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Effects of freeze-drying on the glass temperature of cyclic polystyrenes

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Abstract

The calorimetric glass temperature was measured for three cyclic polystyrenes with apparent molecular weights ranging from 4.0×10^3 to 195.5×10^3 g/mol for both bulk material and for samples freeze-dried from dilute solution. Freeze-drying from dilute solution was found to reduce the glass temperature by 7–14 K depending on the sample. These T_g depressions are 5–12 K greater than those found previously for freeze-dried linear polystyrene. Annealing at 403.2 and 443.2 K (130 and 170 °C) resulted in recovery of the T_g back to the bulk value with the time scales depending on both temperature and the magnitude of the T_g reduction; the low apparent activation energy dependence of the recovery of T_g precludes its being due to viscous flow.

Keywords: Glass transition temperature; Freeze-drying; Polystyrene

1. Introduction

The glass transition temperature is generally depressed by confinement, both in nanometer size pores as first observed by Jackson and McKenna [1,2] and verified by Jonas et al. [3] and in ultrathin films [4–21]. The depression can be as great as 75 K for unsupported polystyrene films [5–7]. In addition, the glass transition temperature is depressed by freeze-drying from dilute solution and by precipitation from dilute solution [22–27]. Neither the depression of T_g at the nanoscale nor the depression due to freeze-drying or precipitation from dilute solution is readily explained in the framework of our current understanding of the glass transition. In fact, one of the leading theories of the glass transition, configurational entropy theory [28], predicts that T_g should increase for supported thin films and for material confined to nanopores [29], neither of which is the general observation although in cases of very strong interaction between the polymer and the substrate, increases in T_g with decreasing film thickness have been reported [30–32] and an increase in T_g with freeze-drying has been reported [33,34] for polyacrylamide which has strong hydrogen bonding.

In prior work by two of the present authors [22], the effects of freeze-drying from a dilute benzene solution (0.1% by weight) on the viscoelastic behavior and the calorimetric glass transition were investigated for linear polystyrenes ranging from low to ultrahigh molecular weights. The freeze-drying process was shown to reduce the entanglement concentration for chains with molecular weights above the entanglement molecular weight (although entanglements were not completely eliminated consistent with NMR work by McGrath et al. [35] which showed interpenetrated chains after freeze-drying). The depression in the calorimetric glass temperature was found to be 2.2 K for the lowest molecular weight polystyrenes which had molecular weights below the entanglement molecular weight, 5.2 K for the polystyrene which could fully entangle in its equilibrium configuration, and 5.2 and 3.0 K for the ultrahigh molecular weight samples which could not fully entangle due to their very long terminal relaxation times. Recovery of the glass temperature occurred on annealing at 423.2 K (150 °C) and was estimated to be in excess of 60 and 90 h for the 16.7 and 390 kg/mol samples, respectively. The results indicate that a reduction in entanglements upon freeze-drying is not the origin of the reduced T_g observed

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and that re-entanglement is not responsible for the recovery of T_g.[2]

Other researchers have also investigated the effects of freeze-drying on the glass transition temperature. Braun and Kovacs [23] reported dilatometric measurements of polystyrene freeze-dried from a 1% solution of toluene; when the freeze-dried material was suspended in a non-solvent, T_g was depressed only about 1–2 K over that of the same sample molded at 453.2 K (180 °C) and equilibrated for up to several weeks near 373.2 K (100 °C). Similarly, Huang et al. observed reductions in the glass temperature of approximately 3 K for polystyrene after rapid precipitation from dilute chloroform solution (10^{-4} g/ml) incurred by flash vaporization of the solvent [24]. On the other hand, Xue and co-workers reported much larger reductions in T_g [26,27] freeze-dried polystyrene from a 0.07% cyclohexane solution was observed to have a calorimetric T_g of 338.2 K (65.0 °C), and polystyrene prepared by spraying a 0.5% benzene solution into methanol showed a T_g of 340.3 K (67.1 °C). On repeated heating scans to 443.2 K (170 °C), the DSC glass transition temperatures of both materials increased, nearly reaching the bulk value on the fourth scan for the freeze-dried material and on the second scan for the sprayed material [26]. The same research group also found that a higher molecular weight polystyrene freeze-dried from a 0.04% cyclohexane solution had a glass temperature of 314.2 K (41 °C) [27]. The T_g for that material increased to 333.2 K (60 °C) in the second and third DSC heating scans which went to 453.2 K (180 °C). The authors suggest that the sample reached equilibrium at this point, and they invoke a new theory to explain the results; however, as shown in the previous paper [22] and in the work reported here, the recovery of the bulk T_g after freeze-drying can take on the order of days even at temperatures far above T_g. Hence, although the large depressions in T_g observed by Xue et al. are intriguing, their interpretation of their data is questionable.

