem. Co.) were prepared and allowed to equilibrate for at least 3 days before use. The freeze-drying process was performed as follows. First, either 25 or 80 ml of the dilute polystyrene solution was slowly injected on the walls of a prechilled 600 ml vial while the vial was immersed in liquid nitrogen; the frozen solution was kept in liquid nitrogen for another 15 min. A vacuum (0.05 Torr) was then applied to the sample in the vial to sublime off the benzene. During the first 10 h when most of the solvent was pumped out, the sample temperature was maintained between −15 and −10 °C. Then the sample temperature was increased to room temperature and the sample exposed to vacuum (0.05 Torr) for an additional 20 h. We note that 2 additional days of pumping at room temperature and 0.05 torr did not change the T_g of the sample and hence, presumably, the residual solvent concentration.

Table 1
Characteristics of the polystyrene samples investigated

Sample designation	M_w (g/mol)	M_w/M_n
Dylene 8	221×10^3	2.38
PS-3680	3.68×10^3	1.08
c-PS2590[5][a]	215×10^3	1.10

[a] The number in the bracket represents the number of fraction of the refractionated sample.

For Dylene 8, nine batches were prepared from 80 ml 0.10% solutions, two batches from 25 ml 0.10% solutions, one batch from 80 ml 0.05% solution, and six batches from 80 ml 0.02% solution. There is good reproducibility between these batches as indicated by a difference of 0.30±0.14 K in T_g of the former nine batches, 0.30 K in T_g for samples taken from each of the 25 ml solution batches, and 1.42±0.62 K for the 0.02% solution batches. For the low molecular weight linear polystyrene, one batch was prepared from 80 ml 0.02% solution. For the cyclic polystyrene, one batch was prepared from 80 ml 0.10% solution.

To remove any adventitious moisture from the bulk sample, it was annealed for 5 h at 150 °C under vacuum at 0.05 Torr prior to T_g measurements; a weight loss of 0.23% accompanied this annealing.

3.2. Measurements of residual solvent

To determine the amount and effects of what is presumably residual solvent, freeze-dried samples were weighed before and after annealing under vacuum at various temperatures ranging from 40 to 140 °C and 0.05 Torr for times ranging from 1.5 min to 24 h; T_g was also measured as a function of annealing conditions as described below. To determine the total amount of residual solvent in each sample, weight loss was measured after annealing under vacuum at 0.05 Torr for 1 h at 100 °C (70 °C for the low molecular weight linear polystyrene due to its reduced T_g) and 1 h at 140 °C with a ramp of approximately 3 °C/min between 100 °C (70 °C) and

140 °C; we show later that this procedure results in T_g reverting back to the bulk value. A Mettler AE240 microbalance was used to measure weight loss, and sample sizes varied from 10 to 25 mg. The temperature at which the vacuum was applied was controlled by placing the sample inside a glass vial immersed in a high precision oil bath from Hart Scientific whose absolute temperature is known to ± 0.01 K. In addition, thermogravimetric analysis (TGA) runs were also performed under nitrogen atmosphere at various isothermal temperatures ranging from 40 to 150 °C for the freeze-dried materials. The temperature of the TGA was calibrated using Alumel, which has a magnetic transition at 154 °C.

3.3. DSC measurements

Differential scanning calorimetry (DSC) was performed on the samples after freeze-drying and after subsequent annealing/vacuum treatments using a Perkin Elmer DSC 7 with an ethylene glycol cooling system maintained at 15 °C. The runs were made under nitrogen atmosphere. Sample sizes varied from 1 to 10 mg. Standard aluminum sample pans were used for both bulk polystyrene and freeze-dried samples. DSC was also performed on samples after freeze-drying and subsequent TGA studies.

