Dynamics of ultra-thin polystyrene with and without a (artificial) dead layer studied by resonance enhanced dynamic light scattering

S. D. B. Vianna,^{1,a)} F. Y. Lin,^{1,a)} M. A. Plum,¹ H. Duran,^{1,2} and W. Steffen^{1,b)}

¹Max Planck Institute for Polymer Research, P.O. Box 3148, 55128 Mainz, Germany

²Department of Materials Science and Nanotechnology Engineering, TOBB University of Economics and Technology, Söğütözü Cad. 43, 06560 Ankara, Turkey

(Received 5 December 2016; accepted 1 May 2017; published online 17 May 2017)

Using non-invasive, marker-free resonance enhanced dynamic light scattering, the dynamics of capillary waves on ultrathin polystyrene films' coupling to the viscoelastic and mechanical properties have been studied. The dynamics of ultrathin polymer films is still debated. In particular the question of what influence either the solid substrate and/or the fluid-gas interface has on the dynamics and the mechanical properties of films of glass forming liquids as polymers is in the focus of the present research. As a consequence, e.g., viscosity close to interfaces and thus the average viscosity of very thin films are prone to change. This study is focused on atactic, non-entangled polystyrene thin films on the gold surface. A slow dynamic mode was observed with Vogel-Fulcher-Tammann temperature dependence, slowing down with decreasing film thickness. We tentatively attribute this relaxation mode to overdamped capillary waves because of its temperature dependence and the dispersion with a wave vector which was found. No signs of a more mobile layer at the air/polymer interface or of a "dead layer" at the solid/polymer interface were found. Therefore we investigated the influence of an artificially created dead layer on the capillary wave dynamics by introducing covalently bound polystyrene polymer brushes as anchors. The dynamics was slowed down to a degree more than expected from theoretical work on the increase of density close to the solid liquid interface—instead of a "dead layer" of 2 nm, the interaction seems to extend more than 10 nm into the polymer. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4983487>]

I. INTRODUCTION

The dynamic properties of polymeric melts confined to the nanoscopic dimensions of thin films, be it free standing or supported, have been extensively studied throughout the last 20 years for their fundamental scientific and technological importance.^{1–3} For some classes of materials, such as, e.g., small glass formers and polymers under confinement, deviations from bulk properties have been shown and attributed to the restricted geometry and/or the influence of a free surface^{4,5} or the interphase developing at the interface^{6,7} to a solid substrate. Although enormous theoretical and experimental efforts have been made to reach a concise view of the dynamic behavior of supported and free-standing ultrathin polymeric films, controversial results have been reported.^{8–19} In particular the so-called α -relaxation, related to the glass transition which in polymers is attributed to the reorientational motion of chain segments and therefore to the main chain backbone²⁰ as well as mechanical properties, is in the focus of interest. There is an ongoing discussion whether and to which degree T_g of ultrathin films is influenced by the confinement imposed by the nanoscopic dimensions of the films, the presence of a solid support, or the free-surface. A number of theoretical treatments directed at the physics of thin polymeric films can be found in

the literature^{21–26} connecting cooperative rearranging regions or fragility to the features observed in the glass transition of thin films.

Some studies on polystyrene (PS) and polymethyl methacrylate (PMMA) concluded that ultrathin polymer films have a reduced T_g . It was attributed, among other reasons, to an increased mobility of polymer chains or segments at the free-surface.^{27–29} The thickness of this mobile layer was recently deduced to be between 4 and 7 nm at T_g .⁵ Other researchers came to the conclusion that the relaxation times related to the mobility of the free-surface are Arrhenius-like.^{30,31} This is in contrast to experiments using ultrasensitive differential scanning calorimetry down to a film thickness of ~ 3 nm and to experiments by dielectric spectroscopy, ellipsometry, and AC-calorimetry, in which careful sample preparation, e.g., annealing and handling conditions, was emphasized to avoid side effects which mimic changes in T_g .^{8,32–35} no deviations in T_g were observed in entangled polystyrene.³⁶

Recent results from computer simulation find a difference in density in close proximity to the gold-polystyrene interface in polystyrene.^{6,37–40} This change in density should lead to a change in the relaxation behavior of the α -process and the viscosity. Thus this region of higher density should have a different glass transition temperature leading to a change of the over the film thickness averaged glass transition temperature. A similar result, gradually varying chain packing/orientation states of polyacrylamide thin films spin-coated on gold substrates, was found via polarized reflection-absorption Fourier

^{a)}S. D. B. Vianna and F. Y. Lin contributed equally to this work.

