Soft Matter

PAPER

Cite this: DOI: 10.1039/c3sm50171j

Received 15th January 2013

Accepted 29th April 2013

DOI: 10.1039/c3sm50171j www.rsc.org/softmatter

Introduction

The emergence of nanotechnology will necessitate the use of polymers restricted to confined geometries at the nanoscale. For instance, polymers processed into the thin film geometry (with thickness (h) < 100 nm) may be exploited for use as templates in microelectronics,¹ active layers in photovoltaic cells,² non-biofouling protective coatings,³ and membranes in separation technologies.⁴ Polymer nanoparticles (with diameter (d) < 500 nm) may find use as vehicles in drug delivery,⁵ components in fluorescent imaging,6 performance reinforcing additives,7 and components in photonic structures.8 Inevitably, in the confined state, the presence of interfaces will have a profound effect in dictating the average material properties. In the above applications, it is the physical properties of the confined polymer (irrespective of thin film or nanoparticle geometry) that are of significant importance. If the properties of polymers change due to physical confinement (i.e., decrease in film thickness or nanoparticle diameter) or interfacial effects, our understanding of such effects will be essential in assessing their potential use in nanotechnology.

Without question, the glass transition temperature (T_{σ}) has been the most thoroughly investigated property of confined polymers in the past two decades.9-27 Undoubtedly, this is, in part, due to the abrupt change in mechanical and thermal properties at T_g and its relevance in dictating the practical use temperature for polymers. Fundamentally, the $T_{\rm g}$ of confined systems has been explored as a means for assessing the characteristic length scales that dictate the glass transition and properties of the glassy state. The T_{g} of polymers can deviate substantially from the bulk with physical confinement to the nanometer length-scale.⁹⁻²⁷ Changes in T_g with confinement have been explained to be a result of (or lack of) interfacial interactions between the polymer and the interface.9-11,14,18,19,23 When attractive interactions between the polymer and interface (substrate) persist, enhancements in T_{g} may be observed.^{10,18,19} On the other hand, repulsive or free-soft interfaces can lead to a reduction in T_g with confinement.^{9,11,14,23} By tuning the interfacial interactions between the substrate and confined polymer, it is possible to systematically change the $T_{\rm g}$.^{16,18} The influence of confinement-interfaces on systematic deviations in T_{g} of polymers has been observed in thin films,9-14,16,18,24 nanoparticles, 20,23,25,28-30 nanocomposites,^{15,17,19,21} and polymer confined in nanopores.^{26,27} Hence, the phenomenon appears to be general with respect to different confining geometries.

Understanding the impact of confinement on the T_{g} of polymers is important, but it alone fails to elucidate other pertinent characteristics of the glass transition. For instance, it fails to provide information about the temperature dependence of the cooperative segmental dynamics at T_{g} , a phenomenon commonly described by the dynamic fragility index. The dynamic fragility index (m) describes how fast dynamics change for glass-forming liquids as T_g is approached.^{31,32} Mathematically, m is defined as:

$$m = \left[\frac{\mathrm{d}\log\tau}{\mathrm{d}(T_{\mathrm{g}}/T)}\right]_{T=T_{\mathrm{g}}} \tag{1}$$

where τ is the relaxation time and T is temperature. Experimentally, the fragility index is normally measured under

Fragility and glass transition temperature of polymer confined under isobaric and isochoric conditions

Chuan Zhang^a and Rodney D. Priestley*^{ab}

It is now well established that the glass transition temperature (T_q) of polymers can deviate substantially from the bulk with nanoscale confinement. Understanding the impact of confinement on the T_{α} of polymers is important but it does not provide information about the temperature dependence of the cooperative segmental dynamics near the T_{q} , a phenomenon commonly referred to as the dynamic fragility. Here, we measure the dynamic fragility index (m) as well as the T_q of confined poly(4-methylstyrene) (P4MS) under isobaric and isochoric conditions. We accomplish this via variable cooling rate differential scanning calorimetry (DSC) studies on aqueous-suspended and silica-capped P4MS nanoparticles. We observe that both the isobaric (m_p) and isochoric (m_v) fragilities decrease with confinement. However, T_q decreases and remains constant with isobaric and isochoric confinement, respectively. The importance of interfaces in the observed trends as well as comparisons to prior studies is discussed.

View Article Online

^aDepartment of Chemical and Biological Engineering, Princeton University, Princeton, NJ 08544, USA. E-mail: rpriestl@princeton.edu

^bPrinceton Institute for the Science and Technology of Materials, Princeton University, Princeton, NJ 08544, USA

isobaric (constant pressure) conditions, and the resulting fragility may be expressed as $m_{\rm p}$, the isobaric fragility. To a limited extent, the isobaric fragility of confined polymers has been investigated.^{33–36} In the case of polystyrene (PS) thin films supported on an Al substrate, $m_{\rm p}$ has been observed to decrease as a function of decreasing film thickness when h < 50 nm.³³ In the absence of strong interfacial interactions either between thin film and substrate or polymer matrix and inorganic nanofiller, the isobaric fragility has generally been reported to decrease with increasing the extent of confinement.^{34–36}

Recent molecular dynamics simulations have investigated the dynamic fragility of polymer nanocomposites and thin films.37,38 In nanocomposites, the confining dimension is the interparticle distance between nanofiller elements. In the case of non-attractive interactions, the dynamic fragility decreased with increasing concentration of the nanofiller.37 Such computations appear in agreement with experiments; however, there is one significant difference. That is, the simulations were performed under isochoric (constant volume) conditions; hence, the reported fragility represents $m_{\rm v}$, the isochoric fragility and not $m_{\rm p}$, which is commonly measured experimentally. In a follow up study, simulations were used to investigate the influence of thermodynamic path (i.e., isobaric versus isochoric conditions) on the dynamic fragility of polymer nanocomposites.³⁸ In summary, a qualitatively similar behavior was observed irrespective of the thermodynamic path. However, quantitatively, the effects of confinement on the isobaric fragility were significantly reduced compared to the isochoric fragility at a similar extent of confinement (i.e., nanoparticle concentration). Experimentally, analogous studies that measure both isobaric and isochoric fragilities of confined polymer have not been reported. In this study, we make the first of such measurement.

