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Polystyrene with different topologies: Study of the glass transition temperature in confined geometry of thin films

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ABSTRACT

The glass transition behaviour of polystyrene (PS) with systematically varied topologies (linear, star-like and hyperbranched) confined in nanoscalic films was studied by means of spectroscopic *vis*-ellipsometry. All applied PS samples showed no or only a marginal depression in glass transition temperature T_g in the order hyperbranched PS (5 K) > star-like PS (3 K) > linear PS (0 K) for the thinnest films analyzed. The T_g behaviour was accompanied by the observation of the film density in dependence of film thickness. A maximum decreased density of about 7% for hyperbranched PS and 5% for star-like PS and again no deviation in density of bulk was found for linear PS. Accordingly, we deduce from these results considering an experimental accuracy of about ± 2 K for T_g and up to ±3% for film density, that the polymer topology only barely influences T_g in the confinement of thin films.

1. Introduction

Although the physics of bulk polymers have been analyzed extensively, the properties of thin polymer films and surfaces are still rather poorly understood and confront scientists with severe problems [1–7]. One of the major current challenges is to determine why thin polymer films can have a glass transition temperature (T_g) strongly differing from the known bulk T_g. Although this has been studied at length and has been the topic of comprehensive reviews [1–5], no consistent picture has yet been obtained.

For linear polystyrene (PS) a vast number of controversial experimental results are reported. Many scientists support the results of Bahar et al. that the length scale of geometrical confinement is just about three repeat units (polymer segments) [8]. In these studies no altered glass transition was found for PS film thicknesses down to about 5 nm [9–17]. Nonetheless, there is a variety of contradicting results which show a depressed T_g in thin films [18–23].

To the best of our knowledge, in most cases exclusively linear homopolymers like poly(methyl methacrylate) (PMMA) or PS were in the focus of such studies [1–5]. However, other polymer topologies like dendritic macromolecules are likely to exhibit properties very different to their linear counterparts due to their branched, globular structure, their high number and density of functional groups as well as their low viscosity attributable to significantly reduced entanglements [24,25]. Due to the often tedious and complicated preparative synthesis these materials have barely been in the focus of glass transition investigations. Serghei et al. investigated the glassy dynamics of a hyperbranched (hb) aromatic polyester with randomly distributed functional groups (acetyl and hydroxyl) using capacitive scanning dilatometry and broadband dielectric spectroscopy [26]. An increase of about 10 K determined by means of capacitive scanning dilatometry was observed with decreasing length-scale while the temperature position of the alpha relaxation peak was shifted by 30 K to lower temperatures. Remarkably, these deviations from bulk T_g started at an unusual high film thickness

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of about 200 nm. Thereupon, we investigated tailor-made linear and hyperbranched polyesters having polar and non-polar end groups and found that T_g in geometrical confinement may increase or decrease, mainly depending on the nature of functional end groups and hence on interfacial interactions between polymer and substrate [27]. However, a critical point in this article was the tendency of functional groups to crosslink at higher temperatures which has significant influence on the glass transition.

In this contribution, we extend the former studies on systematically varied PS samples ranging from linear to star-like and hyperbranched topologies bearing only inert functional groups. Beside the commercially available linear and star-like PS, tailor-made hyperbranched PS was applied, which was synthesized by means of self condensing vinyl polymerization (SCVP) and subsequent polymer analogous reaction. Temperature dependent spectroscopic *vis*-ellipsometry was used in order to investigate the glass transition temperature of polymer films in the thickness range of 10–400 nm. Furthermore, ellipsometry was used to determine the material density in dependence of film thickness.

2. Experimental

2.1. Materials

Linear and star-like atactic PS with different molecular weights (Table 1) were purchased from PSS (Polymer Standards Service GmbH, Mainz, Germany) and used without further purification. 4-Vinylbenzylchloride ($\geqslant$90%) from Sigma–Aldrich was purified by distillation under reduced pressure and subsequent passing over basic alumina. Toluene and dichloromethane (both Sigma–Aldrich, Chromasolv®, HPLC grade) were used as solvent for film preparation. All other substances and solvents were purchased from commercial sources (Sigma–Aldrich, Fluka or Acros) and used as received.

2.2. Preparation of the hyperbranched PS derivative

The hyperbranched polystyrene derivative was synthesized by self condensing vinyl polymerization (SCVP) under ATRP conditions of the inimer 4-vinylbenzylchloride (Scheme 1) [28].

Three milliliter distilled 4-vinylbenzylchloride (21.3 mmol), 665 mg bipyridine (bpy, 4.3 mmol) and 8 ml chlorobenzene were added to a 25 ml Schlenk flask with rubber septum and magnetic stir bar. The solution was thoroughly degassed by three freeze–pump-thaw cycles. Afterwards 211 mg CuCl (2.1 mmol) were added and the mixture was stirred until a homogenous brown solution was formed. Again the solution was degassed, flushed with argon and heated to 115 °C to start the polymerization. After about 5 h the mixture was quenched to room temperatures dissolved in 20 ml THF and stirred at air to deactivate the copper complex. The reaction mixture was passed over neutral alumina to remove the copper compounds and then precipitated in methanol twice. The product was collected and subsequently dried in vacuum at 45 °C to obtain a slightly yellowish polymer with a yield of 60%.