^{b)}Author to whom correspondence should be addressed. Electronic mail: steffen@mpip-mainz.mpg.de

transform infrared spectroscopy (RA-FTIR).⁴¹ An increase of density towards the solid liquid interface was experimentally found by Positron Annihilation Lifetime Spectroscopy (PALS) experiments on PS on gold⁶ and verified by a multiscale computer simulation approach.^{6,37–39}

Our paper describes the results from a dynamic light scattering study utilizing the localized field of surface plasmons as an incident electromagnetic wave by the recently developed marker free method, Resonance Enhanced Dynamic Light Scattering (REDLS).^{42,43} REDLS is sensitive to all regions of films with a thickness of less than about 200 nm (the maximum depends on the combination of refractive indices of the materials⁴⁴). Thus, it enables probing the full range of the solid/polymer/free surface system with 3 different regimes, i.e., the solid-liquid interface, the interior, bulk(like) phase, and the liquid-gas free surface. The experiments reveal a relaxation whose temperature, thickness, and q -dependence agree with those expected for capillary waves at the free surface. The molecular weight dependence of these capillary waves and thus the viscosity from non-entangled to entangled PS are reported. Utilizing a theoretical model for capillary waves in viscoelastic media, the storage shear modulus at different thicknesses of the films is extracted. To enhance the effect of a more dense/dead layer at the solid/liquid interface in the liquid polymer, we grafted PS by introducing thiol as the end-group during the anionic polymerization. This thiol undergoes a covalent bond with gold thus anchoring PS to the gold interface. Subsequently spin coated PS and the effect of the anchor were studied.

II. EXPERIMENT

A. Material and methods

Thin layers of gold on highly polished glass substrates (LaSFN9) have been prepared by thermal evaporation at a constant rate of 0.1 nm/s. To ensure a good adhesion of gold to the glass substrate, a thin layer of chromium (~ 1 nm) was applied beforehand. Immediately after, the polymer was spin coated onto the substrate. The roughness of the gold layer (root mean square, RMS) measured by AFM was smaller than 0.75 nm (area $2.5 \mu\text{m} \times 2.5 \mu\text{m}$). The thickness (h) of the gold film was measured by a profilometer (Tencor P-10) and confirmed by surface plasmon resonance spectroscopy (SPR) to be 47 nm (± 1 nm) in all cases. This is the ideal thickness for the coupling efficiency of the surface plasmon to its resonance at $\lambda = 632.8$ nm and polystyrene as the adlayer.

All polystyrene polymers used in this work were synthesized by anionic polymerization at Max-Planck Institute for Polymer Research. M_w of the main sample, polystyrene (PS2.0), used here is 2.0 kg/mol, PDI = 1.08, and $T_g = 325$ K (DSC, heating rate 1 K/min). M_w of PS (PS-SH) which was modified by a thiol (-SH) group at the end is 3.0 kg/mol, $M_w/M_n = 1.2$. Thin films were prepared by spin coating dilute solutions (from 1% w/w. to 10% w/w) of these low polydispersity polystyrene (PDI ~ 1.05 -1.08) dissolved in toluene (HPLC-grade, Sigma Aldrich). The solutions were filtered through a Millipore Teflon filter (pore size 200 nm). Prior to use, all filters were rinsed with high purity toluene several times to avoid possible impurities and contaminants (as

dust particles or small pieces of Teflon from the filter itself) and dried by blowing filtered and dried nitrogen through it. All the recipients, as well as needles and syringes, were highly clean and dust free. It proved to be necessary to use glass-only syringes in order to avoid common contaminants present in plastic syringes to get into contact with the solution, working as plasticizers and finally decreasing T_g of ultrathin films or inducing dewetting. The same arguments apply to using all-stainless steel needles in order to avoid contamination. The films were spun for 10 min to ensure a good pre-drying, at speeds between 1000 and 5000 rpm depending on the film thickness and molecular weight. To form the thiol-anchor, PS-SH was dissolved in toluene (HPLC-grade, Sigma Aldrich) at a concentration of 1 mM. Then the prepared gold thin film supported by the glass substrate was immersed in the 1 mM PS-SH/toluene solution for 72 h. After 72 h, the substrate with the now covalently attached PS-SH was rinsed with clean toluene 10 times to remove unbound PS-SH. After drying, PS2.0 films were spun onto the thiol anchor. The concentration of PS2.0 for the preparation of the spin coated films had to be adjusted, since for the same spinning conditions films with a thickness 10 nm higher are obtained due to the increased adhesion by the anchor molecules.

After spinning, the films were annealed as follows: The vacuum oven was rinsed several times with dry and filtered nitrogen and then a vacuum of $p < 1$ mbar was applied. Only membrane pumps were used in order to avoid back diffusion of oil to the vacuum chamber. When the vacuum was achieved, the temperature was quasi-statically increased to $T = T_g + 35$ K (heating rate $\ll 1$ K/min to have a quasistatic temperature change) for PS2.0 and $T = T_g + 50$ K for PS of different molecular weights. The samples were kept under these conditions for at least 24 h. The samples were brought back to room temperature under vacuum also quasi-statically to avoid internal stress formation.

As a control experiment, we kept samples at these annealing conditions for increasing lengths of time in order to observe if this produces defects on the sample due to dewetting. No dewetting was observed even after several days under conditions used in the REDLS experiments. It was observed that our films of non-entangled PS2.0 are stable several days even at $T_g + 65$ K, without dewetting.

After annealing, the films were characterized by SPR, REDLS, and AFM. The quality of the ultrathin polymer films can be optically determined by SPR, as well as its thickness. The thickness determined by SPR (assuming the refractive index of bulk PS, $n \sim 1.59$) agreed within the error of ± 1 nm with the profilometer results (Tencor P-10).

