The Dynamic of Confined Polystyrene in Nanoparticles in the Glassy Regime: The Close Packed Morphology

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ABSTRACT: The dynamic of confined polystyrene in nanoparticles was investigated in particles as small as 42 nm in the close packed morphology. The relaxation time was extracted from the dynamic of closure of voids between close packed particles. The particles deform under the effect of the surface tension energy (polystyrene/air), and the deformation is probed via small angle neutron scattering. Both the shift factor and relaxation time of the confined PS were found to follow a bulk dynamic between bulk $T_g$ and $T_g - 50 \degree C$ for particles as small as 42 nm. This data was interpreted to indicate that cooperativity resulting from the contacts between particles inhibits the eventual activation of the surface dynamic.

INTRODUCTION

The dynamic of confined polymers is of considerable scientific and technological interest.\(^1\)\(^-\)\(^35\) This research is motivated by the need for nanometric functional systems for new technologies. The strong dependence of the dynamic on the glass transition ($T_g$), incited several groups to focus their research on the $T_c$ of confined polymers particularly in the thin film geometry.\(^1\)\(^-\)\(^15\) The main finding of this research was the strong shift of the thermal expansion curves in both supported and free-standing thin films, which support the conclusion of the $T_g$ depression in confined polymers.\(^1\)\(^-\)\(^15\) This result lead several groups to directly investigate the dynamic of polymer in thin film using dielectric relaxation spectroscopy (DRS)\(^14\)\(^,\)\(^15\) surface viscosity,\(^17\)\(^,\)\(^18\) and dye reorientation.\(^16\) These experiments suggested a faster dynamic in thin films in accordance with the $T_g$ depression. However DRS experiments from the Kremer group did not report any changes of the molecular dynamic in the supported thin films and they stressed the importance of the thin film processing history in the thin film dynamic.\(^19\) This conclusion was also corroborated by the AC–calorimetry technique from Schick group.\(^19\)\(^,\)\(^20\)

While most of the confinement studies were dedicated to thin film geometry, only a few were being conducted on the nanoparticle geometry.\(^30\)\(^-\)\(^33\) The nanoparticle geometry has several advantages as it leads to a larger surface area than thin films and an isotropic confinement. These particles are synthesized via emulsion polymerization in the aqueous phase with controlled sizes larger than 20 nm. They are used in several applications such as the water-born coating industry.\(^36\)\(^-\)\(^45\) A few groups have investigated the dynamic and the glass transition of polymers confined in particles. For example Sasaki et al., using dynamical scanning calorimetry (DSC) on aqueous suspensions of polystyrene particles, observed a reduction of the heat capacity ($\Delta C_p$) when decreasing the particle size and did not detect any shift of $T_g$.\(^30\) They explained the reduction of $\Delta C_p$ by the presence of a layer surface with a lower $T_g$. A recent report suggested a tremendous $T_g$ shift in suspensions of polystyrene particles containing acrylic acid.\(^34\) The effect of surfactant on $T_g$ reduction of particle suspension was also discussed.\(^35\) When PS particles were dispersed in nanoblends, they were also found to adopt different mechanical properties than bulk particularly for particles smaller than 45 nm.\(^32\)\(^,\)\(^33\) However, the effect of confinement in nanoparticles on the dynamic of polymers still remains an open question. We have shown in previous work that it is possible to directly probe the relaxation time of polystyrene in nanoparticles using the kinetic of void closure between close-packed particles.\(^41\)\(^,\)\(^42\) In these experiments we found that when water is evaporated from the particle suspension in the glassy regime, the particles remain spherical and form close-packed structures separated by interstices (voids).\(^41\)\(^,\)\(^42\) The presence of free surface area within these interstices (Scheme 1) is what gives the confined particularity to the polymer. The air/polystyrene surface tension $\gamma_{P/A}$ ($\gamma_{P/A} = 0.03 \, \text{N/m}^2$) in the voids generates negative

Scheme 1. Three Steps of Void Closure
Laplace pressure \( P_{\text{Lap}} = \gamma / r \sqrt{S_{\text{void}}/V_{\text{void}}} \) (where \( S_{\text{void}} \) and \( V_{\text{void}} \) are the surface and volume of the voids) which close the voids and deform the particles. We demonstrated that particle deformation can be used to quantify the relaxation time of the confined polymer in particles.

