Glass Transition of Disentangled and Entangled Polymer Melts: Single-Chain-Nanoparticles Approach

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ABSTRACT: We study the effect of entanglements on the glass transition of high molecular weight polymers, by the comparison of single-chain nanoparticles (SCNPs) and equilibrated melts of high-molecular weight polystyrene of identical molecular weight. SCNPs were prepared by electrospraying technique and characterized using scanning electron microscopy and atomic force microscopy techniques. Differential scanning calorimetry, Brillouin light spectroscopy, and rheological experiments around the glass transition were compared. In parallel, entangled and disentangled polymer melts were also compared under cooling from molecular dynamics simulations based on a bead-spring polymer model. While experiments suggest a small decrease in the glass transition temperature of films of nanoparticles in comparison to entangled melts, simulations do not observe any significant difference, despite rather different chain conformations.

INTRODUCTION

There has been a great interest to understand the relation between glass transition temperature \( T_g \) and molecular weight \( M_n \) of polymers.1–5 For polystyrene (PS), \( T_g \) significantly increases with \( M_n \) slowly leveling off around the entanglement molecular weight \( M_e \). For short polymer chains of only a few monomers, conformations are still approaching the asymptotic Gaussian structure with increasing chain length, while for molecular weight around \( M_e \), conformations typically are reasonably well represented by a Gaussian coil structure. Thus, beyond \( M_e \), \( T_g \) does not change much with increasing \( M_n \) and approaches a constant value of about \( T_g = 374 \text{ K} \) for high molecular weight PS.6 It is this regime, where entanglements clearly dominate the viscoelastic response of a melt, we are focusing on in the present work.

In general, the relationship between \( T_g \) and \( M_n \) can be expressed in terms of modified version of the well-known Fox and Flory equation:1,2

\[
\frac{1}{T_g(M_n)} = \frac{1}{T_g(\infty)} + \frac{K_c}{M_n}
\]

where \( T_g(\infty) \) is the extrapolated \( T_g \) of a polymer at infinite \( M_n \) and \( K_c \) is an experimentally determined parameter, depending on the particular polymer species. For PS, \( K_c = 0.78 \text{ Da/K} \) and the asymptotic value of \( T_g(\infty) \) is 374 K.7 To rationalize this continued chain length dependency \( (T_g - M_n) \) relationship beyond \( M_n \), two lines of arguments can be found in the literature. The first one proposes that entanglements are central for the remaining shift in and physical properties near \( T_g \).9,10 The alternative explanation is that chain-ends are responsible for the observed behavior. The end groups have higher mobility because of their local excess free volume resulting in larger conformational entropy and deficient intermolecular constraints. Lower \( M_n \) means higher concentration of chain ends and hence higher mobility leading to lower \( T_g \).11–15 Thus, the question we are addressing is to what extent do entanglements play a role for the glass transition. To do this, we have to look for systems identical up to the presence of entanglements. For this, we study experimentally and by simulation equilibrated polymer melts and systems made of disentangled single-chain nanoparticles (SCNPs).

SCNPs can be used to study the effect of entanglements on the properties of long chain polymer melts. Heating SCNPs of high molecular weight above \( T_g \) leads to the formation of a metastable disentangled melt of polymers. Their corresponding properties can be compared to that of an entangled melt of bulk polymers.16–18 SCNPs can be prepared using a variety of techniques such as precipitation,19–22 freeze-drying,16,23,24 crystallization,17,18 spin-casting16, and electrospraying. All these preparation methods have the use of very dilute polymer solutions in common. In electrospraying, electric
fields are applied to facilitate the production of extremely small droplets out of polymer solutions, almost exclusively containing only one polymer chain each. The solvents evaporate, and isolated particles of single polymer molecules are collected. SCNPs can also be used as molecular mass and size standard, biological tracer and to study nano- and microphases where each particle can be considered as a distinct phase.\textsuperscript{27}

