

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/259486924>

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

ARTICLE *in* MACROMOLECULES · OCTOBER 2013

Impact Factor: 5.8 · DOI: 10.1021/ma401523n

CITATIONS

2

READS

35

3 AUTHORS:



Yahya Rharbi

French National Centre for Scientific Research

60 PUBLICATIONS 1,094 CITATIONS

SEE PROFILE



François Boué

French National Centre for Scientific Research

211 PUBLICATIONS 4,454 CITATIONS

SEE PROFILE



Qamar Nawaz

Grenoble Institute of Technology

9 PUBLICATIONS 33 CITATIONS

SEE PROFILE

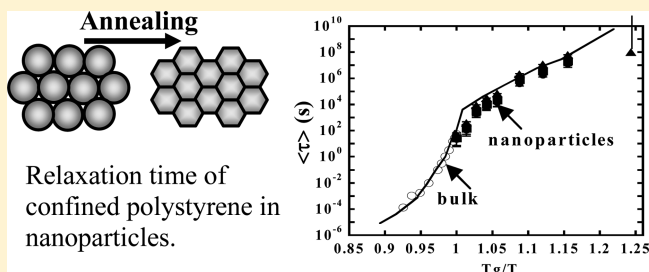
The Dynamic of Confined Polystyrene in Nanoparticles in the Glassy Regime: The Close Packed Morphology

Yahya Rharbi,^{†,*} François. Boué,[‡] and Qamar Nawaz[†]

[†]Laboratoire de Rhéologie et procédés, UJF/INPG/CNRS, BP 53, Domaine universitaire 38041, Grenoble, France

[‡]Laboratoire Léon Brillouin, CEA Saclay, 91191 Gif-sur-Yvettes, France

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 was found to follow a bulk dynamic between bulk T_g and $T_g - 50$ °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.



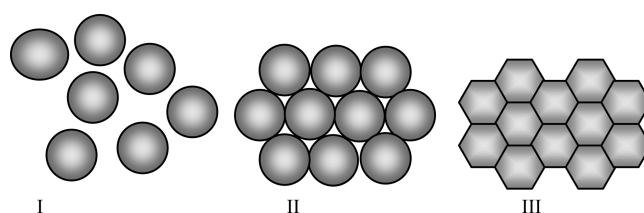
INTRODUCTION

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_g of confined polymers particularly in the thin film geometry.^{1–12} 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 T_g depression in confined polymers.^{1–13} This result lead several groups to investigate directly the dynamic of polymer in thin film using dielectric relaxation spectroscopy (DRS)^{14,15} surface viscosity,^{17,18} and dye reorientation.¹⁶ These experiment 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 films geometry, only a few were being conducted on the nanoparticles geometry.^{30–35} 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 50 reduction of the heat capacity (ΔC_p) when decreasing the

particle size and did not detect any shift of T_g .³⁰ They explained the reduction of ΔC_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 probe directly 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 $\gamma_{p/a}$ ($\gamma_{p/a} = 0.03$ N/m²) in the voids generates negative

Scheme 1. Three Steps of Void Closure



Received: July 19, 2013

Revised: September 8, 2013

Laplace pressure $P_{\text{lap}} = \gamma_{\text{p/a}} S_{\text{void}} / V_{\text{void}}$ (where S_{void} and V_{void} are the surface and volume of the voids) which close the voids and deform the particles.^{38,39,42} We demonstrated that particle deformation can be used to quantify the relaxation time of the confined polymer in particles.^{41,42}

In the present study we investigate the role of the 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.^{30–35} We suggest that the eventual depression of T_g in freestanding particles^{30,34,35} 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.^{34,35} There are several ways for cleaning the latex suspensions; ion exchange, serum replacement and dialysis.^{46–50} Several groups such as the 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 removing ionic surfactants and counterions from polystyrene colloidal suspensions.^{46–49} Our suspensions were cleaned using a mixture of anionic and cationic exchange resins (DOWEX Marathon MR-3, Aldrich). The suspensions was mixed with 50 wt % resin and gently agitated for several hours and then filtered to remove the resin. The cleaning was monitored using the conductivity, which decreases during the cleaning procedure. This was repeated several times until the conductivity no longer changed. The particle surface contained SO_4^- 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.^{46–49} 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 $\mu\text{mol/g}$ of SO_4^- 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 an M_w of 342, 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 ($J(t)$) 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 annealed at 150 °C. A thin layer (10 μm) of Lactite Superglue-3 (cyanoacrylate) 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 τ_{bulk} is estimated from the constitutive equation (eq 1), with $G(t, \tau) = G^0 \exp(-(t/\tau)^\beta)$.^{50–55} The exponent β for