In the present study we investigate the role confinement in the particle geometry on the polystyrene dynamic. We show that this dynamic exhibits a bulk behavior for all temperatures and particle sizes investigated. Our results show that the free surface between the particles does not activate the polystyrene dynamic contrary to what is expected. We suggest that the eventual depression of \( T_g \) in freestanding particles and the activation of the dynamic could be inhibited via dynamical cooperativity between neighboring particles.

## EXPERIMENTAL SECTION

### Polymer Synthesis and Characterization

Polystyrene (PS) suspensions at 10 wt % were prepared in batch emulsion polymerization at 80 °C from styrene (Aldrich, 99%), the surfactant, sodium dodecyl sulfate (SDS, Aldrich, 99%) and the initiator, potassium persulfate (KPS, Aldrich, 98%).

Removing SDS and counterions from the suspensions is crucial for these experiments. There are several ways for cleaning the latex suspions; ion exchange, serum replacement and dialysis. Several groups such as Vanderhoff and co-workers and Steward and co-workers have extensively investigated for over two decades the cleaning procedures and surface characterization of colloidal particles and have concluded that the ionic exchange technique is the most efficient way for removingionic surfactants and counterions from polystyrene colloidal suspensions. Our suspensions were cleaned using a mixture of anionic and cationic exchange resins (DOWEX Marathon MR-3, Aldrich). The suspensions were mixed with 50 wt % resin and gently agitated for several hours and then filtered to remove the resin. The cleaning was monitored using conductivity, which decreases during the cleaning procedure. This was repeated several times until the conductivity no longer changed. The particle surface contained SO₄⁻ groups from decomposition of the persulfate as well as OH groups from the hydrolysis of the radicals during polymerization. The presence of SDS in the suspension was monitored using conductivity, surface tension and elemental analysis.

Two cleaning cycles were sufficient to remove all the SDS. Changing the counterions K⁺ and Na⁺ with H⁺ required more than three cleaning cycles. The particles contain between 10 and 22 μmol/g of SO₄⁻ on their surface, which results from the chain end groups.

Particle diameters were measured using quasi elastic light scattering (QELS) (Malvern 5000) at a 90° angle. The molecular weight \( M_w \) was measured using gas permeation chromatography (GPC) in tetrahydrofuran (THF). This leads to a \( M_w \) of 324, 381, and 281 kg/mol, and a polydispersity PDI of 3.33, 2.17, and 3 for 42, 62, and 93 nm particles, respectively.

Glass transition of bulk polymer was measured by differential scanning calorimetry DSC (Mettler Toledo DSC 823) during the heating step at a rate of 10 °C/min. The \( T_g \) is taken as the midpoint in the DSC. This leads to 102, 103.4, and 104.4 °C for 42, 62, and 93 nm particles, respectively.

Creep compliance measurements \( (\tau(t)) \) were carried out on AR-G2 (TA Instrument) for various temperatures. Cylindrical PS samples with a diameter of 5 ± 0.05 mm were prepared by annealing the PS powder at 150 °C for 6 h in argon environment under pressure of 4 MPa and then for 3 h without pressure. Other samples were prepared by dissolving the PS powder in toluene and removing the solvent at 100 °C for 24 h and then annealing at 150 °C. A thin layer (10 μm) of Lactide (cyanacrylate) was used to improve adhesion of the films onto the tools. The creep compliance was measured in the linear viscoelastic regime under a constant stress of \( \sigma = 20000 \) Pa. The bulk relaxation time \( \tau_{\text{bulk}} \) is estimated from the constitutive equation (eq 1), with \( G(t, \tau) = G^0 \exp\left(-\frac{|t|}{\tau}\right) \). The exponent \( \beta \) for polystyrene is \( \beta = 0.4 \) and \( G^0 \approx 1 \) GPa.