Previous works\textsuperscript{9,10} on the effect of entanglement near $T_g$ are not consistent. Rong et al.\textsuperscript{9} show a decrease in the $T_g$ of PS ($M_n = 3.18 \times 10^5$ Da) in disentangled freeze-dried dilute solution of PS in benzene. However, Zheng and Simon\textsuperscript{29} used the same approach and concluded that the complete removal of benzene is not possible under those conditions. Hence, the reported\textsuperscript{9} $T_g$ decrease could be ascribed to a solvent-induced plasticization and not to the absence of entanglements. Huang et al.\textsuperscript{10} studied the effect of entanglements on the $T_g$ of low-molecular-weight polycarbonates with a mass-average molecular weight $M_n = 1.7 \times 10^4$ Da and polydispersity $M_w/M_n = 1.79$. Because polycarbonate has an entanglement molecular weight $M_e \approx 2500$ Da,\textsuperscript{30} the studied polycarbonate chains have $z = M_e/M_n \leq 5$. Considering this and the rather significant polydispersity make it difficult to clearly identify the cause of the reduction in $T_g$.

In this work, we study PS melts around $T_g$ consisting of disentangled, collapsed high molecular weight single polymer chain nanoparticles (NPs) and compare their properties to the corresponding equilibrated melts. Samples were prepared by electrospraying dilute polymer solutions of PS in dimethylformamide (DMF). The objective of the sample preparation was to minimize entanglements in the melt of long polymer chains. For this, the polymers were dissolved at dilute concentration and then electrosprayed. By working at a concentration well below the overlap concentration ($C < C^*$), solutions essentially without any entanglements have been prepared. Then, by electrospraying, rapidly drying solution droplets were produced which led to the formation of NPs, containing ideally only single chains, having no or only very few entanglements. The idea was that with the application of high voltage, the initially larger droplets containing polymer and solvent would break up into smaller drops containing single polymer chains only, and the solvent would evaporate so quickly that only dry polymers in their collapsed initial conformation would be collected. The time to reach the collector ($t \approx 7$ ms) was orders of magnitude less than the estimated Rouse-time\textsuperscript{31,32} ($\tau_R \approx 1.5$ s) of the polymer chains (details in Section S3 of Supporting Information). The low concentration ($C < C^*$) ensures no interchain entanglements, and the fast evaporation also guarantees no intrachain entanglements (beyond possible very rare intrachain entanglements already existing in the dilute solution). We used different characterization tools like nuclear magnetic resonance (NMR), Fourier-transform infrared spectroscopy and thermal gravimetric analysis (TGA) to rule out the presence of residual DMF in the samples (spectra and graphs in Sections S2.2.2, S2.2.3, and S2.2.4 of the Supporting Information). We applied three different experimental techniques, differential scanning calorimetry (DSC), oscillatory rheology, and Brillouin light scattering (BLS) to analyze melts of disentangled polymer globules in comparison to entangled PS melts. To complement this and to obtain complementary insights into structural aspects, we further employed molecular dynamics (MD) simulations of entangled and disentangled polymer melts. At first glance, our experiments give consistent results of a somewhat lower $T_g$ for the disentangled polymer melt in comparison to the entangled polymer melt, while simulations do not support this shift. Different experimental techniques measure $T_g$ by tracking different dynamical properties during the transition. This can lead to somewhat different absolute $T_g$ values. However, our study is aimed at examining deviations in properties around $T_g$ between disentangled and entangled state of polymer melts but is not focusing on the absolute value of $T_g$ itself.

\section*{NP PREPARATION}

We have used electrospraying to prepare single-chain PS NPs. Chains of $M_n = 1.1 \times 10^6$ Da having polydispersity of $M_w/M_n = 1.27$ were used for our experiments, for more details, we refer to Supporting Information. Different morphologies were obtained by electrospraying polymer solutions of PS in DMF at different concentrations, near, above, and below $C^*$. Figure 1 illustrates the electrospraying technique showing high-speed camera images of jets of polymer solutions coming out of the needle and scanning electron microscopy (SEM) images of different morphologies obtained at different concentrations. Details of materials and characterizations, including the estimate of $C^* \approx 0.95$ wt %, are given in Section S2.1 of Supporting Information.