The films were characterized by SPR before and after the REDLS experiments (Figure S 1 of the [supplementary material](#)). Any dewetting would result in the shift of the position of the resonance, since the combined refractive index of gold, polymer, and gas would change in such a case.

From AFM measurements (Figure S 1 of the [supplementary material](#)), RMS = 0.37 nm over a range of $2.5 \mu\text{m} \times 2.5 \mu\text{m}$ was determined. Insets in Fig S 1 of the [supplementary material](#) are the surface topography (left) and the phase contrast (right) taken after annealing under the above condition. Thus the initial RMS = 0.75 nm decreased with annealing, indicating

a move towards thermal equilibrium of these films. The AFM measurements (area $0.5 \times 0.5 \mu\text{m}$) of the films with the PS-SH anchor revealed “bumps” of 2 nm in height commensurate with isolated PS-SH chains attached to the surface and the radius of gyration of PS of Mw = 3000 as an isolated, unperturbed coil.

B. REDLS experiment

We used REDLS^{42,43,45,46} (Fig. 1), a non-invasive, marker-free method which allows resolving relaxation processes in the time range from 10^{-6} to 10^3 s, to tackle the open questions about the dynamics of supported ultrathin films. In REDLS, the evanescent part of a surface plasmon (ξ is the penetration depth, i.e., the $1/e$ value of the intensity, of the order of 200 nm) on a thin gold layer is used as the incident field in dynamic light scattering at the proximity of the solid-liquid interface.

The SPR part of the experiment is ultrasensitive to changes in the refractive index, e.g., caused by the changing density because of thermal expansion after changing the temperature of the sample. After performing the SPR experiment, we keep the incident angle of the laser at the resonance angle (for a given temperature). Now the scattered light created in the evanescent light field is collected at a specific scattering angle of the dynamic light scattering detector and correlated to perform the DLS part of the experiment.

The scattering vector is $q = |\mathbf{q}| = |\mathbf{k}_s - \mathbf{k}_i| = (4\pi n/\lambda) \sin(\theta_s/2)$. Here, $\mathbf{k}_i$ and $\mathbf{k}_s$ are the wave vectors of the incident and the scattered beams, n is the refractive index of the polymer, λ is the wavelength of the incident laser beam, θ_s is the scattering angle. In the REDLS experiment with films, instead of q the projection of $\mathbf{q}$ on $\mathbf{k}_i$, $q_{||}$ has to be used. The capillary wave propagates along the surface of the film. Therefore the scattering angle θ_s is an off-plane angle, and $q_{||}$, the

component of the scattering vector q parallel to the substrate plane, has to be used:⁴³ $q_{||} = |\bar{\mathbf{q}}_{||}| = |\bar{\mathbf{q}}| \cdot \cos(\frac{180^\circ - \theta}{2})$.

It is important to note that the REDLS experiment as a heterodyne light scattering experiment directly delivers the field autocorrelation function $G_1(q, t)$, the basis of all theoretical predictions. If the correlation function describes several processes, then the correlation curves sum up to the correlation function measured.

Correlation functions from complex systems give generally functional forms that are not a single exponential decay. Be it the diffusion of polydisperse latex particles in solution or the reorientational dynamics in a glass forming system, all have to be described by a distribution of exponential decays, i.e., a distribution in the relaxation time. One widely used procedure is fitting with the Kohlrausch-Williams-Watts (KWW) function the so-called stretched exponential equation, which has the form

$$G(t) = \alpha e^{(-\frac{t}{\tau})^{\beta_{\text{KWW}}}}, \quad (1)$$

where, $G(t)$ is an arbitrary correlation function (in our case, the heterodyne autocorrelation function $G_1(q, t)$, α is the amplitude of the decay, in our case called contrast ($G(0) - G(\infty)$), τ is the relaxation time, and β_{KWW} is the stretching parameter phenomenologically related to the distribution of relaxation times.

The temperature dependence of the α -relaxation or the viscosity η from the liquid to the glassy state is characterized by a more than exponentially decreasing slowing down of molecular motion. For most non-crystalline polymers, this behavior can be described in terms of a Vogel-Fulcher-Tammann-Hesse function (VFT) which is given by

$$\tau(T) = \tau_0 e^{B/(T-T_0)}. \quad (2)$$

In a heterodyne light scattering experiment, the contrast α is determined by the amount of light quasi-elastically scattered from the sample with respect to the elastically scattered light. The two contributions combine to an interference pattern, the speckle field on the detector, i.e., the single mode fiber selecting one of the speckles as the single mode transmitted through the fiber. An advantage of a heterodyne experiment is the

FIG. 1. Schematics for the REDLS setup: A p-polarized He-Ne laser (wavelength $\lambda = 632.8$ nm) is coupled to a metallic layer (1 nm chromium, 47 nm gold) covering a cylindrical prism. On top of the Au-layer is the polymer film. The beam is kept at the resonance angle Ψ_{sp} , exciting a surface plasmon. At a given temperature and scattering angle θ_s , the scattered light is collected. By rotating the DLS-detector, correlation functions at different scattering angles (θ_s) or scattering vector $q_{||}$ can be obtained. The custom-made sample chamber is filled with filtered, dry nitrogen to avoid polymer degradation by oxidation.