\[
\langle \tau \rangle = \int_0^\infty \exp\left(-\frac{t}{\tau}\right) dt
\]

\[
\sigma = \int_0^\infty G(t - \tau) \frac{d \tau_{\text{bulk}}(\tau)}{d\tau} d\tau
\]

### RESULTS

In order to interpret the results obtained in this work and to get insight on the dynamic of confined polymer in nanoparticles, we must first prove that the particles in the close compact structure are, in fact, surrounded by a free surface. The SANS spectra of samples evaporated in the glassy regime lead to well-defined peaks. For the large particles (93 nm), we observe a narrow first order peak followed by a second and third peak, whereas for 62 and 42 nm particles only a second order peak is seen (Figure 1). The contrast in the SANS infers that the particles remain somewhat spherical and separated with voids (Scheme 1, stage II). The SANS spectra can be interpreted to indicate that the particles are organized as a random compact structure at 64 vol % separated by 36 vol % void. This was also confirmed from the volume shrinkage after annealing the films for an extended time above 100 °C. The voids around the
particles lead to a free surface area between the contact zones. If the particles were freestanding and spherical they would have $S/V = 6/D$, which is larger than those of freestanding films 2/h and supported films 1/h. However, the particles in the close-packed array (Scheme 1, stage II) are in contact with around six neighboring particles, which reduces the fraction of free surface. The scattering peaks vanish within a few minutes when the samples are annealed at bulk $T_g$ (Figure 2) but remain unchanged over 3 years when stored at room temperature. The scattering intensity reflects the evolution of the void volume $(V_{void}(t))$ as $I(t) \propto (V_{void}(t))^2 \propto (V_{void}(0))^2 (1 - \varepsilon(t)/0.36)^2$, where $\varepsilon(t)$ is the deformation rate of the particles: $\varepsilon(t) = 0.36(1 - (I(t)/I(0))^{1/2})$ (Figure 3). The driving force for closing the voids is the stress caused by the polystyrene/air surface tension $(\gamma_{p/a})$. The magnitude of this stress can be estimated as $P_{lap} \approx \gamma_{p/a}/R$, where $R$ is the particle radius and $\alpha \approx 6$ for random compact structures.38,39,56 The applied pressure for the smallest particles (42 nm) is $P_{lap} \approx 4$ MPa, which is lower than the yield stress of polystyrene ($\sim 30$ MPa)61 inferring that the deformation occurs in the linear regime. The deformation is creep-like particularly for small $\varepsilon(t)$ values where the stress can be considered constant leading to a linear dependence of $\varepsilon(t)$ on time $\varepsilon(t) \propto t/\tau_{void}$ ($\tau_{void}$ is the characteristic time for void closure). The Frenkel model gives an estimate of $\varepsilon(t) \propto t/\tau_{void} \propto (\gamma_{p/a}/G_oR)/\tau_\alpha$, where $G_o$ and $\tau_\alpha$ are the elastic modulus and the relaxation time of the polystyrene.56 The dependence of $\varepsilon(t)$ on the particle radius described by the Frenkel equation is well depicted in Figure 3, where $\varepsilon(t)$ increases rapidly vs time in small particles.