Previously, we have demonstrated the ability to measure the isochoric fragility of confined PS.39 Isochoric confinement was achieved by capping PS nanoparticles with a rigid inorganic shell layer. The fragility was measured via variable cooling rate differential scanning calorimetry (DSC) (see Experimental/ Results section for more detail). It was demonstrated that with isochoric confinement the fragility index decreased sharply for nanoparticles with d < 260 nm. Such observation is in qualitative agreement with simulations performed under isochoric conditions. In contrast to the simulation findings for polymer nanocomposites (under isochoric conditions), we did not observe a systematic change of $T_{\rm g}$ in proportion with the isochoric fragility. However, in a recent computational study on fragility and $T_{\rm g}$ of supported polymer thin films, it was observed that for the thinner films, the ratio of T_{g} to *m* as a function of film thickness was not constant.40 Furthermore, as illustrated in ref. 40, a large drop in the $T_{\rm g}$ as a function of the distance from the center of the film towards the free surface was not accompanied by a corresponding change in the fragility. Combined, these experimental and simulation studies illustrate the need for further investigations on the influence of thermodynamic path on the dynamic fragility of polymers as well as its relationship to $T_{\rm g}$ under confinement. In this study, we measure both the isobaric and isochoric fragilities, as well as the $T_{\rm g}$, of confined poly(4-methylsytrene) (P4MS). We achieve this *via* DSC studies on aqueous-suspended and silica-capped nanoparticles of P4MS. We show that both isobaric and isochoric fragilities decrease with confinement. On the other hand, $T_{\rm g}$ decreases and remains constant with isobaric and isochoric confinement, respectively. The importance of interfaces in the observed trends as well as comparisons to prior studies is highlighted.

Experimental

Synthesis of P4MS nanoparticles

Bare (aqueous-suspended) P4MS nanoparticles were synthesized from surfactant-free emulsion polymerization. In a representative synthesis to generate \sim 450 nm diameter nanoparticles, 0.037 g of ammonium persulfate (≥98%, Sigma-Aldrich) was initially added to 100 mL of deionized (DI) water in a three-neck flask. The solution was purged with nitrogen for 20 minutes and then heated to 348 K. Subsequently, 2.5 g of 4-methylstyrene (96%, Sigma-Aldrich) was combined with 0.05 g of acrylic acid (99%, Sigma-Aldrich), and the mixture was injected into the flask. Prior to usage, 100 mL of 4-methylstyrene was de-inhibited and dried by stirring the as-received monomer in 1 g of *tert*-butylcatechol inhibitor remover (Sigma-Aldrich) and 1 g of CaH₂ (95%, Sigma-Aldrich) for 1 hour and then filtered. The polymerization reaction was allowed to proceed under reflux conditions for 20 h. After polymerization, the resulting nanoparticle suspension was washed three times by centrifugation and ultimately suspended in DI water. A small portion of the aqueous-suspended sample was dried and then annealed at 413 K for at least 12 hours to form bulk P4MS. Nanoparticle sizes were controlled by changing the starting concentrations of 4-methylstyrene, ammonium persulfate, and/ or acrylic acid in subsequent reactions. We note that the addition of a small amount of acrylic acid (≤ 5 wt% with respect to 4-methylstyrene for all nanoparticle samples) as a co-monomer provided stability to the colloidal suspension.

Silica-capping of P4MS nanoparticles

In order to coat the bare P4MS nanoparticles with a \sim 30 nm silica shell, a modified Stöber method was implemented.41,42 Here, a 4 mL portion of the aqueous-suspended bare P4MS nanoparticles ($c \approx 80 \text{ g L}^{-1}$) was added dropwise into a 10 mL solution containing poly(allylamine hydrochloride) (PAH, Sigma-Aldrich, $M_{\rm w} = 15$ kg mol⁻¹, c = 1.2 g L⁻¹) and NaCl (Fisher Chemical, $c = 1.4 \text{ g L}^{-1}$) in water. The mixture was stirred for 1 hour and then washed twice with DI water. Next, the nanoparticles were dispersed in 10 mL of poly(vinyl pyrrolidone) solution in ethanol (PVP, Sigma-Aldrich, $M_{\rm w} = 360$ kg mol^{-1} , $c = 7 \text{ g L}^{-1}$). The mixture was allowed to stir for 1 hour. Afterwards, the P4MS nanoparticles were washed once with DI water and ultimately suspended in 20 mL of fresh ethanol. Subsequently, 0.3 mL of tetraethyl ortho-silicate (98%, Sigma-Aldrich) and 1.6 mL of ammonium hydroxide (Sigma-Aldrich) were added to the mixture, and the reaction was allowed to proceed for at least 12 hours. The resulting silica-capped P4MS nanoparticles were washed at least three times with DI water

and ultimately suspended in water. Prior to further characterization, a portion of the silica-capped samples were dried under the hood overnight and subsequently annealed under vacuum at 353 K for at least 24 hours. We note that in the modified Stöber method, the bare P4MS nanoparticle surface was covered with a thin layer of PVP prior to silica-coating because P4MS itself does not have a strong attraction to silica, therefore a bare P4MS surface cannot be coated directly with silica. The concentration of PVP used in the current study with respect to nanoparticle concentration should result in a surface coverage of ~60 PVP polymer chains per nm².⁴¹

Characterization

Diameters of P4MS nanoparticles were measured using images obtained from scanning electron microscopy (SEM) (FEI XL-30). Prior to imaging, the aqueous-suspended P4MS nanoparticles were drop-casted onto carbon tape, allowed to dry in the hood for 12 hours, and then coated with a 5 nm thick iridium layer. Shell thicknesses of silica-capped P4MS nanoparticles were determined from transmission electron microscopy (TEM) (Philips CM100). Gel permeation chromatography (Waters 515 HPLC pump, Polymer Laboratories 30 cm PLGel Mixed-C column, Waters 410 differential refractive index detector, tetrahydrofuran eluent) was used to determine the weightaverage molecular weight (M_w) and polydispersity index (PDI) of synthesized P4MS nanoparticles. Thermogravimetric analysis (TGA) (TA Instruments Q50) was used to determine polymer and silica compositions (i.e., wt%) of the silica-capped P4MS nanoparticles. Thermal measurements of aqueous-suspended



Fig. 1 SEM images of bare 361 nm diameter P4MS nanoparticles (a) before and (b) after repeated thermal cycling in DSC measurements under aqueous environment. Scale bar represents 1 μ m. TEM images of the corresponding silica-capped P4MS nanoparticles (c) before and (d) after repeated thermal cycling in DSC measurements. Scale bar represents 500 nm.

P4MS nanoparticles, dried silica-capped P4MS nanoparticles, and bulk P4MS were conducted using differential scanning calorimetry (DSC) (TA Instruments Q2000) at a constant heating rate of 20 K min⁻¹ and cooling rates ranging from 0.5 K min⁻¹ to 40 K min⁻¹. In subsequent thermal analysis of the silicacapped samples, the heat capacity contribution from the silica shell was removed from the total signal using wt% results obtained from TGA and the heat capacity baseline of Stöber silica nanoparticles. Similarly, for the aqueous-suspended bare nanoparticles, the heat capacity contribution from water was removed from the raw DSC signal. Fig. 1(a) shows a SEM image of a representative sample consisting of 361 nm diameter assynthesized bare P4MS nanoparticles from surfactant-free emulsion polymerization, whereas Fig. 1(b) shows the same nanoparticle sample after the heating/cooling protocol employed in the DSC. Fig. 1(c) shows a TEM image of the corresponding 361 nm diameter nanoparticle sample when coated with a \sim 30 nm silica shell, and Fig. 1(d) shows the same sample after the heating/cooling protocol employed in the DSC. In both cases, it is clear that repeated thermal cycling of aqueous-suspended bare P4MS nanoparticles and dried silica-capped P4MS nanoparticles did not destroy the nanoparticle morphology or cause gross aggregation of the nanoparticles.