The glass transition of polystyrene microspheres has also been investigated. Ediger and co-workers recently reported that for spheres ranging from 42 to 548 nm, no significant change in the glass transition temperature was observed although the value of the step change in the heat capacity at T_g (ΔC_p) decreased with decreasing particle size [36]. These results are consistent with those of Gaur and Wunderlich [37] who found that for polystyrene spheres ranging from 85 to 868 nm in diameter no significant change in the glass transition temperature was observed, although the transition was broadened and began at a lower temperature for the smallest particles. In addition Gaur and Wunderlich also found that ΔC_p decreased with decreasing particle size; they attributed the decrease to increasing surface area as particle size decreases. It is important to remark that based on the molecular weight and size dependence of the depression for unsupported polystyrene films [6], the T_g depression for the smallest microspheres examined by Ediger et al. might have been expected to be on the order of 20–40 K; hence, as the authors concluded [36], there is no straight-forward comparison between the microsphere and unsupported film results.

There are few studies that explore the depression of T_g by either confinement or by freeze-drying as a function of polymer architecture—an exception is a recent collaboration of one of the authors with Dutcher where it was observed that the T_g depression in thin unsupported films of polystyrene rings is the same as that observed for their linear counterparts [38]; this result may have been expected since the molecular weight of the rings studied was in the regime [5,6] in which the T_g versus thickness relationship for linear chains shows no significant molecular weight dependence. The purpose of the present work is to examine the effect of molecular architecture on the T_g depression observed upon freeze-drying from dilute solution using cyclic polystyrenes in the form of uncatenated rings. In particular, we examine whether the effects of freeze-drying on cyclic polystyrenes differs from that of the linear polystyrenes studied earlier. We note that cyclic or ring molecules cannot reptate in the conventional sense and the molecular weight dependence of their viscosity and their terminal relaxation time differs from those of their linear counterparts [39].

2. Experimental

2.1. Materials

Three uncatenated cyclic polystyrene samples with apparent molecular weights varying from 4.0×10^3 to 195.5×10^3 g/mol and having low polydispersity were studied. The materials were synthesized at the Institute Charles Sadron (ICS) in Strasbourg and details of preparation have been reported elsewhere. [40–43] Because the rheological studies of the high molecular weight rings showed contamination by linear chains [39], the two higher molecular weight Strasbourg fractions were refractionated in the laboratories of D.J. Plazek at the University of Pittsburgh. The present fractions, PS2583[4] and PS2590[4] are the fourth fractions in this process. The sample designated PS3050 was used as received from P. Lutz at the ICS without further fractionation beyond that done in the ICS laboratories. Table 1 summarizes the materials and their properties. All molecular weights reported are apparent values based on GPC measurements using a linear polystyrene standard.

The cyclic polystyrene samples were studied in their bulk

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[2] In the original work, it was stated that the relaxation times for the 16.7 and 390 kg/mol samples were 10^{-8} and 10^{-2} s, respectively. An error of 2.303 was made in the calculation; the correct times should have been 10^{-3} and 10^{2} s, respectively. The conclusion of the paper still stands that since the difference in the terminal relaxation times are orders of magnitude, whereas the differences in the time scales for recovery are less than one order of magnitude, re-entanglement is not responsible for the recovery of T_g.

Table 1
Characteristics of polystyrene samples investigated

Sample designation[a]	M_n (kg/mol)[b]	M_w/M_n
PS2590[4]	195.5	1.1
PS2583[4]	40.8	1.14
PS3050	4.0	1.09

[a] The number in brackets represents the fraction number of a fractionated sample.

[b] Apparent molecular weight obtained by GPC using a linear polystyrene calibration standard.

or equilibrium configuration, as well as freeze-dried from a dilute solution (0.1% by weight) in benzene (99.9 + % purity, HPLC grade, from Aldrich Chemical Company). The freeze-drying process was performed by placing the dilute polymer solution in a glass flask and holding it in a dry ice/acetone bath until the solution solidified. A high vacuum was then applied to the sample in the flask for at least 12 h to sublime off the benzene. Due to the heat of sublimation coupled with the relatively high melting point of benzene (278.7 K), the sample remained solidified during the drying process. The polystyrene cycles, separated in the dilute solution and immobilized in the frozen benzene matrix, remain so after sublimation because of the slow relaxation rate at temperatures well below T_g. As a result, the entanglement concentration of the freeze-dried product is greatly reduced relative to that of an unfreeze-dried sample, as was verified in the prior work [22] by creep measurements. In that work [22], isothermal thermogravimetric analysis (TGA) runs at elevated temperatures (up to 150 °C for 50 h) showed that the residual solvent level was less than 0.10% in the freeze-dried samples and could not be responsible for the depression in T_g observed. In addition, as part of both this and the prior work, we freeze-dried the same material in several batches and found no difference in the value of the glass temperature between batches.