FIG. 2. REDLS experiments on PS2.0 varying temperature (T): T-dependence ((cyan) circle 343 K, (green) down-pointing triangle 349 K, (blue) up-pointing triangle 354 K, (red) diamond 360 K, (grey) right-pointing triangle 372 K, (black) star 389 K) of $G_1(q, t)$ at $\theta_s = 60^\circ$ ($q = 1.57 \times 10^{-2} \text{ nm}^{-1}$), $h = 45$ nm. Black line: baseline of REDLS on bare gold. Red lines: KWW fits with β_{KWW} close to one, i.e., almost single exponential.

FIG. 3. Scattering configuration: (a) thin films ($h < 200$ nm) are completely in the field of the surface plasmons. (b) Thick films ($h \gg 200$ nm) are the contribution of the free surface which can be assumed to be outside of the field of the surface plasmons. (c) Intensity of the correlation function, the exponential decrease (solid line, fit) points to a process at the surface of the film.

enhanced signal-to-noise ratio which, besides the enhanced, local field of the surface plasmon, renders our experiments feasible. Since in our experiment this elastically scattered part depends to some degree on the temperature, Fig. 2, and surface roughness of the substrates and the films, the contrast of $G_1(q, t)$ changes accordingly. To be able to compare the scattered intensity of films of different thicknesses, we compute the so-called total scattered intensity I_{total} by multiplying the experimental contrast with the average scattered intensity ($I_{\text{total}} = a \times I_{\text{average}}$), Fig. 3. I_{average} is the average of the measured intensity during the DLS experiment. This gives us a measure of the scattered intensity from the sample enabling a direct comparison between different samples.

The electric field or the intensity of surface plasmons decays exponentially with distance to the metal interface. In our case, the $1/e$ -value, the so-called penetration depth ξ is in the range of 200 nm. For most of our samples, the polymer film is thus in the localized field. This decay of intensity with distance from the solid surface has implications for the identification of processes detected in the experiment as shown further down.

III. RESULTS AND DISCUSSION

A. REDLS on PS2.0

Non-entangled PS2.0 films with a thickness ranging from 17 to 440 nm were studied by REDLS at different temperatures and scattering angles.

The experimental field autocorrelation function obtained by REDLS, $G_1(q, t)$ (Fig. 2), where t is the lag time, from PS2.0 can be fitted by an exponential function (Eq. (1), $\beta_{\text{KWW}} = 1$). This mode obtained by REDLS is not the primary or α -relaxation as its correlation function would require to be described by a stretched exponential (KWW) function (Eq. (1)) with $\beta \approx 0.4$ as well as to show q independent relaxation times.^{47,48}

The α -relaxation could not be resolved in the thickness range studied. Due to the very low contrast in DLS, a result of the density fluctuations comprised by the reorientational motions of the segments of polystyrene, the signal of the α -process vanishes in the noise of the very strong density fluctuation of the capillary waves at the fluid-gas interface.

Plotting its negative log of the relaxation times obtained from the correlation functions, e.g., from Fig. 1 versus $1000/T$, the observed mode shows a VFT behavior (Fig. 4), similar in shape to the α -relaxation or viscosity in bulk material. As the film thickness decreases, the relaxation times increase.

The detected scattered light can originate at the free-surface, at the interfacial region near the solid support, or at the inner part of the polymer film. We analyzed the total scattering intensity as a function of film thickness. For the mode observed, a logarithmic decrease of intensity with increasing thickness was observed (Fig. 3(c)). This is consistent with the exponentially decreasing light intensity of the surface plasmons with distance from the interface. We conclude that this mode is dominated by a process at the polymer free-surface.

The fact that the fit to $G_1(q, t)$ is a single exponential rather than a stretched exponential, the T dependence, its q -dependence, and in particular the decreasing scattering intensity with film thickness, indicates that the slow-mode is caused by capillary waves.

For a capillary wave, in general, one expects the functional form

$$G_1(q, t) = \alpha \exp \left\{ -\frac{t}{\tau_{\text{CW}}} \right\} \cos \{ \omega t \}, \quad (3)$$

FIG. 4. $-\text{Log}(\tau)$ obtained for the slow-mode versus $1000/T$ for films of different thicknesses. The corresponding, colored lines through the data are theoretical predictions for capillary wave dynamics given by Eq. (9). For comparison, as full black line the α -relaxation of bulk PS2.0 obtained by the rheological experiment is included.

an exponentially damped cosine function which is the Fourier transform of the Stokes and anti-Stokes lines found in frequency dependent studies as resulting from the Doppler-shift of the moving waves. In the completely overdamped case, this reduces to

$$G_1(q, t) = \alpha \exp \left\{ -\frac{t}{\tau_{cw}} \right\}, \quad (4)$$

a single exponential decay.