Results and discussion

When the temperature is cooled towards the T_g for a glassformer under constant pressure, there occurs both a reduction in the thermal energy and the specific volume of the material.⁴³⁻⁴⁶ Dynamics near the glass transition are thus governed by a combination of thermal activation and volume (*i.e.*, congestion) effects. Because of this, it is possible to define the isobaric fragility, m_p , into two components to describe the relative effects of temperature and volume on the change in molecular dynamics near the glass transition in the following equation:^{43,45}

$$m_{\rm p} = \left(\frac{\partial \log \tau}{\partial (T_{\rm g}/T)}\right)_V + \left(\frac{\partial \log \tau}{\partial V}\right)_T \left(\frac{\partial V}{\partial (T_{\rm g}/T)}\right)_P (T = T_{\rm g}) \quad (2)$$

Here, the first term on the right-hand side of eqn (2) is simply the definition of the isochoric fragility, m_v , which describes the intrinsic effect of temperature, T, on structural relaxation, as volume, V, is held constant (see eqn (1)). For bulk polymeric materials, m_v has not been determined experimentally (presumably due to difficulties in establishing true isochoric conditions), but rather calculated using PVT data and the appropriate equation of state47 or via cross-plotting PVT data to construct isochoric Angell plots.48 The second term on the righthand side of eqn (2) describes the effect of volume on dynamics as both T and pressure, P, are held constant. Hence, the relative magnitudes of the two terms in eqn (2) will provide insights on which component is more dominant in causing the change of molecular dynamics near the glass transition. That is, if the relaxation time, τ , is independent of volume at temperatures close to $T_{\rm g}$, then $m_{\rm p}=m_{\rm v}$, which suggests that there is no volume contribution to glass transition dynamics, and thermal activation is the decisive role in the dynamical behavior. On the other hand, if τ is unchanged as temperature is reduced at a constant volume, then m_v equals zero, which suggests that there is no energetic contribution to the temperature variation of structural relaxation, but rather volume effects is the decisive mechanism governing the change in dynamics.

In the current work, we utilize variable cooling rate DSC to experimentally determine both the isobaric and isochoric fragilities (as well as the T_g) of poly(4-methylstyrene) confined in the nanoparticle geometry. Due to the unique geometry of capping P4MS nanoparticles with a rigid silica shell, isochoric conditions are established, as confirmed previously.^{39,49} As a result, it becomes possible to assess m_v of confined polymer (or even just bulk polymer) in a direct experimental manner. Variable cooling rate DSC was first used by Moynihan and coworkers⁵⁰ to determine the enthalpy relaxation activation energy of glass-formers. Later, Robertson *et al.*⁵¹ and subsequently Wang *et al.*⁵² showed that the dynamic fragility can be determined from the cooling rate, Q, and the fictive temperature, T_f , by first noticing the dependence of the cooling rate on T_f as follows:

$$Q = Q_0 \exp\left(\frac{-E_{\rm g}}{RT_{\rm f}}\right) \tag{3}$$

where Q_0 is a prefactor constant, E_g is the activation energy of the structural relaxation process, and *R* is the gas constant. By comparing the cooling rate (*Q*) to a standard quench rate (Q_{std}) and subsequently taking the logarithm, a relation between the cooling rates and T_f (determined from *Q*) and a standard fictive temperature, $T_{f,std}$ (determined from Q_{std}) can be established:

$$\log\left(\frac{Q}{Q_{\text{std}}}\right) = \frac{E_{\text{g}}}{\ln 10R} \left(\frac{1}{T_{\text{f,std}}} - \frac{1}{T_{\text{f}}}\right) = \left(\frac{E_{\text{g}}}{\ln 10RT_{\text{f,std}}}\right) \left(1 - \frac{T_{\text{f,std}}}{T_{\text{f}}}\right)$$
(4)

Furthermore, by observing that the prefactor term on the right hand side of eqn (4) is simply the definition of the dynamic fragility, m,^{32,53} eqn (4) can be rewritten as:

$$\log\left(\frac{Q}{Q_{\rm std}}\right) = m\left(1 - \frac{T_{\rm f,std}}{T_{\rm f}}\right) = m - m\frac{T_{\rm f,std}}{T_{\rm f}}$$
(5)

here, it becomes apparent that *m* can be extracted from both the slope and the intercept when $\log(Q/Q_{\text{std}})$ is plotted as a function of $(T_{\text{f,std}}/T_{\text{f}})$. In the case where the measurements are conducted under isobaric conditions, $m = m_{\text{p}}$, and under isochoric conditions, $m = m_{\text{v}}$. We note that Q_{std} in the current study is 20 K min⁻¹ and is equivalent to the heating rate used in all cases. Thus, when the heating rate is equal to the cooling rate, $T_{\text{f,std}}$ determined from Q_{std} is equivalent to the T_{g}^{34} and for the sake of subsequent discussion, the two terms are interchangeable. In a recent publication, we have successfully measured m_{v} of silicacapped PS nanoparticles using variable cooling rate DSC,³⁹ the results of which we compare to that of P4MS in a later section.

Fig. 2(a) shows DSC thermograms of representative diameters of aqueous-suspended P4MS nanoparticles (isobaric condition), whereas Fig. 2(b) shows DSC thermograms of representative diameters of dried silica-capped P4MS nanoparticles (isochoric condition). In both panels, the heat capacity is plotted *vs.* temperature upon heating at 20 K min⁻¹ at seven



Fig. 2 DSC thermograms of representative diameters of (a) aqueous-suspended bare P4MS nanoparticles and (b) silica-capped P4MS nanoparticles showing the heat capacity vs. temperature at cooling rates ranging from 0.5 K min⁻¹ to 40 K min⁻¹.

different cooling rates ranging from 0.5 K min⁻¹ to 40 K min⁻¹ for each nanoparticle size. The fictive temperature, defined as the temperature at which the equilibrium liquid has a relaxation value of any macroscopic property the same as that of the system in the glassy state, can be determined for each heating curve using a geometrical argument established by Moynihan and co-workers.⁵⁰ In the Moynihan method, $T_{\rm f}$ is defined from the following mathematical equation:

$$\int_{T_{\rm f}}^{T_2} (C_{\rm liquid} - C_{\rm glass}) \mathrm{d}T = \int_{T_{\rm l}}^{T_2} (C - C_{\rm glass}) \mathrm{d}T \tag{6}$$

where T_1 is a temperature well below T_g at which the measured heat capacity, C, and the glass heat capacity, C_{glass} , are the same, and T_2 is a temperature well above T_g at which C is equal to the liquid heat capacity, C_{liquid} . Fig. 3(a) shows a graphical representation of eqn (6) for a representative DSC trace of 437 nm diameter bare P4MS nanoparticles cooled at 5 K min⁻¹ (and heated at 20 K min⁻¹). Here, T_f is simply the temperature at which the area shaded by forward-slashed lines (*i.e.*, left hand side of eqn (6)) is equal to the area shaded by backward-slashed lines (*i.e.*, right hand side of eqn (6)). From Fig. 3(a), it becomes apparent that as the enthalpy relaxation peak (overshoot) at the glass transition grows, T_f must shift towards lower temperatures to compensate for the emergence of the additional area under the overshoot.