polystyrene is $\beta = 0.4$ and $G^0 \approx 1$ GPa.^{52–54} The average relaxation time is calculated as

$$\langle \tau \rangle = \int \exp(-(t/\tau)^\beta) dt$$

$$\sigma = \int_0^t G(t-t') \frac{d\epsilon_{\text{bulk}}(t')}{dt'} dt' \quad (1)$$

SANS Experiments. The small angle neutron scattering (SANS) experiments were carried out on PAXY instrument at Orphée (Laboratoire Léon Brillouin, CEA-Saclay). The scattered neutrons, collected on an XY bidimensional multidetector, were circularly averaged to obtain spectra of intensities (I) versus the magnitude of the scattering wave vector (Q). The wavelength was 12 Å and the sample–detector distance was 6.7 m, which yields a range of Q values between 4.5×10^{-3} and 3×10^{-2} Å⁻¹.

Cracked films were obtained after evaporating water from the colloidal suspensions at 45 °C. The stock powder was then separated into several samples of 0.2 g placed in glass bottles. Each of these samples was annealed at different temperatures between 100 °C and room temperature for a given time between 1 min and 3 years depending on the annealing temperature. The samples were gently grinded into a powder, and 0.09 ± 0.002 g of it was placed between two pieces of aluminum scotch tape (0.1 mm thick) separated by a spacer of 14 mm inner diameter and 0.8 mm thickness. The powder was then pressed using 15 kg_f to obtain a homogeneous film thickness of 0.8 mm.

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

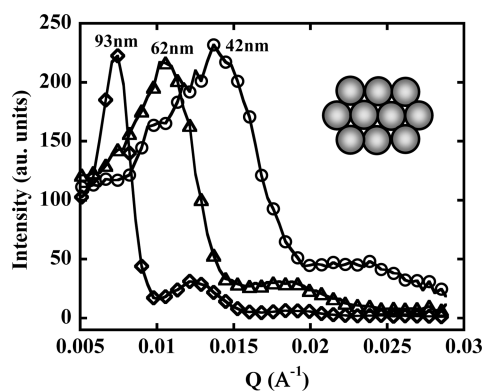


Figure 1. Small angle neutron scattering intensities vs the scattering vector Q for polystyrene particles in the close packed morphology (inset). These structures were made by drying suspensions of PS particles at 60 °C below bulk T_g (45 °C). The diameter of the PS particles is 42 nm (○), 62 nm (Δ), and 93 nm (◇). Inset: scheme of PS particles in the close packed morphology.

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.⁴² This was also confirmed from the volume shrinkage after annealing the films for extended time above 100 °C. The voids around the

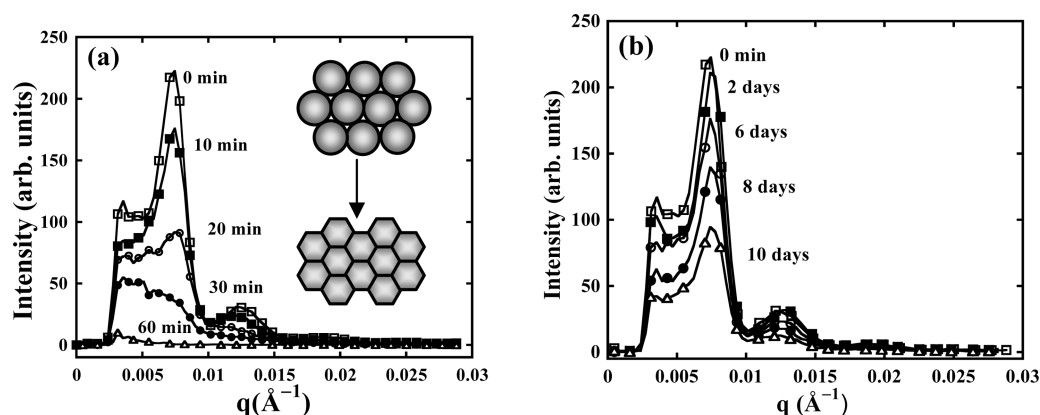


Figure 2. SANS spectra of 93 nm during annealing at 100 °C (a) and at 80 °C (b). Inset: scheme of particle deformation and void closure during annealing.