The limiting fictive temperature, T_f', was calculated using Pyris software from DSC heating scans made at 10 K/min after cooling at 10 K/min from 130 °C. The limiting fictive temperature only depends on the cooling rate. The value of T_f' is known to be approximately equal to the glass transition temperature, T_g, measured on cooling at the same cooling rate [23], although we show in other work that T_f' is 1.0 K lower than T_g for this polymer measured by DSC. [24] However, since the difference between T_f' and T_g is a constant independent of cooling rate, in this work, we use T_f' as our estimate of T_g. DSC runs consisted of the following program: a 1 min hold at 35 °C, a heating scan from 35 to 130 °C at 10 K/min, a 3 min hold at 130 °C, a cooling scan from 130 to 35 °C at 10 K/min, a 1 min hold at 35 °C, and finally a second heating scan from 35 to 130 °C at 10 K/min. The initial heating scan was made in order to examine residual stress effects. We measure T_f' on the second heating scan. The hold at 130 °C (3 min) does not affect the value of T_f' measured [4]. Baseline subtraction was performed for the DSC scans.

Temperature and heat flow calibrations were performed upon heating at 10 K/min with indium ($T_m = 156.6$ °C) and a liquid crystal standard (+)-4-*n*-hexyloxyphenyl-4′-(2′-methylbutyl)-biphenyl-4-carboxylate [25] (CE-3 from Leslie, University of Alabama; smectic to cholesteric transition at 78.8 °C). The temperature and heat flow are considered to be within ± 0.10 K and ± 0.20 J/g, respectively. The calibrations were checked at regular intervals during the DSC studies by performing check runs using CE-3 and indium.

4. Results

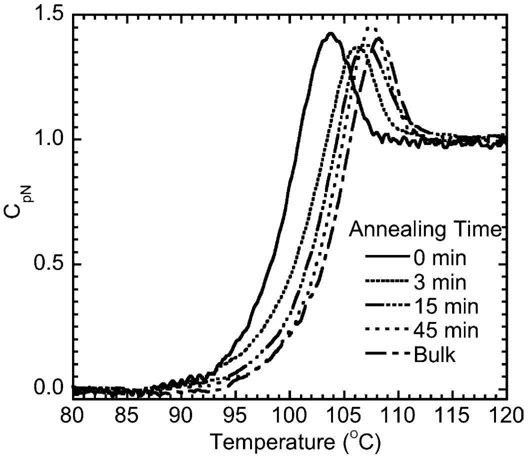

Fig. 1. Normalized heat capacity from DSC heat scans at 10 K/min after cooling at 10 K/min from 130 °C for Dylene 8 polystyrene freeze-dried from 80 ml 0.10% polystyrene solution in benzene as a function of the time of annealing at 80 °C under vacuum at 0.05 torr after freeze-drying.

The normalized heat capacities (C_{pN}) obtained during the DSC heating scans of high molecular weight linear polystyrene (Dylene 8) freeze-dried from 80 ml solution of 0.10% polymer in benzene are shown in Fig. 1 as a function of annealing time under vacuum at 80 °C and 0.05 Torr. C_{pN} is defined as

$$C_{pN} = \frac{C_p - C_{p,g}}{C_{p,l} - C_{p,g}} \tag{1}$$

where C_p is the apparent heat capacity, $C_{p,g}$ is the heat capacity in the glassy regime, and $C_{p,l}$ is the heat capacity in the liquid regime, all three of which are functions of temperature. The original freeze-dried sample shows a 4 K T_g depression, consistent with previous work in the literature [4,6]. After applying vacuum at 80 °C, the glass transition shifts to higher temperatures, and, after annealing under vacuum for 45 min, the transition is nearly that of bulk polystyrene. The heat capacity change at T_g (ΔC_p) is 0.27 ± 0.01 J g^{-1} K^{-1} for both the original freeze-dried samples and the annealed samples, slightly larger than the value of ΔC_p observed on cooling for this same polystyrene (0.25 J g^{-1} K^{-1}) [26].