To obtain SCNPs, first, the conditions for the successful electrospraying had to be optimized. At too high polymer concentration (2.3 wt %), when $C > C^*$, a continuous whipping jet of polymer solution was observed and resulted in the usual electrospinning of nanofibers (NFs) as observed by SEM. The obtained NFs had a diameter of more than 100 nm. When the concentration of the polymer solution was reduced to $C \approx C^*$, a mixture of particles and fibers was obtained. At 0.1 wt %, the initial linear jet of polymer solution broke up in 27 $\mu$m droplets of polymer solution within the first ca. 3 mm from the nozzle as observed in Figure 1. These large droplets are known to undergo secondary splitting in flight,\textsuperscript{33} resulting
in the collected NPs containing single chains, as observed by SEM.

Differences between the obtained structures can be attributed to a combination of the state of the polymers in solution and physical properties of the solutions. Above \( C^* \), because of entanglements present due to the mutual polymer chain overlap, and of the resulting solution viscosity, continuous jets are formed leading to electrospinning of long polymer fibers. At concentrations below \( C^* \), the viscosity of the polymer solution is decreased, and consequently, the same shear force created by the difference of potential can lead to a larger deformation at the nozzle. This steady jet of polymer solution subsequently breaks to form droplets which will undergo secondary splitting later in-flight because of Coulombic and surface tension driven forces. This steady jet of polymer continuous jets are formed leading to electrospinning of long polymer fibers.

Beyond direct visualization by electron microscopy, the size of single chain NPs was verified using atomic force microscopy (AFM). Figure 2a shows an AFM image of NPs prepared from low concentration \((C = 0.1 \text{ wt }\%\) PS in DMF solution. From the profile of different NPs, height and apparent width of the particles were found to be in the range of 15–20 and 55–60 nm, respectively. Taking into account, that the measurement of the apparent width of the particles includes the convolution of the diameter of particles \( \times \) diameter of cantilever-tip, AFM height profiles provide the most accurate measure of the size of the NPs. We further analyzed the SEM image of NPs by measuring the size distribution of \((n = 100)\) randomly selected particles in Figure 1. The histogram (Figure 2b) shows that the average size of the particles is 20 \( \pm 3 \) nm. Assuming melt density of PS, \( \rho \) the diameter of a single chain NP of PS of \( M_n = 1.1 \times 10^6 \) Da should be approx. 20 nm. Details of the calculation are given in Section S4 of the Supporting Information. Thus, we can safely conclude that our NPs typically contain only one polymer chain. We also varied the infuse-rate and applied voltage, but no significant changes were observed in the NP size (Sections S4.1 and S4.2 of the Supporting Information).