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 ($V_{\text{voids}}(t)$) as $I(t) \propto (V_{\text{voids}}(t))^2 \propto (V_{\text{voids}}(0))^2 (1 - \varepsilon(t)/0.36)^2$, 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

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 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 $\log(\tau_{\text{void}}(T)/\tau_{\text{void}}(373))$ where $\tau_{\text{void}}(T)$ 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

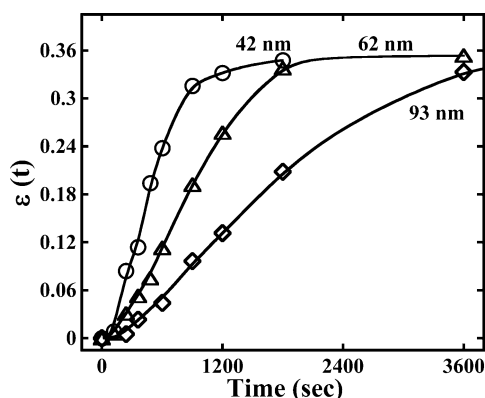


Figure 3. Deformation strain $\varepsilon(t)$ calculated from the intensity peak at 100 °C for various particle size polystyrene.

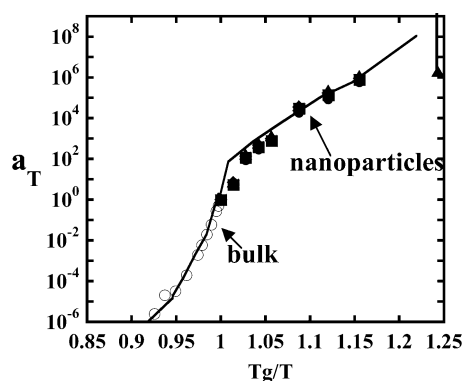


Figure 4. The shift factor a_T vs the inverse of temperature during void closure for particle sizes 42 (◊), 62 (■), and 93 nm (▲). a_T is estimated by shifting the decays to a reference decay at 373 K or as $a_T = \tau_{\text{void}}(T)/\tau_{\text{void}}(373)$, where $\tau_{\text{void}}(T)$ is taken 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 .

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 $P_{\text{lap}} \approx \alpha \gamma_{p/a}/R$, where R is the particle radius and $\alpha \approx 6$ for random compact structures.^{38,39,56–60} The applied pressure for the smallest particles (42 nm) is $P_{\text{lap}} \approx 4$ MPa, which is lower than the yield stress of polystyrene (~ 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 $\varepsilon(t) \propto t/\tau_{\text{void}}$ (τ_{void} is the characteristic time for void closure). The Frenkel model gives an estimate of $\varepsilon(t) \propto t/\tau_{\text{void}} \propto (\gamma_{p/a}/G_0 R)t/\tau_{\alpha}$, where G_0 and τ are the elastic modulus and the relaxation time of the polystyrene.⁵⁶ The dependence of $\varepsilon(t)$ on the particle radius

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 the 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 value of the shift factor. The a_T at room temperature is added in Figure 4 as an indication.

The a_T deviates slightly from the Vogel–Fulcher–Tammann (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.⁵⁰ 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 τ_{void} is found to decrease with decreasing the particle size, the a_T are superposable in this range of particle size. This result proves that the polymer dynamic of polystyrene particles in contact adopt 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 τ_α of the polymer in the nanoparticles.^{38,39,42,56–60} 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.⁵⁶ This leads to $\varepsilon(t) \propto (3/4\gamma_{p/a}/G_0R)t/\tau_\alpha$. 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.³⁹

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

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.⁵⁸ 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.³⁸ This leads to a constitutive equation