The decreasing scattering intensity with film thickness is due to the decreasing light intensity of the surface plasmons with increasing distance from the gold-polymer interface. The dynamic behavior, i.e., the spectrum of capillary waves in viscoelastic media of an arbitrary depth was deduced by Jäckle⁴⁹ with a no-slip boundary condition at the solid/liquid interface. The basis of Jäckle's work is the Maxwell model. A more palatable simplification of Jäckle's results was deduced by calculating the surface dynamic susceptibility by solving the equation of motion.⁵⁰ Apart from assuming a solution of monochromatic form $e^{i(kx - \omega t)}$, a constitutive frequency dependent shear modulus^{51,52}

$$G(\omega) = \mu - i\omega\eta, \quad (5)$$

with μ the real and frequency dependent shear modulus and η the dynamic viscosity was introduced. One has to note that here the Kelvin Voigt model is at the base of the constitutive equations. We follow here the simplification and the surface dynamic susceptibility was calculated⁵⁰ to be

$$S(q_{||}) \cong \frac{k_B T}{\left[\gamma q_{||}^2 + 2\mu q_{||} + 3\mu / q_{||}^2 h^3 \right]}. \quad (6)$$

For highly viscous polymeric systems as in our case, i.e., the capillary waves are overdamped, a Lorentzian shape was deduced⁵⁰ with a width as an inverse of the relaxation time

$$\frac{1}{\tau_{cw}} \approx \frac{1}{\tau_0} + \frac{\mu}{\eta}, \quad (7)$$

where

$$\tau_0 = \frac{\eta}{\gamma} \frac{2[\cosh^2(q_{||} \cdot h) + (q_{||} \cdot h)^2]}{\gamma q_{||} [\sinh(q_{||} \cdot h) \cdot \cosh(q_{||} \cdot h) - q_{||} \cdot h]}. \quad (8)$$

τ_{cw} is the relaxation time of height fluctuations from the free-surface of a viscoelastic film with thickness h on a solid surface observed under a scattering vector $\mathbf{q}_{||}$ (the projection of $\mathbf{q}$ on $\mathbf{k}_i$). $\eta(T)$ and $\gamma(T)$ are the viscosity and surface tension, respectively. μ is the storage modulus G' at infinite (or high) frequencies ($G' = \text{Re}(G)$, G is the shear modulus). G' is according to Ref. 53 for very high probing frequencies independent of frequency and polymer liquids exhibit an almost solid response. This leads to

$$\frac{1}{\tau_{cw}} \approx \frac{1}{\tau_0} + \frac{G'}{\eta}. \quad (9)$$

τ_{cw} slows down when decreasing the film thickness. This slowing down is due to hydrodynamic effects close to the solid surface imposed by the non-slip boundary conditions adopted to derive Eqs. (6)–(9).

The $\mathbf{q}$ -dependence of the slow-mode was studied at a constant temperature in all cases (Fig. 5). It can be described by the

FIG. 5. $q_{||}$ -dependence of the slow mode at $T = 389$ K. The lines are theoretical descriptions of capillary wave dynamics given by Eqs. (8) and (9).

theoretical dispersion relations expected for a capillary wave on a viscoelastic medium of arbitrary thickness. As the theory derived by Jäckle considers the projection component of the total $\mathbf{q}$ -vector on $\mathbf{k}_i$, these curves were plotted against $\mathbf{q}_{||}$ (component parallel to the surface).

Eqs. (6)–(9) describe the VFT behavior (Fig. 4) as well as the $\mathbf{q}$ -dependence (Fig. 5) of the capillary waves dynamics as $\tau_{cw} \propto \eta(T)$. $\eta(T)$ and $G'(\omega, T)$ were experimentally obtained from bulk rheology. To obtain $G'(\omega, T)$, we used τ_{cw} as the probing frequency in bulk rheology. $\gamma(T)$ decreases linearly by increasing temperature in our temperature range and its values were obtained from the literature.⁵⁴ Please note that for $q_{||} \rightarrow 0$, $\tau_{cw} \rightarrow \eta/G'$ as the limiting value. For higher $q_{||}$, the functional form is solely determined by the thickness of the film.

Films of an equal height $h = 45$ nm of PS of different molecular weights (Mw) from below to above the entanglement Mw were studied to understand the Mw dependence of the capillary waves. Capillary waves of all films follow the theoretical model with bulk values for the surface tension and the viscosity (Fig. 6).

It was demonstrated by “atomistically informed coarse-grained molecular dynamics simulations”²⁹ that the decrease in free-standing film T_g with respect to bulk is restricted to a few angstrom in thickness and is more significant for

FIG. 6. Capillary wave dynamics in PS of different molecular weights were tested. The theory of capillary waves (solid lines) describes accurately the observed relaxation mode, when bulk values of viscosity, surface tension, and shear modulus are considered.

FIG. 7. (a) Frequency dependence of the storage shear modulus in bulk PS2.0, measured by rheology (black open circles), and in films of different thicknesses (blue open circles) if G' is treated as a fitting parameter and not taken from bulk rheology. The frequency increases with the film thickness (from $h = 25$ nm to $h = 440$ nm, corresponding to the right-hand side picture). A perfect agreement between bulk and thin films is found when the relaxation mode is described by capillary waves dynamics. (b) Thickness-dependence of the storage shear modulus in PS2.0 thin films at $T = 369$ K.

low Mw compared to high Mw systems.²⁹ A decrease of T_g with the thickness of the film is reported from these simulations for PMMA. We had to use for all molecular weights in PS bulk values for viscosity and surface tension in the calculations.

