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Characteristic Length of the Glass Transition in Isochorically Confined Polymer Glasses

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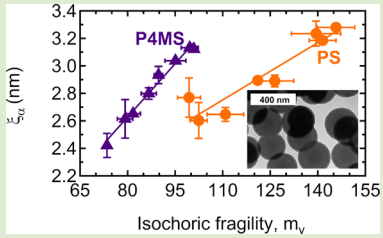
Supporting Information

ABSTRACT: We report the effect of isochoric confinement on the characteristic length of the glass transition (ξ_α) for polystyrene (PS) and poly(4-methylstyrene) (P4MS). Utilizing silica-capped PS and P4MS nanoparticles as model systems, ξ_α values are determined from the thermal fluctuation model and calorimetric data. With decreasing nanoparticle diameter, ξ_α decreases, suggesting a reduction in the number of segmental units required for cooperative motion at the glass transition under confinement. Furthermore, a direct correlation is observed between ξ_α and the isochoric fragility (m_v) in confined polymers. Due to a nearly constant ratio of the isochoric to isobaric fragility in confined polymer nanoparticles, a correlation between ξ_α and m_v also implies a correlation between ξ_α and the volume contribution to the temperature dependence of structural relaxation. Lastly, we observe that when the fragility and characteristic length are varied in the same system the relationship between the two properties appears to be more correlated than that of across different bulk glass-formers.



Polymers under nanoscale confinement can exhibit dramatic changes in glassy properties relative to the bulk. For polystyrene (PS), reductions in the glass transition temperature (T_g) have been observed in a range of confined geometries, including supported thin films,[1] freestanding thin films,[2] nanocomposites,[3] and nanoparticles.[4,5] While significant interest and debate about the origins and existence of T_g deviations with confinement still remain,[6] one way to increase our understanding of glassy behavior in confined polymers is to examine other manifestations of the glass transition, e.g., the fragility. The fragility (m) describes the steepness of the temperature (T) dependence of the cooperative segmental relaxation time (τ) at T_g and is mathematically defined as[7,8]

$$m = \left[\frac{d \log \tau}{d(T_g/T)}\right]_{T=T_g} \quad (1)$$

Glass-formers with high m-values, e.g., PS (m = 150),[9] display a large rate of increase in relaxation time as temperature is reduced toward T_g.

A classical theory to explain the rapid increase in cooperative segmental relaxation time as T_g is approached from higher temperatures is the Adam−Gibbs (AG) theory.[10] The central feature of the AG theory is a growing length scale (ξ) required for cooperative segmental motion or rearrangement, as T is decreased toward T_g. An increase in the cooperative length increases the number of molecules or segmental units (z) in a hypothesized cooperatively rearranging region (CRR), which is reflected in a loss of configurational entropy. From the AG theory, the cooperative segmental relaxation time can be related to z in a CRR[11]

$$\tau = \tau_\infty \exp\left(\frac{zE_\infty}{T}\right) \quad (2)$$

where τ_∞ and E_∞ are constants, representing the high-T relaxation time and activation energy, respectively. In eq 2, z is a function of T; hence, the temperature-dependent activation energy, $E(T)$, is equal to $z(T)E_\infty$. Combining eqs 1 and 2, a relationship between the fragility and the CRR size, as represented by z, can be obtained[12]

$$m = \frac{E_\infty}{T_g} z(T_g) - E_\infty \left.\frac{dz}{dT}\right|_{T_g} \quad (3)$$

Here, the AG theory suggests that the fragility should correlate with both the size of a CRR at T_g, i.e., the characteristic length of the glass transition (ξ_α), and the rate of change in ξ_α with temperature at T_g.