Fig. 3 (a) Application of Moynihan's method to determine the fictive temperature, T_{f_r} of 437 nm diameter bare P4MS nanoparticles cooled at 5 K min⁻¹ and heated at 20 K min⁻¹. Here, the fictive temperature is defined as when the forward-slashed area is equal to the backward-slashed area. (b) Application of the enthalpy method to determine the fictive temperature, T_{f_r} of 437 nm diameter bare P4MS nanoparticles from the DSC trace in (a). Here, the fictive temperature is defined as the intersection between the extrapolated glassy and liquid lines.

Alternatively, the fictive temperature can be determined from the enthalpy method, *i.e.*, the $T_{\rm f}$ is defined as the temperature as which the extrapolated liquid line intersects the extrapolated glassy line in an enthalpy *vs.* temperature plot. Fig. 3(b) shows the enthalpy *vs.* temperature plot generated from integrating the heat capacity *vs.* temperature curve in Fig. 3(a). As expected, $T_{\rm f}$ taken from the intersection of the extrapolated liquid and glassy lines in Fig. 3(b) is identical to the $T_{\rm f}$ derived from Moynihan's method in Fig. 3(a). We note that for the case of silica-capped nanoparticles where the isochoric heat capacity is measured, integration of the DSC curves result in the internal energy. Table 1 tabulates sample values of $T_{\rm f}$ determined from both Moynihan's method and the enthalpy/ energy method for 437 nm diameter P4MS nanoparticles under isobaric and isochoric conditions at cooling rates of 20, 5, and

Table 1Comparison of $T_{\rm f}$ values determined from Moynihan's method and theenthalpy/energy method for cooling rates of 20 K min⁻¹, 5 K min⁻¹, and 1 Kmin⁻¹ (and constant heating rate of 20 K min⁻¹) for 437 nm P4MS nanoparticlesunder isobaric (bare aqueous-suspended) and isochoric (silica-capped) conditions

Condition	Analysis method	Cooling rate (K min $^{-1}$)		
		20	5	1
Isobaric	Moynihan T _f	372.6 ± 0.3	371.0 ± 0.3	368.8 ± 0.3
Isochoric	Moynihan T _f	372.6 ± 0.3 386.3 ± 0.3	371.0 ± 0.3 384.0 ± 0.3	368.9 ± 0.3 381.2 ± 0.3
	Enthalpy T _f	386.3 ± 0.3	383.9 ± 0.3	381.1 ± 0.3

1 K min⁻¹. Here, it is apparent that for each cooling rate at each experimental condition, the $T_{\rm f}$ derived from Moynihan's method is identical, within error, to that from the enthalpy/ energy method. For subsequent analysis, all reported fictive temperatures are determined from Moynihan's method.

A key feature of the representative DSC thermograms shown in Fig. 2(a) is that regardless of the cooling rate for the isobarically confined bare P4MS nanoparticles, the glass transition is shifted towards lower temperatures as the diameter of the nanoparticles is reduced. This observation is qualitatively consistent with the reduced T_g observed for both aqueous-suspended PS nanoparticles^{23,29} and dried PS nanoparticles^{20,25,28} with decreasing size, as well as for P4MS thin films⁵⁴ with decreasing thickness. In contrast, the T_g remains nearly invariant for the isochorically confined silica-capped P4MS nanoparticles with decreasing diameter, as shown in Fig. 2(b), which is qualitatively consistent with previous observations for a lack of significant T_g deviation with confinement for silicacapped PS nanoparticles^{23,39,49} and capped PS thin films.^{55,56}

To quantitatively examine the impact of isobaric and isochoric confinement on the glass transition temperature, Fig. 4 plots $T_{\rm f,std}$ vs. nanoparticle diameter for aqueous-suspended bare P4MS nanoparticles (triangles) and for silica-capped P4MS nanoparticles (squares). Here, the dotted line represents $T_{\rm f,std}$ measured for bulk P4MS created from coalescence of bare P4MS nanoparticle samples at an elevated temperature. It is apparent that for bare P4MS nanoparticles, $T_{\rm f,std}$ (or $T_{\rm g}$) decreases significantly and in a systematic manner as the diameter is reduced, *e.g.*, for 217 nm diameter P4MS nanoparticles, $T_{\rm f,std}$, bulk ≈ -25 K. On the contrary, $T_{\rm f,std}$ hovers around $T_{\rm f,std,bulk}$ for silica-capped P4MS nanoparticles down to ~120 nm in diameter. We note here that the $M_{\rm w}$ of all synthesized P4MS samples range from 40–400 kg mol⁻¹ with a polydispersity index (PDI) of ~3.

We attribute the significant decrease in $T_{f,std}$ with increasing confinement in bare P4MS nanoparticles to an enhanced mobile layer at the polymer-water interface. For polymers which exhibit decreases in T_g with increasing confinement, *i.e.*, no attractive interactions, it is well-accepted that the cause of



Fig. 4 Standard fictive temperature ($T_{f,std}$) of isobarically confined aqueoussuspended bare P4MS nanoparticles (triangles) and isochorically confined silicacapped P4MS nanoparticles (squares) as a function of diameter. The dotted line indicates $T_{f,std}$ measured for bulk samples formed from the coalescence of dried nanoparticles at an elevated temperature. Error bars represent standard deviations from repeated measurements.

the observed T_{g} reductions originate at the polymer free surface (interface), regardless of confining geometry.9-13,23,24,55-61 That is, at the polymer free surface (typically a polymer-air or polymernitrogen interface), cooperative segmental dynamics are enhanced, leading to a decrease in the polymer T_g upon reaching an appropriate confining length-scale. As this lengthscale is further reduced, the polymer $T_{\rm g}$ decreases more significantly, due to a growing volume fraction of the enhanced mobile layer. In polymer thin films, the thickness dependence of T_g has often been described by two-layer models, ^{59,62} which assume the presence of a mobile layer at the polymer-air or polymer-nitrogen interface with enhanced dynamics (or lower T_{o} atop a bulk layer with bulk dynamics (or bulk T_{o}). In a recent publication on the T_g-confinement effect in PS nanoparticles, we have obtained a similar size-dependent T_{g} for PS nanoparticles measured in an aqueous dispersion and for dried PS nanoparticles measured in a nitrogen environment.25 Thus, the polymer-water interface can be equated to a polymer-nitrogen interface in that both cause nearly identical $T_{\rm g}$ reductions in polymer nanoparticles.