Capillary waves are thermally activated travelling or over-damped surface waves. These waves perform in a sense a dynamic mechanical experiment with the relaxation rate, i.e., the inverse relaxation time (cf. Figs. 4 and 5), of the wave as the frequency of testing. In the true sense of the word, nanorheology is performed. Using Eqs. (6)–(9) and fitting either the q -dependent or the temperature dependent correlation functions according to Jägle's theory G' can be obtained as a fitting parameter. Plotting this G' vs. the testing frequency, the same values are obtained as in a Dynamic Mechanical Spectroscopy (DMS) experiment on bulk PS2.0 (Fig. 7(a)). The thickness dependence is a result of the increasing slowing down of the wave with decreasing thickness of the film. By this the probing frequency at a given set of q and T parameters is changing accordingly.

B. REDLS on PS2.0 anchored by PS-SH

Since we did not detect any influence of a more dense/dead layer for PS2.0 on the gold surface, we enhanced the interaction between the solid surface and polymer by introducing a covalently bound anchor. The anchor consist of PS ($M_w = 3000$) with thiol as one endgroup. Thiol is covalently attached to form a brush layer of PS on the gold solid surface. The first indication the principle works was that, with otherwise unchanged spin coating conditions, the layer thicknesses obtained were about 10 nm higher those obtained without the anchor.

The brush layer obtained was studied by AFM (see Figs. S 3 and S 4 of the [supplementary material](#)) and a sparse brush density was found. The height analysis showed polymer brushes of 2 nm commensurate with the radius of gyration for a corresponding unperturbed chain of $M_w 3000$ PS.

Films with three different thicknesses, h , of the subsequently spin coated film of PS2.0: (black) circle 35 nm, (red) up-pointing triangle 60 nm, and (blue) down-pointing triangle 85 nm were produced in the above-described manner and studied. We found a profound difference in the

FIG. 8. Activation plot—comparison of PS2.0 (thickness of film: (black) circle 35 nm, (red) up-pointing triangle 60 nm, (blue) down-pointing triangle 85 nm) anchored by PS-SH to the solid substrate and α -relaxation (solid line) of PS2.0 from bulk rheology experiments. An Arrhenius process bifurcates from the VFT-like capillary wave at lower temperatures for the 85 nm film. The shift of the bulk line vs. the VFT of the 85 nm film from capillary waves is due to the finite thickness (cf. discussion above) as can be seen from the additionally plotted PS2.0, 60 nm on gold ((green) diamond).

dynamical behavior of these films as depicted in the activation plot in Fig. 8. For comparison, we included (green, solid symbols) the dynamics of the capillary waves at $h = 65$ (directly spin coated on gold) and as a black, solid line the VFT of bulk PS2.0 from dynamic mechanical spectroscopy. Only the

FIG. 9. PS-SH/PS2.0 of $h = 85$ nm. (a) The $q_{||}$ -dependence of the mean relaxation rate Γ at different temperatures: ((black) circle) 366 K, ((red) up-pointing triangle) 378 K, ((blue) square) 389 K, and ((magenta) diamond) 398 K. The solid lines represent least-squares fits based on the capillary wave model⁵⁵ represented by Eq. 3.1. (b) Comparison of viscosities: (circle) from fits of the capillary wave model. The experimental error in viscosity is up to 4%. (c) (black) Square. Effective thickness from fits of the capillary wave model. The red, dashed line represents the real thickness of PS. The error in effective thickness is up to 12%.

TABLE I. Viscosity η of PS-SH/PS85 vs. temperature obtained from the capillary wave model fits in Fig. 9(a). Surface tension γ was taken from Ref. 56. The G' values are from the fit. Please note that for $q_{||} \rightarrow 0$, $\tau_{cw} \rightarrow \eta/G'$ as the limiting value. For higher $q_{||}$, the functional form is solely determined by the thickness of the film.

T (K)	h (nm)	γ (mN/m)	η (Pa s)	G' (Pa)
366	85	35.4	8128.3	1341
378	85	34.5	1127.7	5231
389	85	33.7	155.1	7693
398	85	33.1	40.1	5126

thickest of the films displayed a VFT behavior of capillary waves as expected from an ultrathin film, albeit shifted to slower times and agreeing with the $h = 65$ nm film. The $h = 60$ and $h = 35$ nm films on PS-SH rather follow an Arrhenius behavior. An Arrhenius process bifurcates from the VFT-like capillary wave at lower temperatures for the 85 nm film. This Arrhenius process is reminiscent of the Arrhenius process found by Fakhraei and Forrest^{10,30} studying high molecular weight PS by watching the time dependence of the relaxation of nanoholes. Since the molecular weights between ours and their study are quite different, we refrain from a direct comparison.

To get a better insight into the stronger slowing down of the capillary waves of the PS2.0 films on anchor compared to the PS2.0 films directly on gold, we performed q -dependent experiments. As explained above, the $q_{||}$ part of the scattering vector plays a role. The experiments were performed at four different temperatures, ((black) circle) 366 K, ((red) up-pointing triangle) 378 K, ((blue) square) 389 K, and ((magenta) diamond) 398 K, and are assembled in Fig. 9(a). The solid lines in (a) are fits with the aforementioned model. For a good fit, the fit parameter “effective viscosity” was consistently higher as compared to neat PS2.0 in the bulk (Fig. 9(b), Table I).