The recovery of the T_g of the freeze-dried material back to its bulk value by annealing under vacuum is accompanied by a loss of weight, presumably due to loss of residual solvent. The percent weight loss as a function of the square root of time during annealing under vacuum is shown in Fig. 2 for freeze-dried Dylene 8 at various temperatures. The weight loss is initially linear with the square root of time, as might be expected for diffusion-controlled weight loss. The limiting value of weight loss is a strong function of annealing temperature indicating that applying vacuum at temperatures far below T_g, even for very long times, is insufficient for removing what is, presumably, residual solvent. In addition, the results in Fig. 2 show that weight loss is almost imperceptible at 80 °C for a sample subjected to a temperature of 130 °C for 5 min in a sealed DSC pan (which results in a compacted sample due to viscous flow with no change in T_g within the error of the measurements); the lower degree of weight loss in this compacted sample is presumably due to the

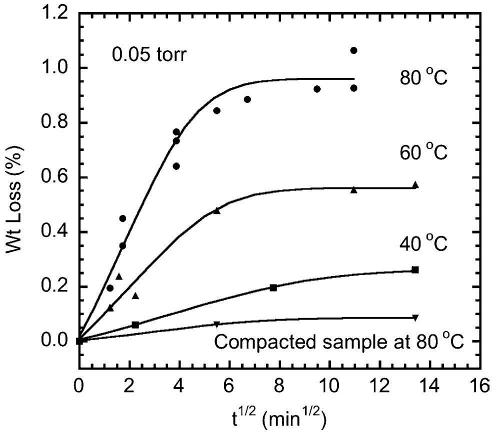

Fig. 2. Weight loss plotted as a function of the square root of the time of annealing under vacuum at 0.05 torr for freeze-dried Dylene 8 polystyrene (80 ml 0.10% solution) at various temperatures. The lower curve shows the results if prior to annealing the sample is compacted by simply heating to 130 °C. Solid lines represent the best fits of Fickian diffusion, Eq. 2.

longer length scale for diffusion. Assuming that the weight loss is due to loss of residual solvent via Fickian diffusion, the experimental data shown in Fig. 2 were fitted using the relation [27]

$$\frac{Q_t}{Q_\infty} = 1 - \sum_{n=0}^{\infty}\left[\left(\frac{8}{(2n+1)^2\pi^2}\right)e^{-(2n+1)^2\pi^2(Dt/h^2)}\right] \qquad (2)$$

where Q_t and Q_∞ are the percent solvent loss at time t and at equilibrium, respectively, h is the initial sample thickness, and D is the diffusion coefficient. The best fit for the equation gives D/h^2 and Q_∞ values of $1.43\times10^{-4}\ \mathrm{s}^{-1}$ and 0.95 at 80 °C, $9.55\times10^{-5}\ \mathrm{s}^{-1}$ and 0.68 at 60 °C, $3.40\times10^{-5}\ \mathrm{s}^{-1}$ and 0.27 at 40 °C for the non-compacted samples. The fact that Q_∞ decreases with decreasing temperature indicates that the residual solvent concentration increases with decreasing annealing temperature. Assuming that the diffusivity follows an Arrhenius temperature dependence, an apparent activation energy (E_a) of 33 ± 8 kJ/mol is obtained for the non-compacted samples, comparable to values for diffusion of small molecules in polymers [28–30] and also in reasonable agreement with values for diffusion of benzene in other polymers: 6–12 kJ/mol in carbon black-filled epoxidized natural rubber [31], 25–57 kJ/mol in non-crosslinked natural rubber [32], and 95 kJ/mol in poly(ethyl acrylate) at zero solvent concentration with E_a decreasing with increasing solvent concentration [33]. The activation energy is similar to the value obtained (52 kJ/mol) for recovery of the depressed T_g in freeze-dried cyclic polystyrene in our previous work [5].

After annealing under vacuum at various temperatures and 0.05 torr for various lengths of time, T_g was measured. The resulting values are plotted as a function of percent weight loss in Fig. 3 for freeze-dried polystyrene (Dylene 8) from 80 ml 0.10% solutions. T_g increases with the percent weight loss and the relationship is independent of annealing temperature and sample state (compacted versus 'fluffy'). At approximately 1.0% weight loss, T_g recovers back to its bulk value.