If the presence of an enhanced mobile layer at the polymerwater interface is indeed the cause of the observed reductions in $T_{\rm f,std}$ for bare P4MS nanoparticles, then removal of the free surface should eliminate any observed deviations in $T_{f,std}$ with confinement. In the case where P4MS nanoparticles are capped with a silica-shell, the polymer-water interface is effectively eliminated since the polymer comes into contact with a rigid surface. As a result, systematic deviations in $T_{f,std}$ (from bulk $T_{\rm f,std}$) with decreasing diameter are not observed (as shown in Fig. 4), which provides evidence for the importance of the polymer-water interface in causing a reduction in $T_{f,std}$ for the bare nanoparticles. Furthermore, by capping the bare P4MS nanoparticles with a rigid silica shell, we have placed the particles under isochoric conditions. However, the recovery of bulk T_{f,std} for silica-capped P4MS nanoparticles should still be explained in terms of the removal of an enhanced mobile layer at the polymer-water interface (which led to an establishment of isochoric conditions). We note a striking similarity in the thin film literature where the thickness dependence of T_g for supported PS thin films was eliminated by coating the films with a 5 nm gold layer on top of the free surface.55

Another important observation in the DSC thermograms in Fig. 2 is that in both isobaric and isochoric cases, as the cooling rate decreases for each nanoparticle size, the relaxation peak, i.e., the overshoot, becomes larger upon heating at a constant rate of 20 K min⁻¹. A growth in the relaxation peak corresponds to a decrease in the fictive temperature due to the excess area. Furthermore, in both cases, as the nanoparticle diameter is decreased, the area under the relaxation peak increases more rapidly with decreasing cooling rate. This is due to a significant broadening of the DSC traces at slow cooling rates for smaller diameters, which we argue is a manifestation of interfacial effects, *i.e.*, polymer-water interface or polymer-silica interface. To extract the values of isobaric and isochoric fragilities for bare P4MS nanoparticles and silica-capped P4MS nanoparticles, respectively, fictive temperatures are first determined for each diameter at each cooling rate. Subsequently, $\log(Q/Q_{std})$ is plotted with respect to $(T_{\rm f,std}/T_{\rm f})$, as shown in Fig. 5 for four representative diameters for each confinement condition. According to eqn (5), both the slope and the intercept of the linear fits of the plots in Fig. 5 correspond to the dynamic fragility index, *i.e.*, $m_{\rm p}$ or $m_{\rm v}$. Under both isobaric (Fig. 5(a)) and isochoric (Fig. 5(b)) conditions, the magnitude of the slope of $\log(Q/Q_{\rm std})$ vs. $(T_{\rm f,std}/T_{\rm f})$ is observed to decrease as nanoparticle diameter is reduced, indicating that P4MS is becoming stronger, *i.e.*, reduced $m_{\rm p}$ or $m_{\rm v}$, under nanoscale confinement.

To quantitatively examine the impact of isobaric and isochoric confinement on the dynamic fragility of P4MS, m_p and m_y are plotted with respect to nanoparticle diameter for bare and silica-capped nanoparticles, respectively, in Fig. 6. Here, the solid line is the m_p value measured for bulk P4MS created through coalescence of bare nanoparticle samples at an elevated temperature. The dotted line is the average m_v value for nanoparticle diameters greater than 420 nm, which we assume to represent the bulk. Hence, $m_{p,bulk} = 129$, which is in good agreement with value from the literature,⁶³ and $m_{\rm v,bulk} = 100$. A key observation in Fig. 6 is that $m_p > m_v$ holds true for each P4MS nanoparticle sample of similar sizes and for the bulk, as one would expect from eqn (2), *i.e.*, the maximum value m_v can take is the value of $m_{\rm p}$. In a previous study, Casalini and Roland examined m_p and m_v data for a range of glass-formers, including molecular liquids, polymers, and hydrogen bonded materials, and subsequently established the following empirical relationship:44

$$m_{\rm p} = (37 \pm 3) + (0.84 \pm 0.05)m_{\rm v} \tag{7}$$



Fig. 5 $\log(Q/Q_{std})$ vs. $(T_{f,std}/T_f)$ for representative diameters of (a) aqueoussuspended bare P4MS nanoparticles and (b) silica-capped P4MS nanoparticles. Solid lines are linear fits to the data.



Fig. 6 Dynamic fragility index as a function of P4MS diameter for isobarically confined bare nanoparticles (triangles) and for the isochorically confined silica-capped nanoparticles (squares). Solid line is the measured m_p of bulk P4MS and dotted line is the average m_v of nanoparticle sizes exhibiting bulk behavior, *i.e.*, for diameters greater than 420 nm. Error bars represent standard deviations from repeated measurements.

Applying the experimentally determined $m_{\rm p,bulk}$ and $m_{\rm v,bulk}$ values from this study show good agreement with eqn (7). Furthermore, comparisons of $m_{\rm p}$ and $m_{\rm v}$ values for nanoparticles of similar diameters suggest that eqn (7) is also valid for confined glasses. The ability to experimentally obtain $m_{\rm p}$ and $m_{\rm v}$ values which satisfy eqn (7) provides additional confirmation that silica-capped P4MS nanoparticles are indeed under isochoric conditions.

From Fig. 6, it is clear that under isobaric and isochoric confinement, P4MS is becoming stronger, *i.e.*, both $m_{\rm p}$ and $m_{\rm y}$ decrease significantly starting at a diameter of ~420 nm, which we presume to be due to interfacial effects, *i.e.*, polymer-water interface or polymer-silica interface, perturbing glass transition dynamics. For example, under isobaric confinement, $m_{\rm p} = 105$ for a 217 nm diameter sample, and under isochoric confinement, $m_v = 79$ for a 189 nm diameter sample. We note that while both m_p and m_v decrease, the observed dynamic fragility indices for confined P4MS are still classified as "fragile" behaviors. That is, a "strong" glassforming material (e.g., SiO₂) which displays nearly Arrhenius behavior in its temperature dependence of structural relaxation has an isobaric fragility index of 20.31 In addition, we observe that the rate of decrease in fragility with nanoparticle diameter appears to be the same, regardless of confinement conditions. In other words, the relative effects of thermal activation and volume contribution on the change in dynamical behavior near the glass transition, which can be assessed *via* the ratio m_v/m_p , remain almost invariant for P4MS under nanoscale confinement. For bulk P4MS, $m_{v,bulk}/m_{p,bulk} = 0.78$, which implies that 78% of the change in molecular dynamics in the supercooled liquid near the glass transition can be attributed to thermal effects, and for ~200 nm diameter P4MS nanoparticles, $m_v/m_p = 0.75$, which is within experimental error of the ratio in the bulk. Casalini and Roland have tabulated $m_{\rm v}/m_{\rm p}$ values ranging between ~0.4 and 0.85 for different glass-formers.⁶⁴ The relatively large ratio of m_v/m_p for P4MS (bulk and confined) determined in the current study suggests a substantial contribution of thermal effects on the temperature dependence of structural relaxation near $T_{\rm g}$.