Experimental studies on various types of bulk glass-formers have suggested that a simple correlation between the fragility and ξ_α may not exist.[13−16] For instance, Qiu and co-workers observed no obvious trend between the two quantities across four glass-forming materials, i.e., glycerol, *o*-terphenyl, sorbitol, and poly(vinyl acetate).[13] The lack of correlation between fragility and ξ_α may be due to the second term on the right-hand side of eq 3 describing the rate of change of the extent of cooperative motion. That is, the contribution from this term has been shown to be more important than z(T_g) in causing changes in the fragility value.[11]

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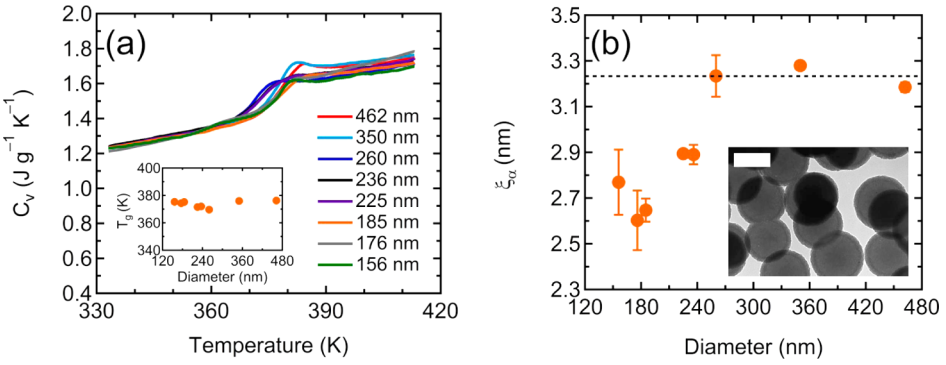

Figure 1. (a) DSC traces of silica-capped PS nanoparticles with diameters ranging from 156 to 462 nm. Inset plots the midpoint T_g vs nanoparticle diameter. (b) ξ_α as a function of diameter for PS. The dotted line represents the bulk ξ_α value for PS (3.23 nm), determined by averaging ξ_α values of nanoparticles exhibiting bulk behavior, i.e., d > 250 nm. Error bars represent standard deviations of repeated measurements. Inset shows a representative transmission electron microscopy (TEM) image of silica-capped 236 nm diameter PS nanoparticles (scale bar equals 200 nm).

Nevertheless, Sokolov and co-workers recently showed that across various types of bulk glass-formers the characteristic length of the glass transition correlated directly with the volume contribution to the temperature dependence of structural relaxation.[14,15] That is, under isobaric conditions, cooling of the polymer toward T_g results in a reduction in both thermal energy and specific volume.[17−19] Hence, the rapid change in dynamics near the glass transition is governed by a combination of thermal and volume effects, and the isobaric fragility (m_p) can be written in terms of the two effects[17,19]

$$m_p = \left(\frac{\partial \log \tau}{\partial(T_g/T)}\right)_V + \left(\frac{\partial \log \tau}{\partial V}\right)_T \left(\frac{\partial V}{\partial(T_g/T)}\right)_P (T = T_g) \quad (4)$$

where V is the volume and P is the pressure. The first term on the right-hand side of eq 4 is simply the definition of the isochoric fragility (m_v), which describes the effect of thermal activation on dynamics as T_g is approached. The second term ($m_p - m_v$) describes the effect of volume on dynamics, as both T and P are held constant. We note that it is this term which is proposed to correlate with ξ_α, at least across different types of bulk glass-formers.[14−16]

In this Letter, we examine the isochoric fragility and the characteristic length of the glass transition in confined polymers to explore correlations between the two properties within the *same system*. We have recently shown that both isobaric and isochoric fragilities decrease with decreasing diameter for polymers confined in the nanoparticle geometry.[9,20] However, the question remains as to whether a corresponding change in the characteristic length at T_g exists for confined systems.[11,12] In this study, we utilize differential scanning calorimetry (DSC) and the thermal fluctuation model (eq 5) to determine the characteristic length of the glass transition for polymers under isochoric confinement. For the case of silica-capped PS and poly(4-methylstyrene) (P4MS) nanoparticles, we show that ξ_α decreases with increasing confinement, i.e., with decreasing diameter (d). Hence, a strong correlation between ξ_α and m_v in confined polymers is reported for the first time. Furthermore, given the unique geometry of silica-capped polymer nanoparticles, a correlation between ξ_α and m_v also implies a correlation between ξ_α and $m_p - m_v$, as detailed below. The results are discussed in the context of the Adam−Gibbs theory and compared with recent works correlating fragility and CRR size across various types of bulk glass-formers[14−16] and in layered thin films.[21]