### GLASS TRANSITION: DSC AND OSCILLATORY RHEOLOGY

First, we compare the apparent glass transition temperature \( T_g \) of different entangled and disentangled melts of PS prepared from the very same batch of polymer and by the same cooling rate. Figure 3 shows the comparison of the glass transition temperature obtained using two different techniques. DSC results of four PS samples are shown: equilibrated bulk PS film, PS NPs, PS SCNPs, and annealed SCNPs. The bulk PS film was prepared by hot pressing 300 mg of PS flakes under a load of 20 kN at 433 K for 1 h. The PS film had a thickness of 100 \( \pm 10 \) \( \mu \)m. The results show that the observed glass transition temperature \( T_g \) of entangled samples (PS films and NPs) are the same within the error (approx. 381 K), despite the strong deformation of the long chains in the fibers. This is remarkable by itself but beyond the scope of the present work. In comparison to that, the apparent \( T_g \) of the melt of disentangled PS NPs (approx. 374 K) is reduced by about 2%, that is, 7°. After annealing the SCNP sample at 433 K for 24 h, \( T_g \) increased to 380 K, similar to \( T_g \) of bulk entangled PS. This increase of \( T_g \) following annealing might be attributed to the development of entanglements in the disentangled SCNP sample, even though polymer globules are known to be metastable.17,37,38 Thus, the question arises, can the apparent lower \( T_g \) be attributed to the higher chain mobility in the disentangled melt in the absence of large number of entanglements? The density of chain ends is the same in each sample. It should be noted that there are no detectable traces of solvent left in the material, see Section S2.2 of the Supporting Information. We have also repeated 10 cycles of heating and cooling of PS NPs (Figure S12 in Supporting Information). The graphs showing 10 heating curves are presented in Section S5 of the Supporting Information. The result shows that the apparently lower \( T_g \) of PS NPs was quite stable and did not change significantly even after 10 cycles of heating and cooling in the range 133–473 K at a rate of 10 K/min, that is a total of 680 min of experiment duration. Though this is significantly longer than the expected overall Rouse time, which is expected to govern the internal relaxation dynamics of the nonentangled particles, no signature of re-entanglement is observed. Experimental17,18,39,40 and theoretical works37,38 on disentangled melts of polymers showed that chains longer than a critical length need to overcome a significant free energy barrier in order to relax from a metastable \( \rightarrow \) fully entangled state. The PS used in our experiments would have \( z = M_n/M_e \approx 66 \) entanglements per chain (considering \( M_n = 1.1 \times 10^6 \) Da and \( M_e = 16,600 \) Da) in a fully equilibrated entangled melt. Thus, heating of our SCNPs of long PS chains is expected to lead to the formation of metastable melts.
To examine this, Figure 3b shows the temperature sweep rheology experiments on entangled and disentangled (SCNPs) PS. The loss modulus ($G''$) measures energy dissipation, and the temperature of the peak value of $G''$ during temperature sweep gives an estimate of the glass transition temperature of polymers. Our oscillatory rheology experiments show an apparent lower glass transition temperature of disentangled PS NPs ($T_g = 379$ K) in comparison to entangled PS ($T_g = 383$ K) in good agreement with DSC. The difference in $T_g$ of entangled and disentangled samples from rheological experiments turns out to be smaller than that observed in DSC experiments. Note that by measuring $T_g$ with oscillatory rheology, we probe local relaxation rather than the overall viscosity of the melts. As in the DSC experiments, lower $T_g$ of disentangled PS NPs was very stable. The samples for rheology experiments were prepared at a temperature of 433 K and the data presented in Figure 3 are from the cooling cycle after the experiments were carried out. The (1,1) mode of the individual SCNPs cannot be resolved for NP surface mobility below $T_g$. Because the BLS intensity strongly decreases with the NP diameter, the fundamental quadrupolar vibration mode, (1,2), cannot be resolved for NP diameter below about 100 nm. In the presence of NP adhesion, however, a new interaction-induced branch (1,1) representative of few NPs vibration is discernible in the BLS spectrum at frequencies lower than the (1,2) mode.

For the present non-transparent as-prepared SCNPs powder, the (1,2) mode of the individual SCNPs cannot be resolved because of their small size ($20 \pm 3$ nm). Figure 4a shows the reduced [intensity ($I$) times frequency ($f$) squared] BLS spectra of as-prepared SCNPs at different temperatures increasing from 294 to 373 K. The (1,1) mode is resolved as anticipated because of the SCNPs adhesion in the SEM image (Figure 1). Upon this first heating, the (1,1) mode undergoes a blue shift (increase of its frequency) at the softening temperature, $T_s \approx 345$ K, and then abruptly changes in the temperature region between 363 and 373 K as indicated by the dashed line in Figure 4a. The strong peak in the BLS spectrum at 373 K is reminiscent of the longitudinal acoustic (LA) phonon in bulk PS at backscattering (BS) and hence indicates the formation of a contiguous film of molten SCNPs. The BLS spectra of the latter are presented in Figure 4b. The interaction-induced (1,1) mode is associated with the acoustic phonon propagation in SCNPs clusters of granular type (lower inset to Figure 4d), and its frequency is sensitive to the interparticle adhesion force. The position of the (1,1) mode is represented by the frequency $f_{(1,1)}$ at maximum intensity in the reduced BLS spectra in Figure 4a, and its temperature dependence is plotted in Figure 4d (black solid circles). As temperature increases above $T_s$ (patterned area), $f_{(1,1)}$ crossovers to the LA phonons in the film of molten SCNPs (upper inset to Figure 4d) in the region 363–373 K. Hence, the $T_g$ of the SCNPs should fall into this temperature range (yellow shaded area in Figure 4d) and is slightly ($\approx 6$ K)

**FIGURE 3.** Comparison of the glass transition temperature $T_g$ of entangled and disentangled PS: (a) DSC experiments: PS NPs, PS NFs, and PS film. PS NPs and NFs were prepared by electrospinning of PS in DMP solution at concentrations C = 0.2 wt % and C = 2.3 wt % using the process parameters: distance $d = 20$ cm and infuse-rate $v = 1.5$ mL/h and applied voltage $V = 15$ kV. PS film was prepared by hot-pressing bulk PS at temperature $T = 433$ K under a load of $L = 20$ kN. (b) Rheological experiment: temperature sweep at frequency $f = 10$ rad/s was used.