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

The $G(t)$ of polystyrene can be considered either monoexponential or stretched exponential with an exponent $\beta = 0.4$.⁵⁰ The averages $\langle\tau\rangle$ from all these models are plotted against the inverse of the 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 α relaxation time $\langle\tau\rangle_\alpha$ 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 α relaxation time at T_g from other techniques such as DRS⁵⁰ and SHG.⁵⁰ The $\langle\tau\rangle$ from the bulk of this study was also found to superimpose with $\langle\tau\rangle_\alpha$ from SHG⁵⁰ for all the temperatures above T_g (Figure 5). This infers that these experiments probe the α 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 of this study.⁵¹

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,

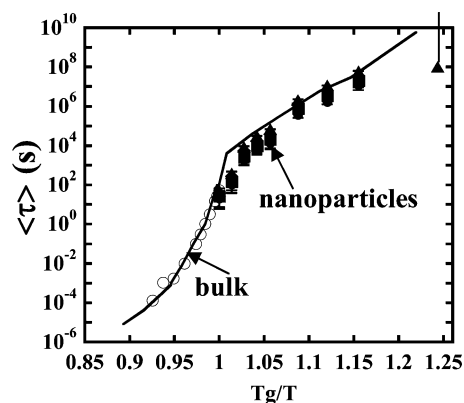


Figure 5. Average relaxation time $\langle\tau\rangle$ vs the inverse of temperature during void closure for particle sizes 42 (◆), 62 (■), and 93 nm (▲). The $\langle\tau\rangle$ for nanoparticles is compared to the $\langle\tau\rangle$ of bulk PS made from the same particles using the creep compliance (○) and to the bulk $\langle\tau\rangle$ from the SHG on other PS sample. The temperature is normalized to the bulk T_g . The error bar is estimated from the various models for calculating $\langle\tau\rangle$.

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 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 $\langle\tau\rangle_\alpha$ 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 represent 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, 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 α -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.⁶²

Beside the dynamic of the polystyrene particles, their glass transition is an important issue.^{30,34,35} 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 ΔC_p , which was interpreted to suggest the presence of a layer with a higher mobility on the free surface.³⁰ On the other hand recent papers stressed the importance of the surface properties on the particle T_g .^{34,35} In one report an important T_g shift (-50 °C for 90 nm particles) was observed in surfactant-free PS particles in water and was attributed to the absence of surfactant.³⁴ Yet

these particles contain sulfate (SO_4^-) 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.³⁵ These findings bring us to discuss the importance of the 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 Vanderhoff team and Steward and coworkers among other.^{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 $\mu\text{mol/g}$ of SO_4^- 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 particles surface suggested from the DSC experiment³⁰ or polarized fluorescence experiment on freestanding polystyrene thin film¹⁶ does not dominate the overall relaxation time of the particles in contact with each others. 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 makes 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 makes the close packed structure to 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.³² 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 particle larger than 40 nm behaves 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 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 .¹⁷ 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 $T_g - 50^\circ\text{C}$, 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 $\langle\tau\rangle_\alpha$. We propose that the cooperativity between particles due to the contacts between them inhibit the eventual activation of the surface dynamic.

AUTHOR INFORMATION

Corresponding Author

*E-mail: (Y.R.) rharbi@ujf-grenoble.fr.

Notes

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 Yousfi and H. Galliard for their help with these experiments.