Monodisperse PS and P4MS nanoparticles with diameters ranging from 110 to 630 nm were synthesized using surfactant-free emulsion polymerization.[4,9,20] Subsequently, the bare PS and P4MS nanoparticles were coated with a ∼30 nm thick silica shell via a modified Stöber method.[9,20,22,23] Silica capping of the polymer nanoparticles resulted in isochoric conditions, as previously shown by comparing the heat capacity jump at T_g for the silica-capped samples to bare nanoparticles or the bulk.[9,20,24] The synthesized silica-capped nanoparticles were dried under the hood overnight and subsequently annealed under vacuum at 353 K for at least 24 h. Thermal measurements were conducted using DSC (TA Instruments Q2000) at constant cooling and heating rates of 10 K/min. The Supporting Information provides details on relevant characterization techniques.

While several experimental techniques, including light scattering[14] and 4-D nuclear magnetic resonance (NMR),[13] have been used in determining cooperative length scales in various glass-formers, an alternative method to calculate ξ_α was derived by Donth[25,26] based on thermal fluctuations in compact subsystems.[27] According to Donth's approach, ξ_α can be determined from the T_g, the isochoric heat capacity (C_v), the density of the glass-former (ρ), and the mean temperature fluctuations across the CRR volume (δT), which is related to the breadth of the glass transition, as follows

$$\xi_\alpha = \left[\frac{k_B T_g^2 \Delta(1/C_v)}{\rho(\delta T)^2}\right]^{1/3} \quad (5)$$

Here, k_B is the Boltzmann constant and $\Delta(1/C_v)$ is equal to $1/C_{v,glass}(T_g) - 1/C_{v,liquid}(T_g)$. Utilizing calorimetric techniques, e.g., DSC or modulated differential scanning calorimetry (MDSC), the parameters C_v, T_g, and δT can be determined in a single experiment. In previous studies, eq 5 has been used to calculate ξ_α in bulk glass-formers, i.e., small molecules[28] and polymers,[16,26,28−31] as well as small molecules confined in nanopores[32] and polymers confined in the nanocomposite geometry.[33]

To confirm the thermal fluctuation model in determining the characteristic length of the glass transition to systems investigated here, eq 5 was first applied to a series of commercially obtained (Sigma-Aldrich or Scientific Polymer) bulk PS with M_w ranging from 1.14 to 250 kg/mol. Detailed

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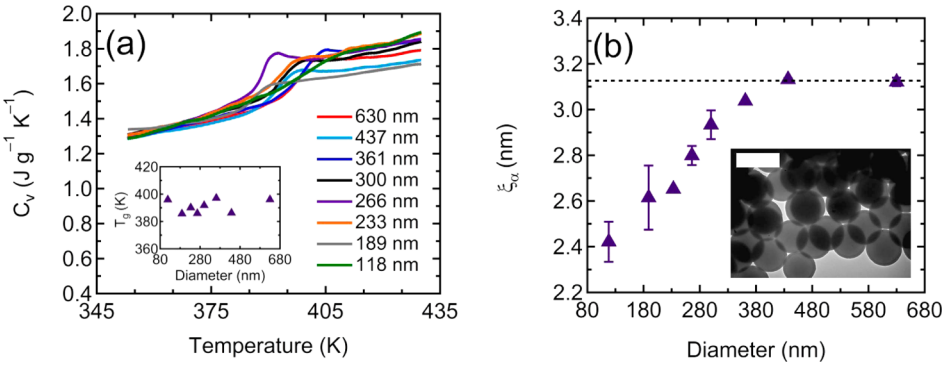

Figure 2. (a) DSC traces of silica-capped P4MS nanoparticles with diameters ranging from 118 to 630 nm. Inset plots the midpoint T_g vs nanoparticle diameter. (b) ξ_α as a function of diameter for P4MS. The dotted line represents the bulk ξ_α value for P4MS (3.13 nm), determined by averaging ξ_α values of nanoparticles exhibiting bulk behavior, i.e., d > 430 nm. Error bars represent standard deviations of repeated measurements. Inset shows a representative TEM image of silica-capped 361 nm diameter P4MS nanoparticles (scale bar equals 500 nm).