2.2. Calorimetry

Differential scanning calorimetry (DSC) was performed using a Perkin Elmer DSC 7 with an ethylene glycol cooling system maintained at 288.2 K (15 °C). The runs were made under nitrogen atmosphere. Sample sizes varied from 3 to 5 mg for the freeze-dried samples. The bulk samples (not freeze-dried) were larger, ranging from 5 to 11 mg. Standard sample pans were used for the bulk cyclic polystyrene, and 50 μL pans were used for the freeze-dried material.

The DSC temperature history used in this work is the same as that used to study the effect of freeze-drying on linear polystyrenes [22]: the sample was held at 403.2 K (130 °C) for 5 min, then cooled from 403.2 to 323.2 K (130 to 50 °C) at a specified cooling rate, followed by a hold at 323.2 K for 1 min, and finally heated from 323.2 to 403.2 K at 10 K/min. Cooling rates ranged from 0.1 to 100 K/min. This temperature history was generally followed by a similar set of scans made at cooling and heating rates of 10 K/min. The heating leg which followed the 10 K/min cooling leg was used as an internal reference to insure that the temperature calibration was unchanged over the course of the experiments. The same procedure was used for all samples. We show later that a hold of five minutes at 403.2 K does not affect our results. A single sample was used for the DSC measurements for each bulk (not freeze-dried) sample; for the freeze-dried samples, a different sample was used for each cooling rate to insure that repeated scans above T_g would not influence the results.

Temperature calibration was performed upon heating at 10 K/min with indium and a liquid crystal standard (+)-4-*n*-hexyloxyphenyl-4′-(2′-methylbutyl)-biphenyl-4-carboxylate [44] (CE-3 from T.M. Leslie, University of Alabama; smectic to cholesteric transition at 352 K). The temperature is known to within ±0.1 K. The calibration was checked at regular intervals during the DSC studies by running the indium standard.

The DSC heating scans were analyzed to find the value of the fictive temperature of a glass associated with a given cooling rate, T_f'. T_f' is also know as the limiting fictive temperature [45] and is equivalent to Plazek and Frund's T_{fg} [46], the value of T_f that approximates T_g at a given cooling rate. We find T_f' by integrating the heat flow curve and then extrapolating the liquid line to the glassy line, a procedure that is consistent with the method proposed by Moynihan et al. [45]:

$$\int_{T_f'}^{T \gg T_g} (C_{pl} - C_{pg})\mathrm{d}T = \int_{T \ll T_g}^{T \gg T_g} (C_p - C_{pg})\mathrm{d}T \qquad (1)$$

where C_{pl} and C_{pg} are the liquid and glass heat capacities, respectively, and C_p is the apparent heat capacity measured by DSC. The standard deviation of the limiting fictive temperature for multiple scans, all measured at 10 K/min after cooling at the same rate, is reported in Section 3. We simply note here that the standard deviation ranges from 0.3 to 1.3 K for the various samples. Since the value of T_f' measured after cooling at a given rate is approximately equal to the value of the glass transition temperature (T_g) which would be measured during cooling at that same rate [45,46], with both T_f' and T_g being only functions of the cooling rate and not of the heating rates, the trends we report for T_f' apply equally as well to T_g. Hence, at times, we will generalize and refer to the glass transition temperature in our discussion. We note that measurement of T_g on cooling is the preferred method for measuring T_g [47,48]; however, because of sensitivity issues, arising in part from the low packing density of the freeze-dried samples, we chose heating and the measurement of T_f' as our estimate of T_g.