**GLASS TRANSITION: BLS**

BLS is a powerful technique for studying dynamics and glass transition of amorphous materials. For transparent films, BLS measures the longitudinal modulus $L(\omega)$ at GHz frequencies, $\omega$. The dispersion, $L(\omega)$, in amorphous polymers is controlled by the main glass-rubber relaxation time, $\tau_r$ and attains the limiting low and high frequency values $L_\infty$ for $(\omega t)^2 \ll 1$ and $L_\infty$ for $(\omega t)^2 \gg 1$, respectively. $T_g$ attains the limiting low and high frequency values $T_g$ for $T_g + 100$ K. The temperature dependence of $L(T) = \rho(T)c(T)^2$, with $\rho(T)$ and $c(T)$ being the density and longitudinal sound velocity, is mainly controlled by $c(T)$ in the vicinity of $T_g$. The different temperature dependences, $c(T < T_g)$ (weak) and $c(T > T_g)$ (strong), enables the determination of $T_g$ in amorphous bulk polymers by BLS. In the case of non-transparent powder of polymeric colloids, BLS determines the glass transition through the temperature-sensitive particle elastic vibrations which disappear upon the formation of the contiguous film at $T_g$.

In addition, BLS identifies a second so-called softening temperature, $T_s$, which is related to the onset of particle surface mobility below $T_s$. Because the BLS intensity strongly decreases with the NP diameter, the fundamental quadrupolar vibration mode, (1,2), cannot be resolved for NP diameter below about 100 nm. In the presence of NP adhesion, however, a new interaction-induced branch (1,1) representative of few NPs vibration is discernible in the BLS spectrum at frequencies lower than the (1,2) mode. The position of the (1,1) mode is represented by the frequency $f_{(1,1)}$ at maximum intensity in the reduced BLS spectra in Figure 4a, and its temperature dependence is plotted in Figure 4d (black solid circles). As temperature increases above $T_s$ (patterned area), $f_{(1,1)}$ crossovers to the LA phonons in the film of molten SCNPs (upper inset to Figure 4d) in the region 363–373 K. Hence, the $T_g$ of the SCNPs should fall into this temperature range (yellow shaded area in Figure 4d) and is slightly ($\approx 6$ K).
Surface mobility might lead to the slightly lower apparent softening temperature $T_g$ of the as-prepared SCNPs (solid red symbols in Figure 4a) at $q = 4\pi n / \lambda = 0.0366 \text{ nm}^{-1}$, where $\lambda = 532 \text{ nm}$ is the laser wavelength and $n = 1.55$ is the refractive index. The change of the decrease rate of $c(T)$ in the annealed film occurred at $T_g = 373 \pm 2 \text{ K}$ (red shaded area in Figure 4e). This is identical to $T_g$ of the bulk PS of fully entangled chains (Supporting Information, S6) and slightly higher than that of the coalescent SCNP film (yellow shaded in Figure 4e). Note that because of different mechanisms and heating rates, the $T_g$ estimated by BLS can be about 7–10 K lower than the corresponding DSC value (Figure 3a).59–61

The BLS results corroborate the notion that the $T_g$ of the as-prepared and coalescent SCNPs samples with disentangled chains is slightly ($\approx 6 \text{ K}$) lower than that of the annealed film with entangled chains. The conceivable $T_g$ suppression effect due to the free surface softening64 is not supported by the similar $T_g$ values in the as-prepared and coalescent SCNPs samples (Figure 4d). Based on this similarity, the local chain structure in these two samples should assume a similar local structure. On a larger length scale, the chain packing in the experimental samples might be not the same compared to the equilibrated structures of the MD simulations.55,56