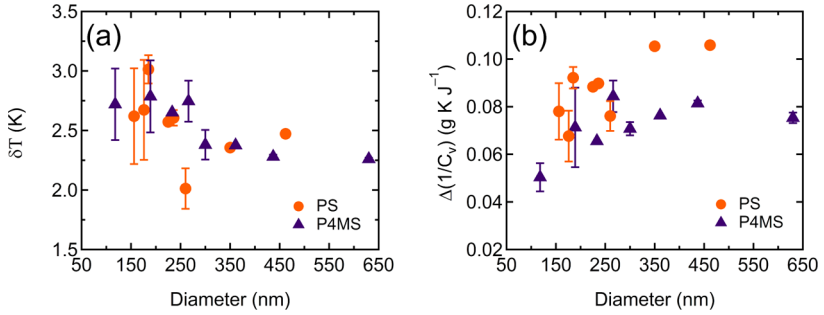

Figure 3. (a) δT and (b) $\Delta(1/C_v)$ as a function of nanoparticle diameter for silica-capped PS (circles) and P4MS (triangles). Error bars represent standard deviations from repeated measurements.

results are highlighted in the Supporting Information (Figures S1 and S2). As the PS M_w is reduced from 250 to 1.14 kg/mol, ξ_α decreases from 3.7 to 2.9 nm. The absolute ξ_α values (and the trend with M_w) determined from Donth's approach are in agreement with that from an alternative technique.[14]

Figure 1(a) shows DSC thermograms for silica-capped PS nanoparticles with diameters ranging from 156 to 462 nm, in which the isochoric heat capacity, C_v, is plotted vs temperature. We note that the PS M_w for all nanoparticle samples ranges from 100 to 400 kg/mol with a polydispersity index (PDI) of ∼3. Here, no systematic deviation (within experimental error) in the midpoint T_g as a function of nanoparticle diameter is observed (Figure 1(a) inset), in agreement with previous works.[4,9,24] By capping bare PS nanoparticles with a rigid silica shell of ∼30 nm in thickness (Figure 1(b) inset), isochoric conditions are established.[9] Due to the unique geometry of silica-capped nanoparticles, the isochoric heat capacity, C_v, is then directly measured via DSC and can be used without further approximations in the thermal fluctuation model.

Figure 1(b) shows the characteristic length of the glass transition as a function of nanoparticle diameter calculated from eq 5 using T_g, $\Delta(1/C_v)$, and δT values extracted from the calorimetric data presented in Figure 1(a). Here, T_g is taken as the midpoint temperature between the extrapolated liquid and glassy lines, and δT is determined as $\delta T = \Delta T/2.5$, where ΔT represents the temperature interval in which the isochoric heat capacity varies between 16% and 84% of the total heat capacity jump at T_g (ΔC_v).[28,31] The dotted line represents the bulk ξ_α value for PS (= 3.23 nm), determined by averaging ξ_α values of silica-capped PS nanoparticles which exhibit bulk behavior, i.e., d > 250 nm. A bulk ξ_α value of 3.23 nm is in close agreement with the size of CRR for bulk PS M_w = 233 kg/mol (ξ_α = 3.38 nm) determined using the frequency of the boson peak and the transverse sound velocity.[14] As shown in Figure 1(b), when the nanoparticle diameter is reduced from 462 to 156 nm, ξ_α decreases from the bulk value of 3.23 to 2.77 nm. The onset diameter in which a reduction in ξ_α is observed for silica-capped PS is ∼260 nm, which is equivalent to the onset diameter at which a reduction in the isochoric fragility was observed in silica-capped PS nanoparticles.[9]