3. Results and analysis

The reduction in the limiting fictive temperature (T_f') caused by freeze-drying can be clearly observed by comparing the DSC traces shown in Fig. 1(a) and (b) for freeze-dried and bulk cyclic polystyrene PS2583[4] ($M_n = 40.8$ kg/mol). The curves shown in Fig. 1(a) are heating scans performed at 10 K/min after cooling at 1 K/min, whereas those shown in Fig. 1(b) are heating scans performed at 10 K/min but after cooling at 10 K/min. For ease of comparison, the normalized heat capacity (C_{pN}) is the ordinate in Fig. 1(a) and (b), and as defined, it is 0.0 in the glassy regime and 1.0 in the liquid:

$$C_{pN} = \frac{C_p - C_{p,g}}{C_{p,l} - C_{p,g}} \tag{2}$$

where C_p is the apparent heat capacity (i.e. the heat flow in units of J g^{-1} K^{-1}), $C_{p,g}$ is the heat capacity in the glassy regime (which is a function of temperature), and $C_{p,l}$ is the heat capacity in the liquid regime (which also is a function of temperature). In addition to showing the depression in the glass transition for the freeze-dried material, the scans show that the enthalpy recovery or annealing peak depends on the ratio of the heating to cooling rate and is larger for the slower cooling rate, as expected. The annealing peak is also broadened and reduced in height for the freeze-dried material. The area under the peaks, however, is not significantly affected by freeze-drying, indicating that the relaxation kinetics associated with the depressed glass temperature in the freeze-dried material are similar to those in the bulk material relative to T_g. The increase in breadth and reduction in height of the enthalpy recovery peak for the freeze-dried material may be attributed to a lower thermal conductivity due to the 'fluffy' nature of the freeze-dried material; it is noted that a broadening of DSC annealing peaks has been shown to arise from thermal lag effects [49], although model calculations show that the broadening observed due to the finite thermal diffusivity of a standard polymeric sample is considerably smaller than the broadening observed here. We note that the height of the step change in the heat capacity at the glass temperature ($\Delta C_p = C_{p,l} - C_{p,g}$) is unaffected by freeze-drying, as indicated by the data reported in Table 2.

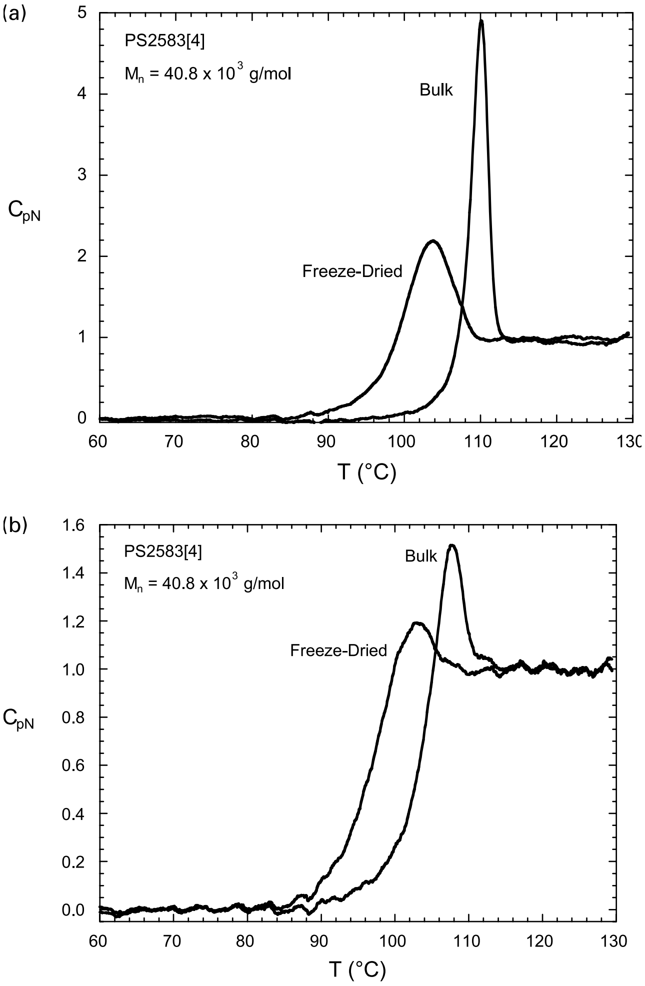

Fig. 1. (a) Normalized heat capacity for heating at 10 K/min after cooling at 1 K/min for both a freeze-dried and bulk sample of PS2583[4] ($M = 40.8$ kg/mol). (b) Normalized heat capacity for heating at 10 K/min after cooling at 10 K/min for both a freeze-dried and bulk sample of PS2583[4] ($M = 40.8$ kg/mol).