In the isobaric case, the decrease in $m_{\rm p}$ with confinement is accompanied (in a sense caused) by a decrease in $T_{\rm f,std}$ (= $T_{\rm g}$) and is in qualitative agreement with a previous study by Fukao and Miyamoto.³³ In that study, reductions in both $m_{\rm p}$ and $T_{\rm g}$ of supported PS thin films were observed with decreasing thickness, presumably caused by an enhanced mobile layer at the polymer interface. Fig. 7(a) plots $m_{\rm p}$ vs. $T_{\rm f,std}$ for the isobarically confined bare P4MS nanoparticles. Here, a clear positive correlation between $m_{\rm p}$ and $T_{\rm f,std}$ is observed, conforming with the general notion that *m* and $T_{\rm g}$ should be positively correlated in bulk glass-formers.³²

Interestingly, in the case of isochoric confinement, a reduction in m_v with decreasing diameter is not accompanied by a decrease in T_g , as exemplified in Fig. 7(b) which shows a lack of correlation between m_v and $T_{\rm f,std}$. The fact that $T_{\rm g}$ does not systematically deviate for silica-capped P4MS nanoparticles suggests that as m_v decreases (*i.e.*, as the glass former becomes stronger) with confinement, cooperative segmental dynamics in the super-cooled liquid are becoming slower. A possible explanation of the origin of slow dynamics in silica-capped P4MS nanoparticles is the existence of a reduced mobility layer at the polymer-silica interface. This reduced mobility layer is then directly responsible for the broadening of the glass transition (and subsequently the broadening of the relaxation peak) at the slowest cooling rates for small diameters, as observed in Fig. 2(b). That is, as the nanoparticle diameter decreases, the surface area to volume ratio (= 6/d) increases significantly. Thus, the effect of the reduced mobility layer becomes more



Fig. 7 (a) $m_{\rm p}$ vs. $T_{\rm f,std}$ for aqueous-suspended bare P4MS nanoparticles showing a positive correlation between the two measured quantities. (b) $m_{\rm v}$ vs. $T_{\rm f,std}$ for the silica-capped P4MS nanoparticles showing a lack of correlation between the two measured quantities. Error bars represent standard deviations from repeated measurements.

significant in smaller-sized nanoparticles, which in turn strongly perturbs molecular dynamics near the glass transition. We note a similar broadening in the DSC traces has been observed for silica-capped PS nanoparticles at the slowest cooling rates for small diameters.³⁹ Additionally, an immobile layer at the polymer–substrate interface has been observed experimentally in the thin film geometry.^{22,65} The fact that $T_{f,std}$ remains invariant, while m_v decreases significantly with size for the silica-capped P4MS nanoparticles suggests a non-trivial relationship between dynamics, *i.e.*, fragility, and thermodynamics, *i.e.*, the calorimetric glass transition, in confined systems,^{66,67} as highlighted in a recent computational study that showed for thin films the ratio of T_g to *m* as a function of film thickness did not remain constant.⁴⁰

Recently, we explored the effect of isochoric confinement on m_v of silica-capped PS nanoparticles.³⁹ Here, we compare those results, as well as results of $T_{\rm g}$ s of aqueous-suspended PS nanoparticles,²³ to that of the current work on P4MS in order to examine the effect of chemical structure on the observed $T_{\rm g}$ - and fragility-confinement effects. Fig. 8(a) compares the observed $T_{\rm g}$ -confinement effect in aqueous-suspended bare P4MS nanoparticles to that of aqueous-suspended bare P5 nanoparticles. The inset shows the chemical structures of the repeat units in P4MS and PS. The main difference between the two is that in P4MS, there exists one methyl group on the 4-position of the phenyl ring. Here, the absolute $T_{\rm g}$ of bulk P4MS is ~10 K higher



Fig. 8 (a) Comparison of $T_g - T_{g,bulk}$ vs. diameter between aqueous-suspended bare P4MS nanoparticles (triangles) and aqueous-suspended bare PS nanoparticles (circles). Data for bare PS nanoparticles are reproduced from ref. 23. (b) Comparison of $m_v - m_{v,bulk}$ vs. diameter between silica-capped P4MS nanoparticles (squares) and silica-capped PS nanoparticles (circles). Dotted line represents no deviation from the bulk, *i.e.*, when $m_v = m_{v,bulk}$. Solid lines are guides for the eye. Data for silica-capped PS are reproduced from ref. 39. Error bars represent standard deviations from repeated measurements.

than bulk PS, due to the fact that the alkyl substituent on the phenyl ring increases bulkiness of the repeat unit, therefore reducing segmental mobility and causing an increase in T_{g} .⁶³ When $T_{g} - T_{g,bulk}$ is plotted *vs.* nanoparticle diameter as shown in Fig. 8(a), no significant difference exists between the observed T_{g} -confinement effect in bare P4MS (triangles) and PS (circles) nanoparticles suspended in aqueous environments. That is, the T_{g} of P4MS deviates in the same manner as the T_{g} -reduction observed for PS with decreasing nanoparticle diameter, *e.g.*, when $d \approx 200$ nm, $T_{g} - T_{g,bulk} = -26$ K and -24 K, respectively.

In the supported thin film geometry, Ellison *et al.*⁵⁴ observed a subtle difference between the T_{g} -confinement effect in P4MS and PS when h < 70 nm, in that the T_{g} of P4MS deviates at a much faster rate with thickness than the T_{g} of PS, *e.g.*, when h =24 nm, $T_{g} - T_{g,\text{bulk}} = -21$ K and -14 K, respectively. The difference was explained in terms of chain rigidity, rather than polymer density, in affecting the T_{g} -confinement effect in a polymer with different repeat units. The fact that poly(4-*tert*butylstyrene)⁵⁴ and polycarbonate⁶⁸ with greater chain rigidity exhibit a much greater T_{g} -confinement effect than P4MS or PS at the same film thickness supports the previous notion. Lastly, we note that in agreement with the results presented in Fig. 8(a), Ellison *et al.* did not observe a significant difference in the onset thickness ($h \approx 70$ nm) at which the T_{g} began to deviate from bulk T_{g} for P4MS and PS.