To examine the effect of chemical structure on the observed ξ_α-confinement effect, calorimetry is conducted on silica-capped P4MS nanoparticles with diameters ranging from 118 to 630 nm as shown in Figure 2(a), in which the isochoric heat capacity is plotted vs temperature. We note that the P4MS M_w for all nanoparticle samples ranges from 40 to 400 kg/mol with a PDI of ∼3. The difference between the chemical structures of PS and the P4MS is the addition of a methyl group on the 4-position of the phenyl ring for P4MS. As shown in Figure 2(a) inset, the midpoint T_g does not deviate systematically (within experimental error) for P4MS with decreasing nanoparticle diameter, in agreement with previous results[20] and the results of silica-capped PS nanoparticles. Here, the absolute T_g of P4MS is ∼10 K higher than PS due to the fact that the alkyl substituent on the phenyl ring increases the bulkiness of the repeat unit, which reduces segmental mobility and causes an increase in T_g.[34]

Figure 2(b) plots the calculated ξ_α for P4MS as a function of nanoparticle diameter using T_g, $\Delta(1/C_v)$, and δT values extracted from the calorimetric data presented in Figure 2(a). The dotted line represents the bulk ξ_α value for P4MS (= 3.13 nm), determined by averaging ξ_α values of nanoparticles

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exhibiting bulk behavior, i.e., $d > 430$ nm, which is in agreement with the literature value.[29] In Figure 2(b), as the diameter is decreased from 630 to 118 nm for P4MS, ξ_α decreases from the bulk value of 3.13 to 2.42 nm. Furthermore, the onset diameter at which a reduction in the characteristic length of the glass transition occurs is ∼420 nm. Analogous to the case of silica-capped PS nanoparticles, the onset diameter of a reduction in ξ_α in P4MS is equivalent to the diameter at which a reduction in the isochoric fragility was observed to occur in silica-capped P4MS nanoparticles.[20] A larger onset diameter of ∼420 nm for P4MS, as compared to PS (∼260 nm), in the ξ_α-confinement effect may be a result of a more pronounced effect of the linear alkyl as flexible spacers in confined systems.[34]

In both silica-capped PS and P4MS, we observe a reduction in ξ_α as nanoparticle diameter is decreased. A reduction in ξ_α suggests that the number of segmental units (z) required for cooperative motion at T_g is reduced as PS and P4MS become more isochorically confined in the nanoparticle geometry. We note that since the T_g of PS and P4MS does not deviate systematically with nanoparticle diameter a reduction in ξ_α is then caused by an apparent increase and decrease in δT and $\Delta(1/C_v)$, respectively, with confinement, as shown in Figure 3. An increase in δT implies a broadening of the glass transition event, i.e., a wider temperature range in which the glass transition takes place. A broader glass transition can be understood as a result of a reduced mobile layer at the polymer/silica interface, and the effect is more pronounced as the nanoparticle diameter is reduced (due to an increase in the surface area to volume ratio). The results are consistent with previous observations of a broadening of the relaxation peak toward higher temperatures in variable cooling rate DSC measurements of silica-capped PS and P4MS nanoparticles for the smaller diameters at the lower cooling rates.[9,20] Furthermore, a decrease in $\Delta(1/C_v)$ with confinement may also be a consequence of the reduced mobile layer.

Figure 4 examines the relationship between ξ_α and m_v for polymers under confinement. Here, a linear correlation between ξ_α and m_v is observed for both silica-capped PS and P4MS nanoparticles, which is a key result of the current study. The values of m_v are taken from refs 9 and 20 in which variable cooling rate DSC was utilized to determine the fragility of silica-capped polymers. While recent studies in the literature have revealed no clear correlation between ξ_α and m_p (or m_v) across various types of bulk glass-formers, ξ_α has been observed to correlate linearly to the volume contribution to the temperature dependence of structural relaxation, i.e., $m_p - m_v$.[14−16] For polymer nanoparticles, we have shown previously that the relative contribution of thermal effects to changes in dynamics as T_g is approached, i.e., the ratio m_v/m_p, remains nearly constant with increasing confinement.[20] A nearly constant m_v/m_p value with confinement implies that the volume contribution to the temperature dependence of structural relaxation, or $m_p - m_v$, should also decrease proportionally with a decrease in m_v in confined polymer. In other words, m_v is proportional to $m_p - m_v$ for all polymer nanoparticle diameters. Hence, if ξ_α correlates linearly to m_v, as shown in Figure 4 for PS and P4MS, then ξ_α should also correlate linearly to $m_p - m_v$. A correlation between ξ_α and $m_p - m_v$ is clearly observed in the inset of Figure 4 for silica-capped P4MS nanoparticles, consistent with the observation that ξ_α correlates with $m_p - m_v$ across various types of bulk glass-formers.[14−16] Furthermore, in a recent experimental study by Arabeche and co-workers on layered polycarbonate (PC)/poly(methyl methacrylate) (PMMA) films, ξ_α was found to correlate linearly with both m_p and $m_p - m_v$ in PC as the layer thickness was reduced from 16 μm to 12 nm.[21] Similarly, for bulk PS of varying M_w, m_p was found to be linearly correlated to ξ_α.[14] It is intriguing to note that those results and the results of the current study suggest that for systems in which the fragility and characteristic length are varied within the *same system* (either through confinement or M_w) the relationship between fragility and ξ_α appears to be more correlated when compared to that of across various types of bulk glass-formers.