The dependence of the limiting fictive temperature on cooling rate for PS2583[4] ($M_n = 40.8$ kg/mol) is shown in Fig. 2 for both bulk and freeze-dried materials. The limiting fictive temperature for the freeze-dried material is an average of 6.9 ± 1.2 K lower than the bulk value for all of the runs performed, somewhat larger than the depression found for the linear polystyrenes [22] (which ranged from 2 to 5 K). We remind the reader here that we report the limiting fictive temperature rather than the midpoint in the step change in the heat capacity because the former takes into account the enthalpy relaxation the occurs on heating, and because, by definition, the limiting fictive temperature

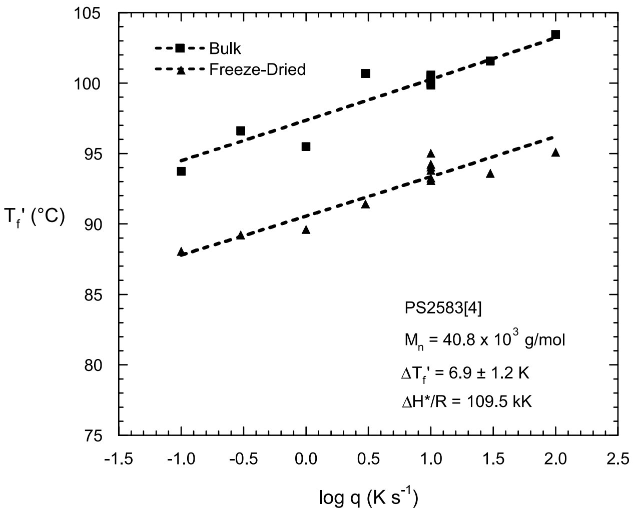

Fig. 2. The limiting fictive temperature (T_f') as a function of the logarithm of the cooling rate q for bulk and freeze-dried PS2583[4] ($M = 40.8$ kg/mol).

Table 2
Summary of calorimetric properties for bulk and freeze-dried polystyrene

Sample designation	M_n (g/mol)	$T_f'(q_{ref})$ (K)[a]		$\Delta T_f'{}_{,ave}$ (K)[b]	ΔC_p (J g^{-1} K^{-1})	
		Bulk	Freeze-dried		Bulk	Freeze-dried
PS2590[4]	195.5×10^3	374.7 ± 1.1	363.5 ± 1.3	11.6 ± 0.9	0.25 ± 0.05	0.27 ± 0.05
PS2583[4]	40.8×10^3	373.4 ± 0.3	367.1 ± 0.7	6.9 ± 1.2	0.25 ± 0.03	0.25 ± 0.02
PS3050	4.0×10^3	373.5 ± 1.1	359.9 ± 0.6	14.3 ± 1.3	0.24 ± 0.02	0.25 ± 0.02

[a] $T_f'(q_{ref})$ is the value of T_f' obtained at a heating rate of 10 K/min after cooling at the reference cooling rate (q_{ref}) of 10 K/min; the values reported are the average for either three runs for samples having a standard deviation above 1.0 K and for six runs for samples having a standard deviation below 1.0 K.

[b] Difference between T_f' for bulk and freeze-dried samples, averaged for all samples over all cooling rates.

should equal the glass temperature that would be obtained on cooling [45,46]; i.e. both T_f' and T_g are only functions of the cooling rate. As shown in Fig. 2, the limiting fictive temperature for both freeze-dried and bulk samples increases with the logarithm of the cooling rate (q), as expected. Although the data are consistent with the expected Williams–Landel–Ferry (WLF) [50] or Vogel–Tammann–Hesse–Fulcher (VTHF) [51–53] temperature dependence, an Arrhenius fit is shown since the WLF/VTHF parameters could not be unambiguously determined due to the limited range of the data. From the Arrhenius fit, an apparent activation energy of 218 kcal/mol is obtained. This is equivalent to a value of $\Delta H^*/R = 110$ kK in the Tool–Narayanaswamy–Mohynihan (TNM) [54–56] model of structural recovery. In comparison, the universal WLF equation with constants of 17.44 for C_1 and 51.6 K for C_2 gives an apparent activation energy of 215 kcal/mol at $T_g = 373.2$ K and a $\Delta H^*/R$ of 108 kK. Fitting DSC enthalpy overshoots yields values of $\Delta H^*/R$ ranging from 53 to 110 kK for linear polystyrene, [57] whereas fitting the temperature dependence of the time required to reach equilibrium for enthalpy yielded a value of 101 kK [58]. Our measurements are consistent with these values; i.e. the time (or cooling rate) dependence of the calorimetric glass transition temperature for cyclic polystyrene, both in the bulk and freeze-dried, is the same within the error of the measurements as that of linear polystyrene. This finding is consistent with the prior rheological work of McKenna et al. on linear and cyclic polystyrene [43], in which it was reported that the Vogel temperature dependence was independent of architecture.