Fig. 8(b) plots $m_v - m_{v,\text{bulk}} vs.$ diameter for silica-capped P4MS (squares) and PS (triangles) nanoparticles. In contrast to the T_{g} confinement effect shown in Fig. 8(a) for P4MS and PS, the effect of size on m_v is largely dependent on the chemical structure of the backbone. That is, for silica-capped P4MS nanoparticles, the decrease in m_v with confinement starts at a much larger lengthscale ($d \approx 420$ nm) than for silica-capped PS nanoparticles ($d \approx$ 260 nm). However, m_v decreases at a slower rate with respect to diameter for silica-capped P4MS than for silica-capped PS. For both PS and P4MS, we note that $T_{\rm g}$ is independent of diameter under isochoric confinement due to removal of the mobile interface. The earlier onset diameter of size effects on m_y for P4MS is likely to be related to the addition of the methyl group on the phenyl ring. The smaller rate of change of m_v with confinement for P4MS as compared to PS is due to the weaker effect of the polymer-silica interface in reducing interfacial chain dynamics. In future work, we will further investigate the impact of chemical structure and interfacial interactions on the isochoric fragility of confined polymers.

Conclusions

We have successfully measured the dynamic fragility and $T_{\rm g}$ of P4MS confined under both isobaric and isochoric conditions. Utilizing a unique confining geometry, *i.e.*, silica-capped P4MS nanoparticles, thermal measurements of polymer confined under isochoric conditions were conducted in a manner not feasible for the thin film geometry. By measuring the fictive temperature as a function of cooling rate in differential scanning calorimetry, we showed that both the isobaric and isochoric fragilities decreased in the same manner for bare and silica-capped P4MS nanoparticles, respectively. However, $T_{\rm g}$

decreases and remains constant with isobaric and isochoric confinement, respectively. We explained the observed experimental results based on interfacial effects perturbing glass-forming dynamics. Furthermore, we compared the observed $T_{\rm g}$ -confinement effect in bare P4MS nanoparticles and the observed $m_{\rm v}$ -confinement effect in silica-capped P4MS nanoparticles to our previous studies on bare and silica-capped PS nanoparticles. We observed no significant deviation in the $T_{\rm g}$ -confinement effect for bare PS and P4MS nanoparticles at the length-scales explored here, in contrast to what has been observed in the thin film geometry. However, P4MS exhibited a decrease in $m_{\rm v}$ at a larger length-scale, but at a slower rate, as compared to PS. Further studies on the impact of chemical structure and interfacial interactions on the $T_{\rm g}$ - and fragility-confinement effects are currently underway.

Acknowledgements

We acknowledge usage of the PRISM Imaging and Analysis Center, which is supported in part by the NSF MRSEC program through the Princeton Center for Complex Materials (DMR-0819860). C.Z. acknowledges support by the Department of Defense (DoD) through the National Defense Science & Engineering Graduate Fellowship (NDSEG). R. D. P. acknowledges the donors of the American Chemical Society Petroleum Research Fund (PRF 49903-DNI10) and the 3M-nontenured faculty grant program for partial support of the work.

References

- 1 Y. Y. Noh, N. Zhao, M. Caironi and H. Sirringhaus, *Nat. Nanotechnol.*, 2007, **2**, 784–789.
- 2 X. N. Yang, J. Loos, S. C. Veenstra, W. J. H. Verhees, M. M. Wienk, J. M. Kroon, M. A. J. Michels and R. A. J. Janssen, *Nano Lett.*, 2005, 5, 579–583.
- 3 W. K. Cho, B. Y. Kong and I. S. Choi, *Langmuir*, 2007, 23, 5678–5682.
- 4 W. Yave, A. Car, J. Wind and K. V. Peinemann, Nanotechnology, 2010, 21, 395301.
- 5 K. S. Soppimath, T. M. Aminabhavi, A. R. Kulkarni and W. E. Rudzinski, *J. Controlled Release*, 2001, **70**, 1–20.
- 6 M. E. Gindy and R. K. Prud'homme, *Expert Opin. Drug Delivery*, 2009, **6**, 865–878.
- 7 X. Wang, J. E. Hall, S. Warren, J. Krom, J. M. Magistrelli, M. Rackaitis and G. G. A. Bohm, *Macromolecules*, 2007, 40, 499–508.
- 8 T. Still, W. Cheng, M. Retsch, U. Jonas and G. Fytas, *J. Phys.: Condens. Matter*, 2008, **20**, 404203.
- 9 J. L. Keddie, R. A. L. Jones and R. A. Cory, *Europhys. Lett.*, 1994, 27, 59–64.
- 10 J. L. Keddie, R. A. L. Jones and R. A. Cory, *Faraday Discuss.*, 1994, **98**, 219–230.
- 11 J. A. Forrest, K. Dalnoki-Veress, J. R. Stevens and J. R. Dutcher, *Phys. Rev. Lett.*, 1996, 77, 2002–2005.
- 12 J. Mattsson, J. A. Forrest and L. Borjesson, *Phys. Rev. E: Stat. Phys., Plasmas, Fluids, Relat. Interdiscip. Top.*, 2000, **62**, 5187– 5200.