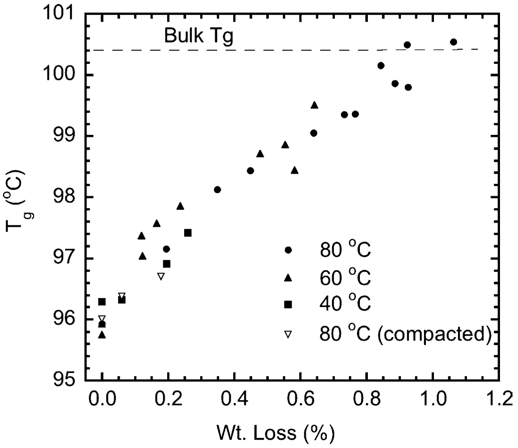

Fig. 3. Glass transition temperature (T_g) as a function of percent weight loss during annealing at 80 °C under vacuum at 0.05 torr after freeze-drying from 80 ml 0.10% polystyrene solution in benzene for Dylene 8. T_g was obtained by DSC upon heating after cooling at 10 K/min from 130 °C.

TGA runs were also performed at various temperatures ranging from 40 to 150 °C, and the results are presented in Fig. 4 for the freeze-dried polystyrene (Dylene 8) from 80 ml 0.10% solution. After days of annealing at 40 and 80 °C, the fresh freeze-dried samples show 0.27 and 0.70% weight loss, respectively, whereas the sample annealed at 150 °C only shows 0.55% loss. The results are consistent with what was observed above in Fig. 2: the total weight loss and the rate of weight loss both increase with increasing annealing temperature below T_g; however, once the temperature is high enough to compact the 'fluffy' freeze-dried sample, the rate of diffusion decreases. Furthermore, the absence of vacuum in the TGA measurements may also lower the rate of diffusion. However, the relationship between the T_g increase after annealing and the weight loss is the same as observed in Fig. 3. Accompanying the weight loss during TGA measurements, T_g has changed to 96.9, 98.8, and 98.0 °C for the samples annealed at 40, 80, and 150 °C, respectively.

As already alluded to, we suggest that the weight loss observed during annealing under vacuum and in the TGA

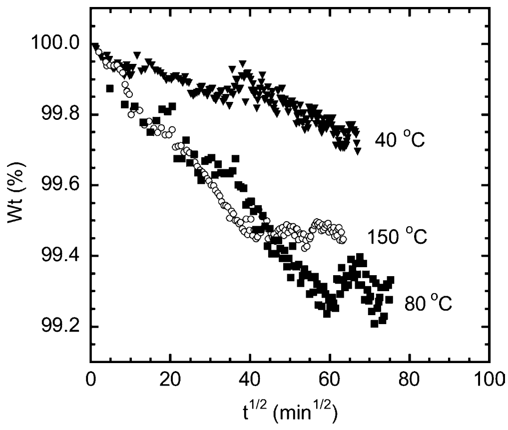

Fig. 4. Weight loss from TGA measurement plotted as a function of the square root of the time of annealing at 40, 80, and 150 °C for freeze-dried polystyrene (Dylene 8) from 80 ml 0.10% solution in benzene.

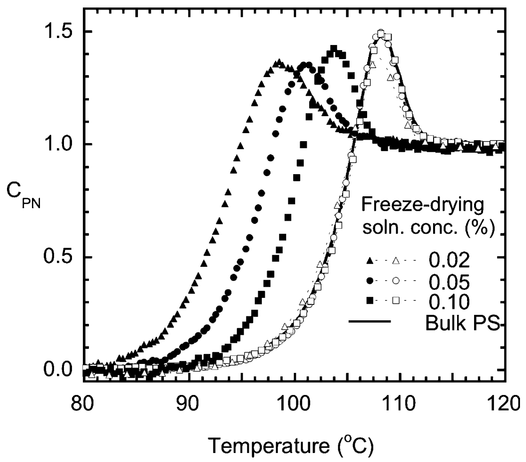

Fig. 5. The effect of annealing on the normalized heat capacity obtained from DSC heating scan after cooling at 10 K/min from 130 °C for bulk Dylene 8 polystyrene and freeze-dried samples from 80 ml 0.10, 0.05, and 0.02% solutions in benzene. Solid symbols represent initial freeze-dried samples; open ones represent annealed freeze-dried polystyrenes. The solid heavy line represents the annealed bulk sample. The annealing was performed under 0.05 torr vacuum for 1 h at 100 °C and 1 h at 140 °C with a ramp of approximately 3 °C/min between 100 and 140 °C.