A reduction in the limiting fictive temperature was also found for the other two cyclic polystyrenes, PS2590[4] and PS3050, having molecular weights of 195.5 and 4.0 kg/mol, respectively. As shown in Figs. 3 and 4, respectively, the glass transition temperature is depressed 11.6 ± 0.9 K for the 40.8 kg/mol material and 14.3 ± 1.3 K for the 4.0 kg/mol material, with both values obtained by averaging the limiting fictive temperature over all runs and cooling rates. Surprisingly, for the three cyclic materials examined, the 4.0 kg/mol sample, which should not be entangled at all, is the sample which shows the largest reduction in the glass temperature corroborating our past conclusion that a reduction in entanglement concentration is not responsible for the reduction in T_g observed in freeze-dried materials. In addition, we note that the bulk T_g associated with cooling at 10 K/min is 373.5 ± 1.1 K (100.3 ± 1.1 °C) for the 4.0 kg/mol sample and is the same within the scatter of the measurements as those for the higher molecular weight samples. The fact that T_g does not depend on molecular weight for the cyclic polystyrenes differs from the results on linear polystyrenes where T_g decreases with decreasing molecular weights, but the result is in agreement with the previous rheological work by McKenna et al. on polystyrene cycles [43] which showed that the viscosity followed essentially the same WLF or Vogel temperature dependence independent of ring size; the result is also consistent with experimental [59,60] and theoretical [61] work which indicates that T_g for cycles should increase rather than decrease at very low molecular weights. The Arrhenius fits to the cooling rate dependence of T_f' give apparent activation energies of 169 and 166 kcal/mol ($\Delta H^* R = 85$ and 83 kK, respectively) for the 195.5 and 4.0 kg/mol samples, respectively.

The reduction in the limiting fictive temperature due to freeze-drying can be eliminated by sufficient annealing above the glass temperature. To determine the time scale for this recovery back to the bulk or equilibrium behavior, we

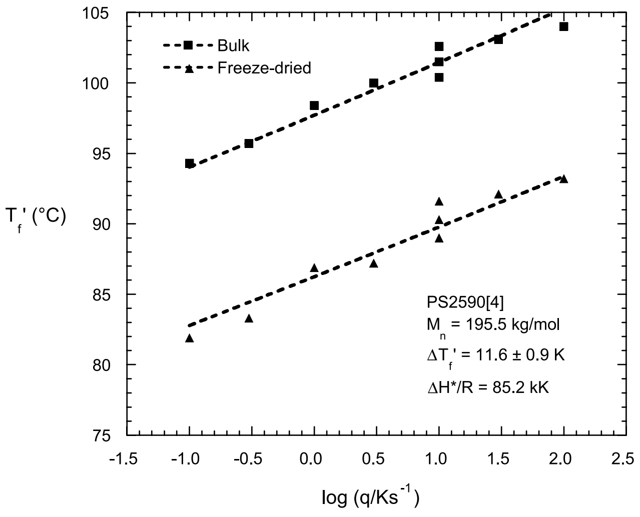

Fig. 3. The limiting fictive temperature (T_f') as a function of the logarithm of the cooling rate q for bulk and freeze-dried PS2590[4] ($M = 195.5$ kg/mol).

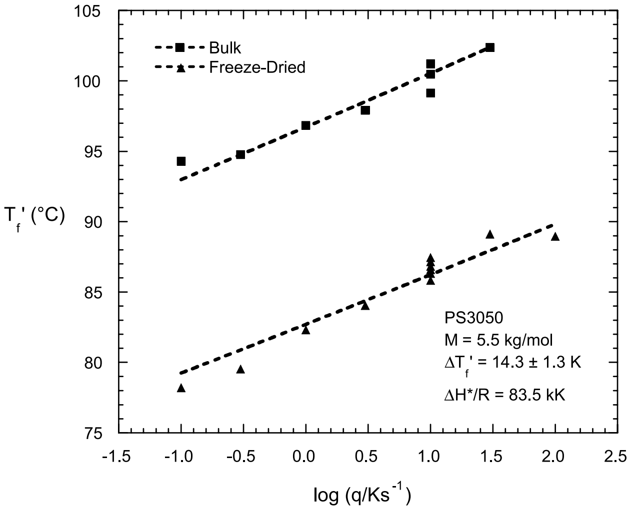

Fig. 4. The limiting fictive temperature (T_f') as a function of the logarithm of the cooling rate q for bulk and freeze-dried PS3050 ($M = 4.0$ kg/mol).