- 13 C. J. Ellison and J. M. Torkelson, *Nat. Mater.*, 2003, **2**, 695–700.
- 14 C. B. Roth and J. R. Dutcher, *Eur. Phys. J. E*, 2003, **12**, S103–S107.
- 15 B. J. Ash, R. W. Siegel and L. S. Schadler, *J. Polym. Sci., Part B: Polym. Phys.*, 2004, **42**, 4371–4383.
- 16 C. H. Park, J. H. Kim, M. Ree, B. H. Sohn, J. C. Jung and W. C. Zin, *Polymer*, 2004, 45, 4507–4513.
- 17 A. Bansal, H. C. Yang, C. Z. Li, K. W. Cho, B. C. Benicewicz, S. K. Kumar and L. S. Schadler, *Nat. Mater.*, 2005, 4, 693–698.
- 18 R. D. Priestley, M. K. Mundra, N. J. Barnett, L. J. Broadbelt and J. M. Torkelson, *Aust. J. Chem.*, 2007, **60**, 765–771.
- 19 P. Rittigstein, R. D. Priestley, L. J. Broadbelt and J. M. Torkelson, *Nat. Mater.*, 2007, **6**, 278–282.
- 20 Y. Rharbi, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2008, 77, 031806.
- 21 H. Oh and P. F. Green, Nat. Mater., 2009, 8, 139-143.
- 22 S. Napolitano and M. Wubbenhorst, *Nat. Commun.*, 2011, 2, 260.
- 23 C. Zhang, Y. Guo and R. D. Priestley, *Macromolecules*, 2011, 44, 4001–4006.
- 24 O. Bäumchen, J. D. McGraw, J. A. Forrest and K. Dalnoki-Veress, *Phys. Rev. Lett.*, 2012, **109**, 055701.
- 25 C. Zhang, V. M. Boucher, D. Cangialosi and R. D. Priestley, *Polymer*, 2013, **54**, 230–235.
- 26 A. Schönhals, H. Goering, C. Schick, B. Frick and R. Zorn, *Eur. Phys. J. E*, 2003, **12**, 173–178.
- 27 Y. P. Koh, Q. X. Li and S. L. Simon, *Thermochim. Acta*, 2009, 492, 45–50.
- 28 J. F. Ding, G. Xue, Q. P. Dai and R. S. Cheng, *Polymer*, 1993, 34, 3325–3327.
- 29 S. Feng, Z. Li, R. Liu, B. Mai, Q. Wu, G. Liang, H. Gao and F. Zhu, *Soft Matter*, 2013, **9**, 4614–4620.
- 30 C. Zhang, Y. Guo and R. D. Priestley, J. Polym. Sci., Part B: Polym. Phys., 2013, 51, 574-586.
- 31 R. Böhmer, K. L. Ngai, C. A. Angell and D. J. Plazek, J. Chem. Phys., 1993, 99, 4201–4209.
- 32 Q. Qin and G. B. McKenna, *J. Non-Cryst. Solids*, 2006, 352, 2977–2985.
- 33 K. Fukao and Y. Miyamoto, Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys., 2001, 64, 011803.
- 34 Y. P. Koh and S. L. Simon, J. Polym. Sci., Part B: Polym. Phys., 2008, 46, 2741–2753.
- 35 S. Napolitano and M. Wubbenhorst, *Polymer*, 2010, **51**, 5309–5312.
- 36 N. T. Qazvini and E. Chehrazi, J. Macromol. Sci., Part B: Phys., 2011, 50, 2165–2177.
- 37 F. W. Starr and J. F. Douglas, *Phys. Rev. Lett.*, 2011, **106**, 115702.
- 38 B. A. Pazmino Betancourt, J. F. Douglas and F. W. Starr, Soft Matter, 2013, 9, 241–254.
- 39 C. Zhang, Y. Guo, K. B. Shepard and R. D. Priestley, J. Phys. Chem. Lett., 2013, 4, 431–436.
- 40 P. Z. Hanakata, J. F. Douglas and F. W. Starr, *J. Chem. Phys.*, 2012, **137**, 244901.
- 41 C. Graf, D. L. J. Vossen, A. Imhof and A. van Blaaderen, *Langmuir*, 2003, **19**, 6693–6700.

- 42 L. Zhang, M. D'Acunzi, M. Kappl, G. K. Auernhammer, D. Vollmer, C. M. van Kats and A. van Blaaderen, *Langmuir*, 2009, 25, 2711–2717.
- 43 K. Niss, C. Dalle-Ferrier, G. Tarjus and C. Alba-Simionesco, J. Phys.: Condens. Matter, 2007, **19**, 076102.
- 44 R. Casalini and C. M. Roland, *Phys. Rev. E: Stat., Nonlinear,* Soft Matter Phys., 2005, 72, 031503.
- 45 G. Floudas, M. Paluch, A. Grzybowski and K. Ngai, *Molecular Dynamics of Glass-Forming Systems*, Springer, Heidelberg, Germany, 2011.
- 46 L. Hong, V. N. Novikov and A. P. Sokolov, J. Non-Cryst. Solids, 2011, 357, 351–356.
- 47 R. Casalini, K. J. McGrath and C. M. Roland, *J. Non-Cryst. Solids*, 2006, **352**, 4905–4909.
- 48 D. H. Huang, D. M. Colucci and G. B. McKenna, J. Chem. Phys., 2002, **116**, 3925–3934.
- 49 Y. Guo, C. Zhang, C. Lai, R. D. Priestley, M. D'Acunzi and G. Fytas, ACS Nano, 2011, 5, 5365–5373.
- 50 C. T. Moynihan, A. J. Easteal, M. A. Debolt and J. Tucker, *J. Am. Ceram. Soc.*, 1976, **59**, 12–16.
- 51 C. G. Robertson, P. G. Santangelo and C. M. Roland, *J. Non-Cryst. Solids*, 2000, **275**, 153–159.
- 52 L. M. Wang, V. Velikov and C. A. Angell, J. Chem. Phys., 2002, 117, 10184–10192.
- 53 D. J. Plazek and K. L. Ngai, *Macromolecules*, 1991, 24, 1222–1224.
- 54 C. J. Ellison, M. K. Mundra and J. M. Torkelson, *Macromolecules*, 2005, **38**, 1767–1778.
- 55 J. S. Sharp and J. A. Forrest, *Phys. Rev. Lett.*, 2003, **91**, 235701.

- 56 J. A. Forrest, K. Dalnoki-Veress and J. R. Dutcher, *Phys. Rev.* E: Stat. Phys., Plasmas, Fluids, Relat. Interdiscip. Top., 1997, 56, 5705–5716.
- 57 Z. H. Yang, Y. Fujii, F. K. Lee, C. H. Lam and O. K. C. Tsui, *Science*, 2010, **328**, 1676–1679.
- 58 S. Peter, H. Meyer and J. Baschnagel, *J. Polym. Sci., Part B: Polym. Phys.*, 2006, 44, 2951–2967.
- 59 K. Fukao and Y. Miyamoto, *Phys. Rev. E: Stat. Phys., Plasmas, Fluids, Relat. Interdiscip. Top.*, 2000, **61**, 1743–1754.
- 60 R. M. Papaleo, R. Leal, W. H. Carreira, L. G. Barbosa, I. Bello and A. Bulla, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2006, 74, 094203.
- 61 D. Qi, Z. Fakhraai and J. A. Forrest, *Phys. Rev. Lett.*, 2008, **101**, 096101.
- 62 J. A. Forrest and J. Mattsson, *Phys. Rev. E: Stat. Phys., Plasmas, Fluids, Relat. Interdiscip. Top.*, 2000, **61**, R53–R56.
- 63 K. Kunal, C. G. Robertson, S. Pawlus, S. F. Hahn and A. P. Sokolov, *Macromolecules*, 2008, **41**, 7232–7238.
- 64 R. Casalini and C. M. Roland, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2004, **69**, 062501.
- 65 S. Napolitano and M. Wubbenhorst, *J. Phys. Chem. B*, 2007, 111, 9197–9199.
- 66 V. Lupaşcu, S. J. Picken and M. Wubbenhorst, *J. Non-Cryst. Solids*, 2006, **352**, 5594–5600.
- 67 V. M. Boucher, D. Cangialosi, H. J. Yin, A. Schonhals,
 A. Alegria and J. Colmenero, *Soft Matter*, 2012, 8, 5119–5122.
- 68 C. L. Soles, J. F. Douglas, W. L. Wu, H. G. Peng and D. W. Gidley, *Macromolecules*, 2004, 37, 2890–2900.