### MD Simulations

Despite three different experiments, addressing qualitatively different quantities to locate the glass transition of the two different polymer systems, the conclusion as to whether $T_g$ for entangled and disentangled long chain polymer melts is the same or not is not entirely clear. To complement this, we resort to simulations studies. By looking at model systems, simulations have the clear advantage to study perfectly defined systems. This comes with the disadvantage that the cooling rate which can be reached in simulations typically is much higher than in experiments. Because we follow exactly the same cooling protocol for both systems, for the current study, this is not a problem. If there is a difference in $T_g$, very fast cooling is expected to increase this difference. Here, we employ MD simulations, which are a very powerful tool to understand the structural and thermal behavior of polymer melts. We study a recently developed coarse-grained model57,58 which does not suffer from artificial chain straightening under cooling and performed MD simulations in the isothermal–isobaric ensemble (NPT). To compare entangled and disentangled melts, we follow a strategy similar to experiment and compare a melt of fully equilibrated chains to a melt of collapsed, disentangled globules. To produce a disentangled melt, we start with isolated good solvent chains, which are contracted a melt of fully equilibrated chains to a melt of collapsed, disentangled globules. To produce a disentangled melt, we start with isolated good solvent chains, which are contracted to a melt of fully equilibrated chains to a melt of collapsed, disentangled globules. To produce a disentangled melt, we start with isolated good solvent chains, which are contracted to a melt of fully equilibrated chains to a melt of collapsed, disentangled globules. 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globules, as also a primitive path analysis (PPA) reveals. To compare the glass transition, both systems were cooled down following exactly the same cooling protocol. Because we focus on potential differences in $T_g$ rather than the exact value of $T_g$, this is an adequate approach. The cooling rate of $10^{-7}$/($k_B\tau$) was chosen such that around the highest temperature $T = 1/e/k_B\tau$, subchains of the order of $N_e$ easily can relax. The observed glass transition temperature $T_g$ was obtained from the change of volume $V$ as a function of temperature. The intersection of the linear extrapolation of $\ln V(T)$ between the liquid branch ($\ln V_{\text{liquid}} = a_{\text{liquid}} + a_{\text{liquid}}/T$) and the glass branch ($\ln V_{\text{glass}} = a_{\text{glass}} + a_{\text{glass}}/T$) can be used to estimate $T_g$. Here, $a_{\text{liquid}}$ and $a_{\text{glass}}$ are thermal expansion coefficients for polymer melts in the liquid state and the glassy state, respectively. Furthermore, we checked whether the melt of globular chains did not significantly re-entangle during the simulation by performing a PPA. The longest straight pieces in PPA have lengths of the order of the whole chains, proving that the disentangled globules remain intact during the simulation. Results of $\ln V$ plotted versus $T$ for both entangled (with the entanglement length $N_e = 28$ obtained from the PPA of chains with bending parameter, $k_B = 1.5^{61,62}$ used in the current work) and disentangled polymer melts each containing 1000 chains of polymerization degree $N = 1000$ with a starting monomer density $\rho = 0.85\sigma^{-3}$. The glass transition occurs at $T_g = 0.670(2) e/k_B$ for the disentangled and the entangled polymer melt at pressure $P = 0.0e/\sigma^3$. For comparison, for a melt of short chains of $N = 50$ and the identical quench rate, we find $T_g = 0.638(4)e/k_B$.^{57,58}

It is obvious from Figure 6 that there is no detectable difference in $T_g$ for the two systems. Also, the densities of the two different systems are almost indistinguishable ($\rho = 0.95\sigma^{-3}$). Furthermore, the monomer packing, as shown by the radial nonbonded monomer–monomer distribution function $g(r)$ shown in Figure 6b, reveals that the local melt structures are identical. A $T_g$ shift of about 2% as in the initial DSC experiment certainly would have been detected. Also, the different contributions to the energy of the melts are indistinguishable, as revealed by Figure 7 for the bonded (a) and the nonbonded part (b). To observe any detectable deviation, we have to closely look at individual contributions to the energy. Figure 7c shows the temperature dependence of the repulsive part of the bonded interaction along the backbone. Up to a very small shift in absolute value, the shapes are identical all the way up to tiny details. Thus, there are no observable compensation effects from different contributions, which might be affected differently by the presence/lack of entanglement constraints.