annealed several freeze-dried samples at 403.2 and 443.2 K (130 and 170 °C) in the DSC and periodically scanned the samples from the annealing temperature to 323.2 K (50 °C) and back to the annealing temperature using cooling and heating rates of 10 K/min. The results of annealing above T_g are shown in Fig. 5 with the data plotted as the difference between the fictive temperature measured during annealing and the average bulk value versus time of annealing. The data shows that the time scale to eliminate the effects of freeze-drying is approximately 25 h at 443.2 K (170 °C) for PS2583[4], which had the lowest reduction of T_g, and in excess of 30 h for the other samples and at 403.2 K (130 °C). It appears that the rate of recovery may be related to the magnitude of the T_g reduction. This, and the long time scales involved, are consistent with the results found in our prior work [22] on linear chains. We emphasize that the TGA results in our prior work [22] showed that residual solvent levels were less than 0.1% indicating that the recovery cannot be attributed to loss of residual solvent.

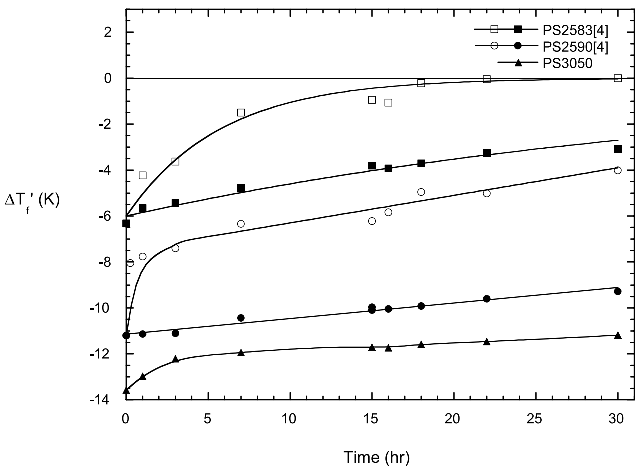

Fig. 5. The depression in the limiting fictive temperature ($\Delta T_f' = T_f' - T_{f',\text{bulk}}$) as a function of annealing time at 403.2 K (closed symbols) and at 443.2 K (open symbols) for the samples indicated. The curves drawn show the trend in the data only.

We can estimate the apparent activation energy for the recovery of the limiting fictive temperature back to its bulk value based on the temperature dependence shown in Fig. 5. The difference in the logarithmic time to reach a given recovery value at two temperatures may be related to the apparent activation energy for the process:

$$\ln t_2 - \ln t_1 = -\frac{E}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{3}$$

where t_2 and t_1 are the times to reach a given $\Delta T_f'$ value at temperatures T_2 and T_1, respectively; E is the apparent activation energy and R is the gas constant. We fit the data shown in Fig. 5 assuming an exponential decay:

$$\Delta T_f' = \Delta T_{f0}' \, e^{-ct} \tag{4}$$

where $\Delta T_f'$ is the difference between the limiting fictive temperature and the bulk value at any given time t, $\Delta T_{f0}'$ is the initial difference in $\Delta T_f'$ after freeze-drying, and c is a constant at a given temperature. The apparent activation energy can then be determined from the temperature dependence of the values of c :

$$\frac{E}{R} = \frac{\ln c_2 - \ln c_1}{(1/T_2 - 1/T_1)} \tag{5}$$

where the subscripts indicate temperatures 1 and 2, respectively. For the PS2583[4] sample, having an apparent molecular weight of 40.8 kg/mol, the apparent activation energy is 16.6 ± 1.1 kcal/mol (69.6 ± 4.6 kJ/mol). The error in the activation energy is based on the error in the constant c obtained from the fit of Eq. (4) to the data. For the PS2590[4] sample, having an apparent molecular weight of 195.5 kg/mol, the apparent activation energy was found to be 15.1 ± 4.5 kcal/mol (63.2 ± 18.8 kJ/mol); the larger error arises from the poorer fit of the data to Eq. (4). The apparent activation energies for the two samples are the same indicating that the same molecular mechanism is responsible for the recovery. In addition, the values are much lower than the apparent activation energy for viscous flow, which we calculated from the zero-shear viscosity data of McKenna et al. [43] for several cyclic polystyrenes to range from 76.7 kcal/mol at 403.2 K (130 °C) to 43.3 kcal/mol at 443.2 K (170 °C). The low apparent activation energy for recovery of the T_g depression relative to that for viscous flow indicates that viscous flow is not responsible for the recovery observed. This is in agreement with the conclusions from our prior work [22] studying the effect of freeze-drying on linear polystyrene. In addition, we note that we can use the activation energy for PS2583[4] to estimate the time scale to reach equilibrium at 323.2 K (150 °C). In this case, it is 67 h, which is similar to the time scales observed for the 16.7 and 390 kg/mol linear polystyrenes previously studied [22].