measurements is due to residual solvent. In order to investigate the effect of solvent content on T_g rather than the weight loss on T_g, the total amount of residual solvent in each freeze-dried sample needs to be determined. To do so, freeze-dried samples were annealed under vacuum at 0.05 Torr for 1 h at 100 °C plus 1 h at 140 °C with a ramp of approximately 3 °C/min between the two temperatures. The effect of this annealing schedule is shown in Fig. 5, where the DSC normalized heat capacity before and after annealing is plotted as a function of freeze-drying solution concentration for the Dylene 8 polystyrene freeze-dried from 80 ml solutions. Initially, T_g is depressed and the glass transition region is broadened. These effects are more pronounced for more dilute freeze-drying solution concentrations. With annealing, the transition shifts back to that of bulk polystyrene. Table 2 summarizes the weight loss after the 100 °C/140 °C annealing schedule, the T_g before and after annealing, and ΔC_p. Samples freeze-dried from more dilute solutions showed larger depressions in T_g and larger losses in weight during annealing. Further annealing for 4 h at 140 °C under vacuum results in no change in the sample weight for any of the samples. Hence, the weight loss reported in Table 2 is considered to be the total amount of residual solvent in the sample. We note that the magnitude of the T_g change after annealing at 0.05 torr for the 100 °C/140 °C annealing schedule is much larger than that observed even after 4 days of annealing at 150 °C at atmospheric pressure, further indicating that TGA is not the best measure of residual solvent in these systems.

Similar results were found for the low molecular weight linear polystyrene (3680 g/mol) and the cyclic polystyrene (215×10^3 g/mol). For the former, due to its lower T_g, annealing to obtain the total residual solvent content was performed at 0.05 Torr for 1 h at 70 °C plus 1 h at 140 °C with a ramp of approximately 3 °C/min between the two temperatures. The results are shown in Table 3.

The effect of solvent content on the T_g depression of Dylene 8 and on the normalized T_g depression of all of the polystyrenes investigated is shown in Fig. 6, along with the prediction of the Jenckel and Heusch's model [34,35]. This model can be written as

$$T_g = w_1 T_{g1} + w_2 T_{g2} + b(T_{g2} - T_{g1}) w_1 w_2 \tag{3}$$

where T_g, T_{g1}, T_{g2} are the glass transition temperatures of the mixture, solvent, and polymer, respectively, w_1 and w_2 represent the weight percent of solvent and polymer, and b is a parameter, which characterizes the solvent quality of the plasticizer. For the polystyrene/benzene system, T_{g1} is taken to be 131 K [36] and b is found to be −1.02 by fitting Jenckel and Heusch's experimental data [34]. For the normalized T_g depression, Eq. (3) can be rearranged into

$$\frac{T_g - T_{g2}}{T_{g2} - T_{g1}} = w_1(b w_2 - 1) \tag{4}$$

a form that is independent of T_{g2} (which differs for the three materials studied). Hence, the normalized T_g depression is expected to have the same dependence on the solvent concentration for all our samples. For most of the freeze-dried samples, this is the case as shown in Fig. 6. There is also

Table 2
Change in the calorimetric properties and weight loss for the bulk and freeze-dried Dylene 8 polystyrene after annealing at 0.05 Torr for 1 h at 100 °C and 1 h at 140 °C with a ramp of approximately 3 °C/min between 100 and 140 °C