Figure 2 shows the time and temperature dependence of the particle deformation. The void closure dynamic slows down when the temperature decreases as predicted by the time–temperature superposition. We first analyze the particle dynamic using the behavior of the time–temperature superposition shift factor $(a_T)$, which is an intrinsic parameter and is model independent. The $a_T$ is calculated either from shifting the decays to a reference decay at bulk $T_g = 373$ K or by plotting $\log(\tau_{void}(T)/\tau_{void}(373))$ where $\tau_{void}(T)$ is taken from the linear dependence of $\varepsilon(t)$ in the early closure time. In Figure 4 we compare $a_T$ for nanoparticles and bulk between 100 and 50 °C. The bulk $a_T$ is taken from the creep compliance measurements on the same sample as well as from the second harmonic generation (SHG) results from ref 50. The data is plotted against $T/T_g$ to compare the present experiment to the SHG results. Within the error bar of our experiment, the $a_T$ values from the nanoparticles are similar to the bulk $a_T$ for all temperatures between bulk $T_g$ and $T_g - 50$ °C and for all the particle sizes investigated here 42, 62, and 93 nm. Annealing the sample at room temperature for over 3 years did not give any significant void closure, which leads to an estimate of the lower

Figure 3. Deformation strain $\varepsilon(t)$ calculated from the intensity peak at 100 °C for various particle size polystyrene.

Figure 4. The shift factor $a_T$ vs the inverse of temperature during void closure for particle sizes 42 (▲), 62 (■), and 93 nm (▲). $a_T$ is estimated by shifting the decays to a reference decay at 373 K or as $a_T = \tau_{void}(T)/\tau_{void}(373)$, where $\tau_{void}(T)$ is taken from the linear dependence of $\varepsilon(t)$ in the early closure time. The $a_T$ for nanoparticles is compared to the shift factor of bulk PS made from the same particles using the creep compliance (○) and to the bulk $a_T$ from the SHG on other PS. The temperature is normalized to the bulk $T_g$. 
value of the shift factor. The $a_\tau$ at room temperature is added in Figure 4 as an indication.

The $a_\tau$ deviates slightly from the Vogel–Fulcher–Tamman (VFT) behavior below bulk $T_g$ and then exhibits the Arrhenius behavior below 90 °C. The activation energy in the glassy regime is found to be 56 kcal/mol for all these particles, which is similar to that estimated from the SHG for bulk PS. This suggests that far below bulk $T_g$ the void closure adopts a bulk behavior. This behavior was observed for all the particle sizes investigated here 93, 62, and 42 nm. Though the $\tau_{\text{void}}$ is found to decrease with decreasing the particle size, the $a_\tau$ are superposible in this range of particle size. This result proves that the polymer dynamic of polystyrene particles in contact adopts the bulk behavior in the Arrhenius regime with the bulk activation energy for all confinement dimensions between 42 and 93 nm.

After this model independent shift factor analysis, we can now perform a quantitative investigation by estimating the relaxation time $\langle \tau_\alpha \rangle$ of the polymer in the nanoparticles. The PS/air surface tension in the interstices, deforms the particles and closes the voids. This process can be quantified using several models. One is the Frenkel model, which balances the interfacial tension force with the free surface area of the particles and the viscous force. This leads to $e(t) \propto (3/4\pi \rho_a G_0 R) / \tau_\alpha$. A modified version of this model was developed for particles in close packed geometry by averaging the stress and the strain over all the orientations.

$$\frac{2\gamma_{p/a}}{R} = \int_0^t G(t - t') \frac{d\varepsilon}{dt'} dt' \tag{2}$$

where $G(t)$ is the time dependent elastic modulus. Another model for estimating the relaxation time during void closure uses the Hertzian model, which uses the JKR formalism for the deformation of elastic particles. The Hertzian model can be generalized for the particle deformation in close packed geometry by introducing viscoelasticity in the JKR formalism and averaging the stress and strain over all the orientations.

This leads to a constitutive equation

$$\frac{6.69(1 - \nu)\gamma_{p/a}}{R} = \int_0^t G(t - t') \frac{d\varepsilon^{1/2}}{dt'} dt' \tag{3}$$

The $G(t)$ of polystyrene can be considered either a monoeponential or stretched exponential with an exponent $\beta = 0.4$. The averages $\langle \tau \rangle$ from all these models are plotted against the inverse of temperature and compared to the bulk values (Figure 5). The difference between the $\langle \tau \rangle$ from these models is integrated within the error bar.