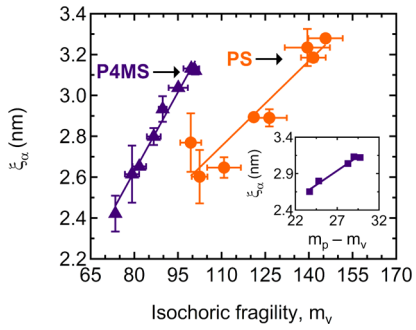

Figure 4. ξ_α as a function of the isochoric fragility, m_v, for both silica-capped PS (circles) and P4MS (triangles) nanoparticles. Values of the isochoric fragility are taken from refs 9 and 20. Inset shows ξ_α vs $m_p - m_v$, i.e., the volume contribution to the temperature dependence of structural relaxation, for P4MS, where the isobaric fragility, m_p, is taken from ref 20. Solid lines are linear fits to the experimental data, and error bars represent standard deviations from repeated measurements.

An interesting and unique observation in the current study is that while both m_v and ξ_α decrease with increasing confinement in silica-capped polymer nanoparticles the T_g remains invariant (Figures 1(a) and 2(a) insets). In the context of the Adam−Gibbs theory, the fragility should be a function of $z(T_g)$ (or ξ_α), dz/dT at T_g, E_∞, and the T_g, as shown in eq 3. Hence, if the T_g is constant and both $z(T_g)$ and fragility are reduced with confinement, one implication from the AG theory is that E_∞ must also remain constant with confinement. As a result, for the T_g to be constant while $z(T_g)$ decreases at $\tau = 100$ s, the prefactor, τ_∞, in eq 2 must increase with confinement. Alternatively, if τ_∞ is to remain constant, then the E_∞ value must grow with increasing confinement to compensate for a shrinking $z(T_g)$ to get the same T_g. In this scenario, when T_g is constant while E_∞ increases and $z(T_g)$ decreases, the first term on the right-hand side of eq 3 is more or less constant; hence, the only term which will contribute to the decrease in fragility with confinement observed in the current work is the dz/dT term. Currently, the exact scenario in which our results satisfy the AG theory cannot be confirmed. However, future experiments using frequency-based techniques, e.g., dielectric relaxation spectroscopy, may shed more light. Lastly, we note that in recent computational studies on polymer nanocomposites it has been shown that the change in the dz/dT term with confinement contributes to the fragility much more than the size of the CRR itself.[11,12]

In summary, the characteristic length of the glass transition, ξ_α, was calculated using the thermal fluctuation model proposed by Donth[25,26] for a series of silica-capped PS and P4MS nanoparticle samples with diameters ranging from 118 to 630 nm. In both cases, with increasing the degree of isochoric confinement, i.e., decreasing nanoparticle diameter, ξ_α was found to decrease below an onset diameter. We then showed

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that ξ_α correlated directly to the isochoric fragility, m_v, under confinement. Furthermore, the observed correlation between ξ_α and m_v in confined polymer was found to be consistent with the correlation of ξ_α and $m_p - m_v$ observed across various types of bulk glass-formers[14−16] and with layered thin films.[21]

■ ASSOCIATED CONTENT

Supporting Information

Full characterization details and application of the thermal fluctuation model toward bulk polymers are given. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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