REFERENCES

- (1) Alcoutlabi, M.; McKeena, G. B. *J. Phys.: Condens. Matter* **2005**, *17*, 461.
- (2) Forrest, J. A. *Eur. Phys. J. E* **2002**, *8*, 261.
- (3) Forrest, J. A.; Dalnoki-Veress, K.; Stevens, J. R.; Dutcher, J. R. *Phys. Rev. Lett.* **1996**, *77*, 2002.
- (4) Keddie, J. L.; Jones, R. A. L.; Cory, R. A. *Europhys. Lett.* **1994**, *27*, 59.
- (5) Kawana, S.; Jones, R. A. L. *Phys. Rev. E* **2001**, *63*, 021501.
- (6) DeMaggio, G. B.; et al. *Phys. Rev. Lett.* **1997**, *78*, 1524.
- (7) Ellison, C. J.; Torkelson, J. M. *Nat. Mater.* **2003**, *2*, 695.
- (8) Varnik, J.; Baschnagel, F.; Binder, K. *Phys. Rev. E* **2002**, *65*, 021507.
- (9) Riggleman, R. A.; Yoshimoto, K.; Douglas, J. F.; dePablo, J. J. *Phys. Rev. Lett.* **2006**, *97*, 045502.
- (10) Forrest, J. A.; Mattsson, J. *Phys. Rev. E* **2000**, *61*, R53.
- (11) Shin, K.; Obukhov, S.; Chen, J.-T.; Huh, J.; Mok, S.; Dobryal, P.; Thiagarajan, P.; Russell, T. P. *Nature Mater.* **2007**, *6*, 961.
- (12) Kim, S.; Torkelson, J. M. *Macromolecules* **2011**, *44*, 4446.
- (13) Baumchen, O.; McGraw, J. D.; Forrest, J. A.; Dalnoki-Veress, K. *Phys. Rev. Lett.* **2012**, *109*, 055701.
- (14) Fukao, K.; Miyamoto, Y. *Phys. Rev. E* **2000**, *61*, 1743.