■ CONCLUSIONS

In this study, we have compared the glass transition of melts of highly entangled polymers to that of disentangled polymers of the very same molecular weight by three different experimental techniques and computer simulations. Chains in experiments contain about $66M_e$ based on an entanglement molecular weight of $M_e = 16,600$ Da,^{61} while the chain length in our simulation study corresponds to about $36N_e$. Thus, in equilibrium, both systems are in the fully entangled regime. In both, simulations and experiments, great care has been taken to produce films/systems of disentangled SCNPs. For the simulations, this is confirmed by a PPA. From the simulations, we know that the local packing of the monomers in both cases is identical and that we study a sample with a homogeneous density. Thus, in contrast to the experiments, the simulation systems are perfectly characterized. Both a careful analysis of the specific volume during the temperature change and a very detailed analysis of different contributions to the energy do not reveal any change in $T_g$ or of behavior around $T_g$ of any other tested property. For the experimental analysis, this is less obvious. DSC and oscillatory rheology suggest a $T_g$ shift, which is comparable to the difference in $T_g$ between chains of a molecular weight of about $M_e$ and that of...
highly entangled chains. Using eq 1 to compare PS of $M_n = M_g = 16,600$ Da and $M_n = 1.1 \times 10^6$ Da, a difference of approximately 6 K in $T_g$ is expected\textsuperscript{3,7} which is very close to the shift observed in our experimental study. In contrast to the simulation results, such an agreement points to a possible critical role of entanglements in this context. The lower $T_g$ of the disentangled melt of high molecular weight PS SCNPs was very stable and recovered the state of entangled melts only after annealing for 24 h at a temperature of $T = 433$ K, much higher than $T_g$ of PS. The heterogeneous distribution of entanglements makes the relaxation of disentangled melts very slow. This delay originates from the deformation of the heterogeneous network (of entangled and disentangled regions) in the course of relaxation.\textsuperscript{3,7} To shed even more light onto this dichotomy, BLS was performed on the very fi

**METHODOLOGY**

**Electrospraying.** PS was dissolved in varying amounts of DMF and mechanically stirred overnight to prepare the PS in DMF solution with different concentrations of 0.1, 0.5, and 2.3 wt %. The resulting solutions were filled into a syringe and then electrosprayed at 20–25% relative humidity and room temperature onto an aluminum foil support. The diameter of the tip of the needle is 0.8 mm. The distance between the collector and tip is 20 cm. The feeding rate was varied from 0.5 to 1.5 mL/h. The applied voltage was varied from 11 to 19 kV. To prepare SCNPs in larger quantity, a 0.2 wt % PS in DMF solution was electrosprayed.

**Scanning Electron Microscopy.** The electrosprayed samples were collected on aluminum foils during electrospraying process for SEM imaging. The morphology of electrosprayed samples was observed by SEM (Hitachi SU8000, Japan).

**Atomic Force Microscopy.** For AFM, the measurement device (Dimension Icon with ScanAsyst) was operated under tapping mode in air. The cantilever (NanoWorld Tapping Mode AFM Probe, Model: ARRO-NCR) used had a resonant frequency of 285 kHz and a spring constant of 42 N/m. Such cantilevers have reflective aluminum coating on the back side. For AFM, samples were collected on a silicon wafer for 30 s only to avoid multilayer formation of NPs. We further focused on a small area having a monolayer of NPs.

**Differential Scanning Calorimetry.** All DSC experiments were carried out on a 204F1/ASC PhoNix (Netzsch, nitrogen flow of 20 mL/min) at heating and cooling rates of 10 K/min. Only heating cycles are reported.