Sample	T_g (°C)[a]		ΔC_p (J g^{-1} K^{-1})[a]		Weight loss upon annealing (%)
	Original	Annealed	Original	Annealed	
Bulk	99.1±0.2	100.4±0.3[b]	0.27	0.27	0.23±0.04[b]
80 ml 0.10%	96.1±0.3[c]	100.8±0.2[b]	0.27	0.27	1.14±0.10[b]
25 ml 0.10%	90.4±0.2[c]	100.3	0.26	0.27	2.06
80 ml 0.05%	91.1±0.2[d]	100.4	0.26	0.27	2.12
80 ml 0.02%	88.5±1.4[c]	100.3±0.4[b]	0.25	0.26	2.94±0.17[b]

[a] Values obtained from DSC heating scan after cooling at 10 K/min from 130 °C.
[b] Values averaged for three different samples, respectively.
[c] Values averaged for samples taken from each of the prepared batches.
[d] Values averaged for three samples taken from the same batch.

Table 3
Change in the calorimetric properties and weight loss for the freeze-dried low molecular weight linear polystyrene and cyclic polystyrene after annealing at 0.05 Torr for 1 h at 70 °C (100 °C for cyclic sample) and 1 h at 140 °C with a ramp of approximately 3 °C/min between the two temperatures

Sample	T_g (°C)[a]		ΔC_p (J g^{-1} K^{-1})[a]		Weight loss upon annealing (%)
	Original	Annealed	Original	Annealed	
PS-3680 (80 ml 0.02%)	63.2 ± 0.5[b]	72.1	0.25	0.27	3.24
c-PS2950[5] (80 ml 0.10%)	93.6 ± 0.2[c]	101.0	0.26	0.27	1.39

[a] Values obtained from DSC heating scan after cooling at 10 K/min from 130 °C.

[b] Values averaged for two samples taken from the same batch.

[c] Values averaged for three samples taken from the same batch.

good agreement between the model and our data, which supports our contention that the observed T_g depression in the freeze-dried samples is due to the effects of residual solvent. To further test this conclusion, we purposefully added 2.9 wt% benzene to a freeze-dried Dylene 8 sample after its T_g had recovered back to the bulk value; this sample (marked by an × in the figure) shows the same T_g versus solvent relationship as the other freeze-dried/annealed samples. However, some of our data, especially for 0.02% solutions, show T_g slightly higher than the model predicts. This may indicate a 1–3 K increase in T_g after freeze-drying from a 0.02% solution in the absence of residual solvent effects. Additionally, Chow's model [37], which has no adjustable parameters, was also used and the prediction compared to the observed plasticization effects of benzene on the T_g of polystyrene. The model of Chow predicts a greater depression than does that of Jenckel and Heusch and falls 6 K below the data at 2.90% solvent concentration. Hence the Jenckel and Heusch model provides a better empirical description of the results albeit with an adjustable parameter (*b*).

To further examine why larger residual solvent concentrations are observed for materials freeze-dried from more dilute solutions, we plot the normalized weight loss of freeze-dried polystyrene (Dylene 8) annealed at 80 °C and 0.05 torr in Fig. 7 as a function of freeze-drying solution concentration. The freeze-drying solution concentration clearly affects the rate of solvent diffusion out of the polymer. As shown in the figure, the limiting value of the normalized percent weight loss decreases with decreasing freeze-drying solution concentration, where the normalized weight loss is simply the weight loss normalized by the total weight loss (i.e. normalized by the total weight percent residual solvent—see Table 2). For samples prepared from 0.02% solution and annealed for 1 h at 80 °C and 0.05 torr, only 40% of the residual solvent was removed, whereas for samples prepared from 0.10% solution, 85% of the solvent was removed under the same conditions. This result seems to be counter-intuitive: samples freeze-dried from more dilute solution have finer texture and more surface area—one would expect that this would lead to easier solvent removal rather than the opposite. A possible explanation may