- (15) Rotella, C.; Napolitano, S.; Wübhenhorst, M. *Macromolecules* **2009**, *42*, 1415.
- (16) Paeng, K.; Swallen, S. F.; Ediger, M. D. *J. Am. Chem. Soc.* **2011**, *133*, 8444.
- (17) Fakhraai, Z.; Forrest, J. A. *Science* **2008**, *319*, 600.
- (18) Qi, D.; Fakhraai, Z.; Forrest, J. A. *Phys. Rev. Lett.* **2008**, *101*, 096101.
- (19) Serghei, A.; Huth, H.; Schick, C.; Kremer, F. *Macromolecules* **2008**, *41*, 3636.
- (20) Tress, M.; Erber, M.; Mapesa, E. U.; Huth, H.; Müller, J.; Serghei, A.; Schick, C.; Eichhorn, K.-J.; Voit, B.; Kremer, F. *Macromolecules* **2010**, *43*, 9937.
- (21) Boucher, V. M.; Cangialosi, D.; Yin, H.; Schonhals, A.; Alegria, A.; Colmenero, J. *Soft Matter* **2012**, *8*, 5119.
- (22) O'Connell, P. A.; McKenna, G. B. *Science* **2005**, *307*, 1760.
- (23) Si, L.; Massa, M. V.; Dalnoki-Veress, K.; Brown, H. R.; Jones, R. A. L. *Phys. Rev. Lett.* **2005**, *78*, 127801.
- (24) Gasemjit, P.; Johannsmann, D. *J. Polym. Sci., Part B* **2006**, *44*, 3031.
- (25) Papaleo, R. M.; Leal, R.; Carreira, W. H.; Barbosa, L. G.; Bello, I.; Bulla, A. *Phys. Rev. B* **2006**, *74*, 094203.
- (26) Reiter, G.; Hamieh, M.; Damman, P.; Sclavons, S.; Gabriele, S.; Vilmin, T.; Raphaël, E. *Nat. Mater.* **2005**, *4*, 754.
- (27) Bodiguel, H.; Fretigny, C. *Phys. Rev. Lett.* **2006**, *97*, 266105.
- (28) Roth, C. B.; Dutcher, J. R. *Phys. Rev. E* **2005**, *72*, 021803.
- (29) Frank, B.; Gast, A. P.; Russel, T. P.; Brown, H. R.; Hawker, C. *Macromolecules* **1996**, *29*, 6531.
- (30) Sasaki, T.; Shimizu, A.; Mourey, T. H.; Thureau, C. T.; Ediger, M. D. *J. Chem. Phys.* **2003**, *119*, 8730.
- (31) Herminghaus, S.; Seemann, R.; Landfester, K. *Phys. Rev. Lett.* **2004**, *93*, 017801.
- (32) Rharbi, Y. *Phys. Rev. E* **2008**, *77*, 031806.
- (33) Yousfi, M.; Porcar, L.; Lindner, P.; Boué, F.; Rharbi, Y. *Macromolecules* **2009**, *42*, 2190.
- (34) Zhang, C.; Guo, Y.; Priestley, R. D. *Macromolecule* **2011**, *44*, 4001.
- (35) Shuo, F.; ZhiYun, L.; Ran, L.; BiYun, M.; Qing, W.; GuoDong, L.; HaiYang, G.; FangMing, Z. *Soft Matter* **2013**, *9*, 46140.
- (36) Winnik, M. A. Latex film formation. *Curr. Opin. Colloid Interface Sci.* **1997**, *2*, 192.
- (37) Steward, P. A.; Hern, J.; Wilkinson, M. C. *Adv. Colloid Interface Sci.* **2000**, *86*, 195.
- (38) Russel, W. B.; Wu, N.; Man, W. *Langmuir* **2008**, *24*, 1721.
- (39) Routh, A. F.; Russel, W. B. *Langmuir* **1999**, *15*, 7762.
- (40) Nawaz, Q.; Rharbi, Y. *Macromolecules* **2008**, *41*, 5928.
- (41) Rharbi, Y.; Yousfi, M.; Porcar, L.; Nawaz, Q. *Can. J. Chem.* **2010**, *88*, 288.
- (42) Nawaz, Q.; Rharbi, Y. *Langmuir* **2010**, *26*, 1226.
- (43) Cabane, B.; Chevalier, Y.; Pichot, C.; Graillat, C.; Joanicot, M.; Wong, K.; Maquet, J.; Lindner, P. *Colloid Polym. Sci.* **1992**, *270*, 806.
- (44) Rharbi, Y.; Boué, F.; Joanicot, M.; Cabane, B. *Macromolecules* **1996**, *29*, 4346.
- (45) Dingenouts, N.; Ballauff, M. *Langmuir* **1999**, *15*, 3283.
- (46) Vanderhoff, J. W.; Van Den Hull, H. J. *J. Macromol. Sci. Chem. A* **1973**, *7*, 677.
- (47) Kamel, A. A.; El-Aasser, M. S.; Vanderhoff, J. W. *J. Colloid Interface Sci.* **1982**, *87*, 537.
- (48) Ahmed, S. M.; El-Aasser, M. S.; Powli, G. H.; Poehlein, G. W.; Vanderhoff, J. W. *J. Colloid Interface Sci.* **1980**, *73*, 388.
- (49) Wilkinson, M. C.; Hearn, J. U.; Steward, P. A. *Adv. Colloid Interface Sci.* **1999**, *81*, 77.
- (50) Dhinojwala, A.; Wong, G. K.; Torkelson, J. M. *J. Chem. Phys.* **1994**, *100*, 6047.
- (51) Roland, C. M.; Casalini, R. *J. Chem. Phys.* **2003**, *119*, 1838.
- (52) Plazek, D. J. *J. Polym. Sci., Part A-2: Polym. Phys.* **1968**, *6*, 621.
- (53) Lin, Y.-H. *J. Phys. Chem. B* **2005**, *109*, 17654.
- (54) Inoue, T.; Osaki, K. *Macromolecules* **1996**, *29*, 1595.
- (55) Kohlrausch, R. *Ann. Phys. (Leipzig)* **1847**, *12*, 393. (b) Williams, G.; Watts, D. C. *Trans. Faraday Soc.* **1970**, *66*, 80.
- (56) Frenkel, J. *J. Phys. (Paris)* **1945**, *9*, 385.
- (57) Bellehumeur, C. T.; Kontopoulou, M.; Vlachopoulos, J. *Rheol. Acta* **1998**, *37*, 270.
- (58) Johnson, K. L.; Kendall, K.; Roberts, A. D. *Proc. R. Soc. London, Ser. A* **1971**, *324*, 301.
- (59) Lin, F.; Meier, D. J. *Langmuir* **1995**, *11*, 2726.
- (60) Lin, F.; Meier, D. J. *Langmuir* **1996**, *12*, 27774.
- (61) Strobl, G. *The Physics of Polymers*, 2nd ed.; Springer-Verlag: Berlin, 1997.
- (62) Zhang, C.; Boucher, V. M.; Cangialosi, D.; Priestley, R. D. *Polymer* **2013**, *54*, 230.
- (63) Yousfi, M.; Rharbi, Y. Submitted for publication.