**Oscillatory Rheology.** Oscillatory rheology experiments were performed using an ARES (TA Instruments). Oscillatory shear deformation was applied with controlled deformation amplitude in the range from 0.02 to 1% such that it was kept in the range of the linear viscoelastic response. Plate–plate geometry was used with a plate diameter of 6 mm. The rheology experiments were carried out on cylindrical pellet samples of PS (one made of bulk PS flakes and other one of SCNPs) with a radius of 3 mm and a thickness of 1 mm. The pellets were prepared by hot-pressing 30 mg of PS at 433 K under 5 kN load. Experiments were performed in a dry nitrogen atmosphere in the temperature range between 363 and 473 K. Oscillatory rheology spectra (values of storage ($G'$) and loss ($G''$) shear modulus as well as loss tangent ($\tan \delta = G''/G'$) as a function of temperature were obtained at a radial frequency $f = 10$ rad/s. The data were obtained at various

![Figure 7. Temperature dependence of the average bonded and bending (a) and nonbonded (b) potential energies per monomer and repulsive part of the bonded potential energy per monomer pairs (c).](https://dx.doi.org/10.1021/acs.macromol.0c00550)
constant temperatures maintained to within ±0.1 K and at a heating/cooling rate of 2 K/min.

**Brillouin Light Spectroscopy.** BLS is a nondestructive technique for probing the thermal density fluctuations of a material by measuring the inelastic scattered light from thermally-activated phonons. The probing wave vector \( q = k_i - k_f \) is defined as the difference between scattering light \( k_i \) and incident light \( k_f \). In the transparent media, such as a PS film, the probing wavevector is selected with the scattering geometry. We used transmission geometry to record the spectra of transparent annealed PS films, where \( q = \frac{4 \pi \sin \theta}{\lambda} \) is independent of the refractive index; \( \lambda = 532 \) nm is the wavelength of incident light, and \( \theta \) is the scattering angle. The BLS spectra consist of a doublet with a Doppler frequency shift with magnitude \( f = \pm c q / 2 \lambda \) at a given \( q \), where \( c \) is the sound velocity in the media. In the turbid media, such as fresh SCNPs, \( q \) is ill-defined because of the strong multiple light scattering. Consequently, the BLS spectrum reveals the resonance modes of the clusters, uniquely defined by the geometric, elastic characteristics, and adhesion of particles. In temperature-controlled BLS experiments, the temperature is monitored with platinum resistance temperature detectors and controlled within ±0.5 K of the set-point value with a custom temperature controller. Samples are isothermally equilibrated at each temperature for at least 20 min before recording a spectrum.

**Simulation.** The polymer chains are described as beads (monomers) connected with springs\(^{37,58,63}\) (the simulation details and model parameters are given in the Section S7). This model reproduces the characteristic non-Arrhenius behavior that the viscosity of polymer melts in the liquid state dramatically increases close to \( T_T \) while the chain conformations only marginally change upon cooling as has been observed for polymers in many experiments. The simulations were performed for both entangled\(^{30,64,65}\) and disentangled\(^{38}\) polymer melt systems with the very same interaction potentials at the same monomer density \( \rho = 0.85 \sigma^{-3} \). Hoover barostat with Langevin thermostat\(^{36,66}\) (implemented in ESPResSo\(^{+}\)\(^{68}\)) was used at constant temperature \( T \) by a stepwise cooling\(^{39}\) and constant pressure \( P = 0.0 c / \sigma^3 \). Each system consisted of 1000 chains of degree of polymerization (chain length) \( N = 1000 \approx 36 N_0 \). Thus, chains in the entangled polymer melt system are highly entangled. The temperature was decreased in steps of \( \Delta T = 0.025 c / k_b \). A relaxation time of \( \Delta t = 30,000 \tau_T \) \((\tau_T = 2.89 \times N^2 \sigma^2 \tau_0 \) being the Rouse-time at the starting temperature \( T = 1.0 c / k_b \)) was allowed between steps. This resulted in a cooling rate of \( \Gamma = \Delta T / \Delta t = 8.3 \times 10^{-7} c / (k_b T) \), which is by far too fast for entanglement effects between chains to become relevant.

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**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.0c00550.

Molecular weight distribution (GPC experiments) of the experimentally studied PS; viscosity, surface tension, and hydrodynamic radius of PS in DMP at different concentrations; TEM images of PS NPs; NMR graphs of PS NPs and NFs; TGA scan of PS NPs and bulk PS; graph showing effects of voltage and infuse-rate on size of PS NPs; simulation model; chain conformations in both entangled and disentangled polymer melts; and the collective structure of melts (PDF)

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**ABBREVIATIONS**

IR, infrared; NMR, nuclear magnetic resonance; UV, ultraviolet
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