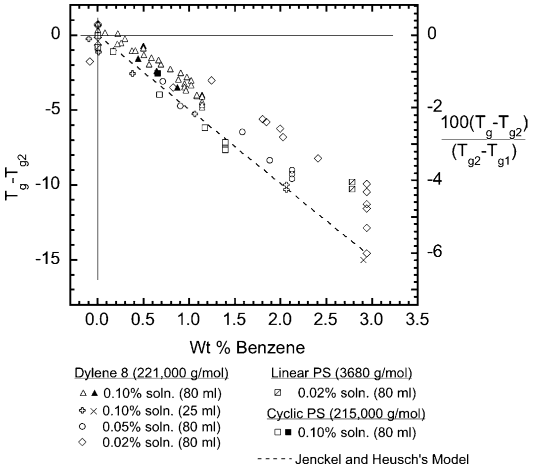

Fig. 6. The depression in the glass transition temperature from the bulk value ($T_g - T_{g2}$) and the normalized T_g depression ($(T_g - T_{g2})/(T_{g2} - T_{g1})$) of freeze-dried linear and cyclic polystyrenes plotted as a function of residual solvent concentration. Open symbols represent the solvent concentration and T_g obtained from annealing under vacuum; solid symbols represents values obtained after TGA measurements. The × symbolizes the freeze-dried Dylene 8 polystyrene from 25 ml 0.10% solution to which 2.9% solvent was added after its T_g had recovered back to the bulk value. The dashed line represents the prediction from Jenckel and Heusch's model [34]. The left-hand *y*-axis applies only to Dylene 8 samples. The right-hand *y*-axis applies to all samples.

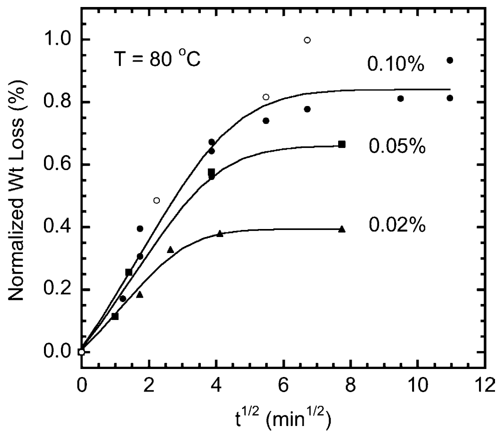

Fig. 7. Normalized percent weight loss (normalized by the total amount of residual solvent reported in Table 2) plotted as a function of the square root of the time of annealing under vacuum at 0.05 Torr at 80 °C for Dylene 8 polystyrene freeze-dried from 25 (open symbols) or 80 ml (solid symbols) solution in benzene with various concentration (0.10, 0.05, 0.02%). The solid lines show the fits of Fickian diffusion, Eq. 2.

be that the increase in surface area results in an increase in the equilibrium amount of physisorbed solvent, which leads to a decrease in the T_g of the surface and also in the measured T_g. This suggestion is also consistent with the temperature dependence of the residual solvent shown in Fig. 2.

5. Discussion

The results presented here demonstrate a strong residual solvent effect on the observed T_g depression and its recovery in freeze-dried polystyrene. This well-known plasticization effect is described by the Jenckel and Heusch model [34], and our results of T_g versus residual solvent concentration for polystyrene freeze-dried from 0.10 and 0.05% polymer solutions agree very well with the model. On the other hand, the data from material freeze-dried from 0.02% polymer solutions are 2–3 K above model predictions, indicating that in the absence of residual solvent effects, we may have an increase in T_g of this magnitude for polystyrene freeze-dried from the 0.02% solutions. In support of such a conclusion is the observation of an elevated T_g for single-chain polystyrene glasses obtained via a microemulsion process [38] and the fact that entropic considerations would predict such an elevation of T_g for freeze-dried polymers [12] and for polymers confined to thin films [39].