Although the results presented corroborate the prior conclusion [22] that reduced entanglement density is not responsible for the depression in the glass temperature in freeze-dried polystyrene, it is not clear what the origin of the reduced T_g of freeze-dried samples is, nor is it clear why the cyclic polystyrenes show significantly larger reductions than their linear counterparts for the conditions used in this and the previous study (which were the same). In addition, it is not clear why the magnitude of the reductions ranges from 7 to 14 K for the three cyclic samples studied and from 2 to 5 K for the five linear samples previously studied [22]. In both studies, no systematic dependence of the T_g depression on molecular weight was observed. One might have expected that the magnitude of the T_g depression arising from freeze-drying from a given concentration would be inversely related to molecular weight for molecular weights at which entanglements occur since the critical concentration for chain interpenetration [62] varies as $M^{-1/2}$, but this is clearly not the case. The reproducibility of the depression between different freeze-dried batches, and even between different laboratories [since a sample of the linear polystyrene freeze-dried by Plazek over twenty years ago showed the same T_g depression (within less than 2 K) for his freeze-dried sample as for ours when we redissolved and re-freeze-dried the sample using a similar freeze-drying technique], leads us to conclude that there is some as yet unidentified sample-specific detail that influences the magnitude of the T_g depression observed. Furthermore, we recall the studies of Xue et al. [26,27] for polystyrene freeze-dried from cyclohexane that showed even larger effects than those we have found, suggesting that the T_g depression upon freeze-drying is extremely sensitive to the details of the process.

The differences observed between freeze-dried polystyrene and that confined to microspheres [36,37] seems, at first glance, to indicate that different mechanisms are involved in the two phenomena. In the freeze-dried material, a reduction of T_g is observed and no change in ΔC_p is observed. On the other hand, in the microspheres, a reduction in ΔC_p is observed with no change in T_g. However, an explanation of the microsphere data has been given in terms of a two-layer model [35,63], in which the surface layer has a depressed T_g associated with the 'missing' ΔC_p and the inner layer shows bulk behavior. We note that two-layer models have also been proposed to explain the T_g depression in ultrathin polymer films [5], as well as by Park and McKenna [4] to explain the simultaneous occurrence in glass-formers confined to nanopores of a reduced T_g (presumed to be in the interior) and an increased T_g (presumably at the interface). More recent work from Schonhals and co-workers suggests that there may be competing size and surface effects [64,65]. A more complex picture is also supported by the recent study by Ellison and Torkelson [21], in which not only a distribution of T_gs in thin films was reported, but also that the gradient in T_g depends on film thickness. The supposition that the observed changes in the glass transition for materials confined to thin films, nanopores, and microparticles may arise from the same competing mechanisms as those which cause the depression of T_g in freeze-dried materials requires further investigation. Finally, the fact that molecular architecture has such a significant influence on the magnitude of the T_g reduction for freeze-dried material suggests that additional work is warranted to understand this intriguing effect.

4. Conclusion

The effects of freeze-drying from dilute solution on the glass transition temperature for three cyclic polystyrenes, with molecular weights ranging from 4.0 to 195.5 kg/mol, have been studied by DSC. Freeze-drying is found to depress the glass transition from 7 to 14 K and the effect does not vary systematically with molecular weight over the range studied. The depressions observed for the cyclic polystyrenes are considerably greater than the 2–5 K depressions observed for linear polystyrenes freeze-dried under the same conditions. Recovery of the bulk T_g occurs with sufficiently high temperature annealing. Complete recovery for the 40.8 kg/mol sample, which showed the smallest reduction in T_f' after freeze-drying, occurred at approximately 25 h at 443.2 K (170 °C), whereas recovery was longer for the other samples and at 403.2 K. The recovery time appears to be related to the magnitude of the depression of the glass temperature rather than to molecular weight or viscosity. The apparent activation energy for recovery is 16.6 ± 1.1 kcal/mol for the 40.8 kg/mol sample and was 15.1 ± 4.5 kcal/mol for the 195.5 kg/mol sample, both considerably lower than the activation energy for viscous flow. The origin of the reduction in T_g observed after freeze-drying is unknown, but the data corroborates our previous conclusion that the depression is not due to a reduced entanglement concentration.

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