Another way to fit (not depicted) is to keep the viscosity at its bulk value and use h , the thickness of the film, as a fit parameter.

Thus we obtained the effective thickness of a PS2.0 film without an anchor.

The anchors strongly changed the mobility of the polymer films. While a PS2.0 film with a height of 85 nm film still shows the expected VFT behavior of the capillary waves apart from an extra Arrhenius process, the thinner films display a completely different relaxation behavior for which there is so far no theoretical explanation.

IV. CONCLUSIONS

Using REDLS, we were able to detect the dynamics of ultrathin polymer films with high precision and sensitivity in the vicinity of a solid surface. With the example of PS on gold substrates, we found the following:

- A relaxation mode showing a VFT behavior with the parameters of viscosity, surface tension, and storage shear modulus of the bulk polymer.
- The mode is located at the free-surface.
- The mode is slowed down by decreasing film thickness due to hydrodynamic coupling with the gold-PS interface.

- The mode can be fitted for its q -, h -, and T -dependence with a capillary wave model including the viscoelastic behavior.

A highly mobile-free surface layer of a considerable thickness compared to the thickness h of the film with, e.g., a Arrhenius behavior should alter substantially the behavior of the capillary waves.

Therefore our experiments on ultrathin films of polystyrene do not support the hypothesis that a more mobile layer of considerable extent exists at the free surface of PS above the glass transition. This is in agreement with the findings in Ref. 5 where a highly mobile layer for $T > T_g$ was not observed, albeit it was observed there for temperatures below T_g , a range inaccessible to us studying capillary waves. This is in disagreement with similar experiments on polybutadiene,⁶ albeit there the measurement temperatures have been very far above T_g while for polystyrene these experiments here were relatively close to T_g . The capillary waves for PS are well described with bulk values of viscosity, shear modulus, and surface tension. If at all this “highly mobile” layer cannot extend beyond the topmost polymer segments in the angstrom range, consider that the amplitude of capillary waves is already in the sub-nanometer scale in the temperature range of our experiments.

Analyzing our experiment in terms of a dynamical mechanic spectroscopy utilizing the thermally activated capillary waves as probes with the rate of the waves as probing frequency, we obtain the values for G' . The values obtained are again the same as those determined by a classical DMS experiment on a bulk sample.

The experiments anchoring PS2.0 with PS-SH, i.e., PS with a thiol group as the endgroup for covalently bonding PS to the gold interface, revealed the high sensitivity of the polymer dynamics for an alteration of the local mobility. The 1-2 nm more dense layer as found in the computer simulations⁶ of PS on gold would not be sufficient to explain this behavior.

SUPPLEMENTARY MATERIAL

See [supplementary material](#) for experimental details about sample preparation including AFM pictures of the surfaces, determination of T_g by SPR, and details about the mechanical spectroscopy on bulk material.

ACKNOWLEDGMENTS

Financial support by DFG within the SPP 1369 “Polymer-Solid Contacts: Interfaces and Interphases” (Project Nos. Ra 796/5 and BU 1556/31-1) is gratefully acknowledged.

¹S. Granick *et al.*, *J. Polym. Sci., Part B: Polym. Phys.* **41**, 2755 (2003).

²S. C. Bae and S. Granick, *Annu. Rev. Phys. Chem.* **58**, 353 (2007).

³H. Huth, A. Minakov, and C. Schick, *J. Polym. Sci., Part B: Polym. Phys.* **44**, 2996 (2006).

⁴C. L. Jackson and G. B. McKenna, *J. Non-Cryst. Solids* **131-133**, 221 (1991).

⁵K. Paeng, R. Richert, and M. D. Ediger, *Soft Matter* **8**, 819 (2012).

⁶H. J. Butt *et al.*, *Macromolecules* **47**, 8459 (2014).

⁷F.-Y. Lin and W. Steffen, *J. Chem. Phys.* **141**, 104903 (2014).

⁸O. K. C. Tsui and T. P. Russell, *Polymer Thin Films* (World Scientific, 2008), p. 267.

⁹A. Raegen *et al.*, *Eur. Phys. J. E: Soft Matter Biol. Phys.* **27**, 375 (2008).