Figure 5 shows a comparison $\langle \tau \rangle$ of confined PS to the $\langle \tau \rangle$ bulk relaxation time taken from the creep compliance measurements on the same sample as well as $\alpha$ relaxation time $\langle \tau_\alpha \rangle$ from the SHG results (ref 50). The $\langle \tau \rangle$ for the bulk PS made from our particles was found to be $\langle \tau \rangle \approx 50$ s at 100 °C, which is similar to the $\alpha$ relaxation time at $T_g$ from other techniques such as DRS and SHG. The $\langle \tau \rangle$ from the bulk of this study was also found to superimpose with $\langle \tau_\alpha \rangle$ from SHG for all the temperatures above $T_g$ (Figure 5). This infers that these experiments probe the $\alpha$ relaxation and therefore one does not expect any dependence of $\langle \tau \rangle$ on the polymer molecular weight for $M_w > 10^5$ g/mol, which is the case of the PS in this study.

The $\langle \tau \rangle$ of the confined PS at the bulk $T_g$ is found to be similar to the bulk $\langle \tau \rangle$ for all the particles investigated here, within the error bar of $\langle \tau \rangle$. One notices that $\langle \tau \rangle$ of the particles decreases by a factor of 2 with decreasing particle size from 93 to 42 nm independently from the models. This small reduction of $\langle \tau \rangle$ is not significant enough to conclude that there is an activation of the dynamic, because one expects, a large variation of the relaxation time in response to small changes in the temperature close to $T_g$.

Within the error bar of our experiment, the $\langle \tau \rangle$ from nanoparticles is found to be similar to the bulk $\langle \tau_\alpha \rangle$ from the SHG for temperatures between bulk $T_g$ and $T_g - 50$ °C for all the particle sizes between 93 and 42 nm. The $\langle \tau \rangle$ at room temperature represents an estimate of the lower limit of the relaxation time and is added in Figure 5 as indication. All aspects of the present experiment; shift factor, the relaxation time and the dependence on the particle size tend to confirm that the relaxation of the polystyrene in the close packed particles behave like bulk for particles between 42 and 90 nm particularly in the glassy regime. These results prove beyond a doubt that the dynamic of polystyrene in particles adopts the bulk $\alpha$-relaxation in the glassy regime when the particles are in a close packed morphology.

### Discussion

The absence of any deviation from bulk dynamic in close packed particles suggests a number of possibilities. (1) The particles adopt a bulk $T_g$ in contrast with the suggestion of refs 34 and 35. (2) The dynamic cooperativity of the particles via the contacts between the particles inhibits the activation of the dynamic of the individual particles. (3) The eventual $T_g$ reduction of the particles is not accompanied by the activation of the polymer dynamic.