We noted in the introduction that several groups have recently invoked that the T_g changes are due to changes in entanglement concentration [6,8,13]. In an attempt to estimate the effect of reducing entanglement density on T_g, we adapt the following equation suggested by Stutz, Illers, and Mertes, initially derived for crosslinked materials [40]

$$T_g = T_{g,u}[1 + K_2X_c/(1-X_c)] \qquad (5)$$

where T_g is the glass transition of crosslinked polymer, $T_{g,u}$ is the glass transition of an unentangled polymer here (rather than the uncrosslinked polymer in original work of Stutz et al.), K_2 is a constant, and X_c is the entanglement (rather than the crosslink) density, expressed by the mole fraction of entanglements in the system. Here, we assume that crosslink points and entanglement points have the same effect on T_g; this may overestimate the influence of entanglements but it provides an estimate of the magnitude of any T_g depression that might be observed from changes in entanglement concentration. By choosing $K_2=0.82$ [41], we estimated that the T_g change for a change in the molecular weight between entanglements (M_c) from the bulk value of 17,300 [42] to 34,600 g/mol, is only a 0.9 K decrease. We note that a change in M_c of this magnitude would occur with an increase in J_N of 100% on freeze-drying, which is greater than that observed in creep measurements [4]. The result corroborates our prior work [4,5] and the results presented here that a decrease in entanglement density cannot be the origin of the observed T_g depression; it is also consistent with results for thin polymer films, which also indicate that reduced entanglements are not the origin of the T_g depressions observed [20–22].

We conclude our discussion by emphasizing that T_g depressions are not observed for polymers freeze-dried, or rapidly dried by other techniques, from solutions that are less dilute than a critical value (ca. 1×10^{-3} g/ml for polystyrene). [6,9–11,15] It is not at all clear why it becomes more difficult to remove residual solvent from materials freeze-dried from more dilute solutions. The benzene vapor pressure of 0.1 wt% benzene in polystyrene is 0.26 Torr at 15 °C, based on the chain-of-rotators equation of state [43,44], indicating that nearly complete removal of the solvent should be achievable at room temperature under moderate vacuum in contrast to our experimental results (as shown, for example, in Fig. 7). It is suggested that our observations could be due to physisorbed solvent, which may increase with increasing sample surface area, i.e. with decreasing freeze-drying solution concentration. The result has implications for the interpretation of the T_g depression of freeze-dried materials [2–14], as well as for the behavior of other properties of materials freeze-dried from dilute solution [7,45–48], since previous experimental protocols involve removal of solvent by freeze-drying and/or annealing under vacuum at low temperatures. The results also have practical implications for the general use of freeze-drying as a materials preparation technique.

6. Conclusion

An investigation of the residual solvent effect on the calorimetric glass transition of freeze-dried linear and cyclic polystyrene has been performed. Upon freeze-drying, T_g was found to be depressed by 4–15 K depending on the sample preparation. After annealing under vacuum at moderate temperatures and 0.05 torr, weight loss, presumably due to loss of residual solvent, occurs and T_g increases. The amount of solvent present in the original freeze-dried samples was determined from the weight loss observed after annealing under vacuum at 0.05 Torr for 1 h at 100 °C (70 °C for the low molecular weight linear polystyrene) and 1 h at 140 °C with a ramp of approximately 3 °C/min between 100 and 140 °C. The calorimetric glass temperature was measured as a function of the fraction of the residual solvent. A linear correlation was found between the T_g depression and the residual solvent concentration, in agreement with data in the literature. The amount of residual solvent in the freeze-dried samples unexpectedly increases with decreasing polymer concentration of the freeze-drying solution, as well as with decreasing annealing temperature, such that residual solvent cannot be removed by annealing under vacuum at temperatures far below T_g; this has significant implications for the majority of work in the literature performed on materials freeze-dried from dilute solutions, as well as for the use of freeze-drying as a general materials preparation technique. We conclude that the residual solvent has a significant effect on the T_g depression observed for polymers freeze-dried from dilute solution; no depression or even a slight increase in T_g is expected in the absence of residual solvent.

Acknowledgements

The authors gratefully acknowledge funding from the National Science Foundation for support of this work through NIRT grant NSF DMR- 0304640. Useful discussions with Prof D.J. Plazek and Prof G.B. McKenna are also acknowledged.

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