- ¹⁰Z. Fakhraai and J. Forrest, *Phys. Rev. Lett.* **95**, 025701 (2005).
- ¹¹J. Sharp, J. Teichroeb, and J. Forrest, *Eur. Phys. J. E* **15**, 473 (2004).
- ¹²C. Ellison and J. Torkelson, *Nat. Mater.* **2**, 695 (2003).
- ¹³J. Forrest, K. Dalnoki-Veress, and J. Dutcher, *Phys. Rev. E* **56**, 5705 (1997).
- ¹⁴J. Forrest *et al.*, *Phys. Rev. Lett.* **77**, 2002 (1996).
- ¹⁵J. Keddie, R. Jones, and R. Cory, *Europhys. Lett.* **27**, 59 (1994).
- ¹⁶D. Qi, Z. Fakhraai, and J. Forrest, *Phys. Rev. Lett.* **101**, 096101 (2008).
- ¹⁷Z. Fakhraai, S. Valadkhan, and J. Forrest, *Eur. Phys. J. E* **18**, 143 (2005).
- ¹⁸Z. Fakhraai, J. Sharp, and J. Forrest, *J. Polym. Sci., Part B: Polym. Phys.* **42**, 4503 (2004).
- ¹⁹S. Napolitano and M. Wübbenhorst, *J. Phys. Chem. B* **111**, 9197 (2007).
- ²⁰D. A. Savin, G. D. Patterson, and J. R. Stevens, *J. Polym. Sci., Part B: Polym. Phys.* **43**, 1504 (2005).
- ²¹S. Herminghaus, K. Jacobs, and R. Seemann, *Eur. Phys. J. E: Soft Matter Biol. Phys.* **5**, 531 (2001).
- ²²J. Lipson and S. Milner, *Eur. Phys. J. B* **72**, 133 (2009).
- ²³D. Long and F. Lequeux, *Eur. Phys. J. E: Soft Matter Biol. Phys.* **4**, 371 (2001).
- ²⁴S. Mirigian and K. S. Schweizer, *J. Chem. Phys.* **141**, 161103 (2014).
- ²⁵K. Ngai, A. Rizos, and D. Plazek, *J. Non-Cryst. Solids* **235-237**, 435 (1998).
- ²⁶T. Salez *et al.*, preprint [arXiv:1502.01900](https://arxiv.org/abs/1502.01900) (2015).
- ²⁷C. R. Daley *et al.*, *Soft Matter* **8**, 2206 (2012).
- ²⁸S. Ge *et al.*, *Phys. Rev. Lett.* **85**, 2340 (2000).
- ²⁹W. Xia, D. D. Hsu, and S. Ketten, *Macromol. Rapid Commun.* **36**, 1422 (2015).
- ³⁰Z. Fakhraai and J. Forrest, *Science* **319**, 600 (2008).
- ³¹Z. Yang *et al.*, *Science* **328**, 1676 (2010).
- ³²M. Erber *et al.*, *Macromolecules* **43**, 7729 (2010).
- ³³E. Mapesa *et al.*, *Eur. Phys. J.: Spec. Top.* **189**, 173 (2010).
- ³⁴A. Serghei *et al.*, *Phys. Rev. E* **71**, 061801 (2005).
- ³⁵A. Serghei *et al.*, *Macromolecules* **41**, 3636 (2008).
- ³⁶M. Y. Efremov *et al.*, *Phys. Rev. Lett.* **91**, 085703 (2003).
- ³⁷K. Johnston and V. Harmandaris, *Soft Matter* **8**, 6320 (2012).
- ³⁸K. Johnston and V. Harmandaris, *Macromolecules* **46**, 5741 (2013).
- ³⁹K. Johnston and V. Harmandaris, *Soft Matter* **9**, 6696 (2013).
- ⁴⁰M. Y. Efremov *et al.*, *Macromolecules* **37**, 4607 (2004).
- ⁴¹X. Lu and Y. Mi, *Eur. Polym. J.* **63**, 247 (2015).
- ⁴²M. A. Plum *et al.*, *Opt. Express* **17**, 10364 (2009).
- ⁴³M. A. Plum *et al.*, *Rev. Sci. Instrum.* **82**, 015102 (2011).
- ⁴⁴M. A. Plum, Ph.D. dissertation (Johannes Gutenberg-Universität Mainz, 2010).
- ⁴⁵M. A. Plum *et al.*, *New J. Phys.* **12**, 103022 (2010).
- ⁴⁶M. A. Plum *et al.*, *Soft Matter* **7**, 1501 (2011).
- ⁴⁷H. Lee, A. Jamieson, and R. Simha, *Macromolecules* **12**, 329 (1979).
- ⁴⁸G. Patterson, C. Lindsey, and J. Stevens, *J. Chem. Phys.* **70**, 643 (1979).
- ⁴⁹J. Jäcke, *J. Phys.: Condens. Matter* **10**, 7121 (1998).
- ⁵⁰Z. Jiang *et al.*, *Phys. Rev. Lett.* **98**, 227801 (2007).
- ⁵¹J. Harden, H. Pleiner, and P. Pincus, *J. Chem. Phys.* **94**, 5208 (1991).
- ⁵²H. Nakanishi and S. Kubota, *Phys. Rev. E* **58**, 7678 (1998).
- ⁵³M. Rubinstein and R. Colby, *Polymer Physics* (Oxford University Press, New York, 2003).
- ⁵⁴G. T. Dee and B. B. Sauer, *J. Colloid Interface Sci.* **152**, 85 (1992).
- ⁵⁵H. Kim *et al.*, *Phys. Rev. Lett.* **90**, 68302 (2003).
- ⁵⁶D. W. Van Krevelen and K. Te Nijenhuis, *Properties of Polymers: Their Correlation with Chemical Structure; their Numerical Estimation and Prediction from Additive Group Contributions* (Elsevier, 2009).