Beside the dynamic of the polystyrene particles, their glass transition is an important issue. The first DSC experiment on free-standing PS particles in water reported a kink in the $T_g$ traces at the bulk $T_g$ and a reduction of the $\Delta C_p$, which was interpreted to suggest the presence of a layer with a higher mobility on the free surface. On the other hand recent papers stressed the importance of the surface properties on the particle $T_g$. Yet...
these particles contain sulfate (SO₄⁻) and acrylic acid groups on their surface. Another paper suggested that removing the ionic surfactant by dialysis reduces the $T_g$ of free-stranding particles. These findings bring us to discuss the importance of latex cleaning on the particle $T_g$. The characterization of the latex surface was a subject of extensive investigation for more than two decades by the Vanderhoff team and Steward and co-workers among others.46–49 They concluded that the ion exchange resins technique is the most efficient way for removing ionic species from polystyrene suspension and showed that dialysis against water is not efficient for removing several surfactants.49 In the present study we follow the procedures of Vanderhoff et al. for removing the surfactant from the suspensions prior to film formation using ionic exchange resins. Conductive titration, surface tension and elemental analysis demonstrate the absence of any traces of SDS after ion exchange cleaning. The particle surface contains 10–20 μmol/g of SO₄⁻ in addition to OH groups, which results from the hydrolysis of the polymerization radicals. The polystyrene from these particles was found to exhibit a strong reduction of the apparent $T_g$ when spin-coated as thin film or deposited as particles on substrate.63 In these experiments, temperature dependence of pyrene fluorescence was studied in supported thin films made from pyrene-labeled PS particles.63 This yielded the same depression of the apparent $T_g$ in thin films as those reported by Torkelson et al.7 A similar experiment was carried out on supported PS particles on a substrate using pyrene labeled particles.63 These experiments showed that the shift of the apparent $T_g$ measured by fluorescence was dominated by the amount of free surface.63 This demonstrates that even if these particles give a strong apparent $T_g$ reduction when they are supported on a substrate or deposited as thin films, they exhibit a bulk dynamic when they are in contact with each other. The strong $T_g$ shift reported in refs 34 and 35 for the surfactant-free polystyrene particles in water is not followed by the activation of the dynamic when the particles are in contact.

The existence of a mobile layer on the particle surface suggested from the DSC experiment, or polarized fluorescence experiment on freestanding polystyrene thin film does not dominate the overall relaxation time of the particles in contact with each other. One can imagine that the deformation of the particles observed during void closure requires the movement of a large fraction of the particles and not only their surface. This could suggest that the dynamic cooperativity between the core and the surface causes the overall particles to behave dynamically as bulk. An alternative possibility is that cooperativity between the particles in contact could inhibit the activation of surface dynamic and make the close packed structure behave as bulk.

It is also worth comparing the present finding to the mechanical property of PS particles dispersed in soft poly(butyl methacrylate) matrix. In these experiments, the PS particles were found to exhibit a bulk behavior for particles larger than 40 nm and deviate from this behavior only in particles smaller than 40 nm. The critical particle size for which we observed confinement effect in nanoblend is much lower than the critical diameter for $T_g$ depression reported in refs 34 and 35 and is lower than the particle size investigated here. These two sets of experiments could infer that particles larger than 40 nm behave dynamically and mechanically as bulk when surrounded either by a soft polymeric matrix or air. However one should take into consideration the role of the confining environment on the properties of the polymer before drawing such a conclusion.

Furthermore, the present results corroborate partially the surface healing experiments on polystyrene film by Forrest et al., which reported a bulk relaxation time around bulk $T_g$. On the other hand the reduction of the activation energy in the glassy regime observed in that experiment does not agree with the bulk activation energy of the present work. The difference between the two results could be due to the dynamic cooperativity resulting from the contacts between the particles of the present experiment.

## CONCLUSION

The dynamic of confined polystyrene in nanoparticles was investigated in particles as small as 42 nm in close packed morphology. The relaxation time was extracted from the kinetic of void closure between close packed particles. The particles deform under the effect of the surface tension energy (polystyrene/air) and the deformation is probed via small angles neutron scattering. The shift factor of the confined PS was found to follow a bulk dynamic in the glassy regime between bulk $T_g$ and $T_g$—50 °C, with the bulk activation energy for particles between 93 and 42 nm. The relaxation time of the confined PS was also found to be similar to the bulk $\langle \tau \rangle_a$. We propose that the cooperativity between particles due to the contacts between them inhibit the eventual activation of the surface dynamic.

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The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

The French neutron facility at the CEA Saclay and the Laboratoire Léon Brillouin are gratefully acknowledged for the neutron equipment. We thank Dr. A. Lapp (LLB) for his help in the neutron scattering experiment and for stimulating discussions and Mohamed Youssi and H. Galliard for their help with these experiments.

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