Table 1
Characteristics of studied PS samples.

Sample	M_w [gmol^{-1}]^a	$M_w/M_n$$^{a)}$	T^∞_g^{b}
Linear PS	27,500	1.04	99 °C
Star-like PS	41,200	1.05	99 °C
Star-like PS	749,000	1.10	103 °C
Hb PS	11,200	3.69	27 °C

[a] Determined by means of SEC-MALLS.
[b] Bulk T_g determined by DSC at 2 Kmin^{-1}.

In order to obtain a hyperbranched PS counterpart all functional chlorine groups were chemically converted into inert hydrogen groups using $LiAlH_4$ as modification agent [28]. The successful modification (>99 %) and the purity of this product were confirmed by NMR spectroscopy measurements (^{1}H NMR (500 MHz, 25 °C, $CDCl_3$) δ (ppm): 7.08, 5.69 & 5.19 (focal group), 3.04–1.92 ^{13}C NMR *(*125.74 MHz, 25 °C, $CDCl_3$, δ (ppm): 143–135, 130–125, 48–32, 21).

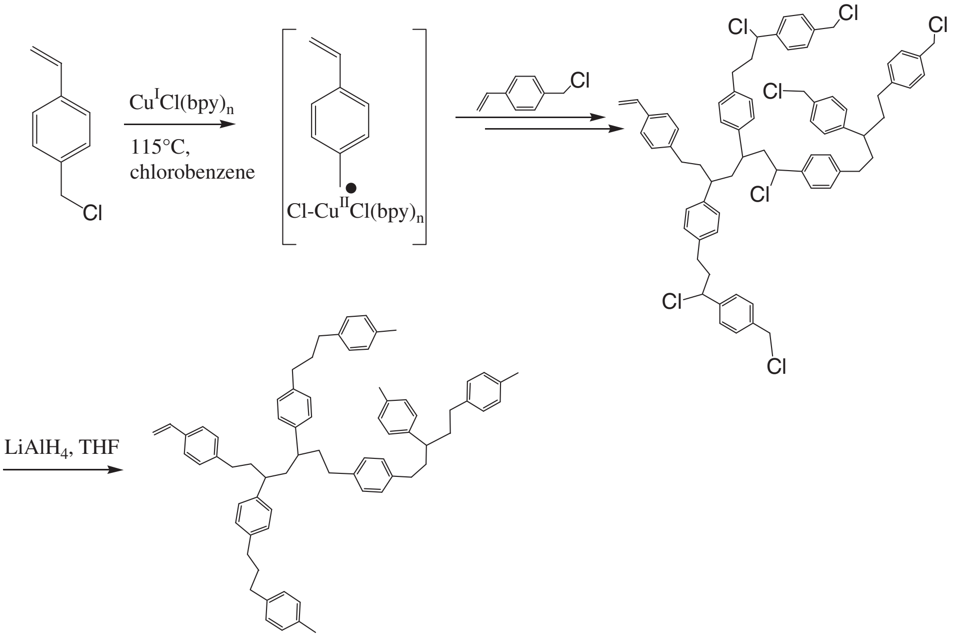
2.3. Film preparation

Highly polished silicon wafers with a native oxide layer ($d \sim 2$ nm) were used as substrates for film preparation. Any inhomogeneities (*e.g.* dust particles or organic contaminations) were thoroughly removed in an ultrasonic bath first in dichloromethane and afterwards in acetone. In an additional step, the substrates were placed in an alkaline hydroperoxide solution mixture (Milli-Q® ultrapure water (resistivity: 18.2 MΩ cm at 25 °C), hydrogen peroxide (30%) and ammonia solution (25%), in the volume ratio 5:1:0.05) for 20 min resulting in hydrophilic surfaces with a static water contact angle below 10°. The substrates were carefully rinsed in ultrapure water and directly used. The root mean square roughness (rms) of the silicon surfaces was around 0.3 nm as examined by AFM. All films were prepared by spin-coating at moderate spinning speed (3000 rpm) and spinning time (30 s) from differently concentrated solutions (toluene for linear and star-like PS, dichloromethane for hb PS).

The quality of all applied polymer films was carefully checked by optical microscopy and AFM before and after annealing, guaranteeing that the samples were neither dewetted nor inhomogeneous. The rms values for all investigated polymer films were below 1 nm (Fig. 1).

2.4. Spectroscopic vis-ellipsometry

In general, ellipsometry measures a change in polarization of polarized light that is reflected from a bare surface or a thin film. The polarization change is represented as amplitude ratio ($\tan\Psi$) and phase difference (Δ). The measured response is dependent on optical properties (refractive index n, extinction coefficient k) and the thickness d of each film. Further details on ellipsometric fundamentals are given in the references [29]. Temperature dependent spectroscopic ellipsometry measurements were carried out at a fixed angle of incidence (70°) using a multi-wavelength (370–1680 nm) rotating compensator ellipsometer (RCE) M2000VI (J.A. Woollam Co., Inc., USA) connected with a heat cell (INSTEC Inc., USA). The real temperature



Scheme 1. Synthetic approach towards a fully hydrogen terminated hyperbranched polystyrene derivative.

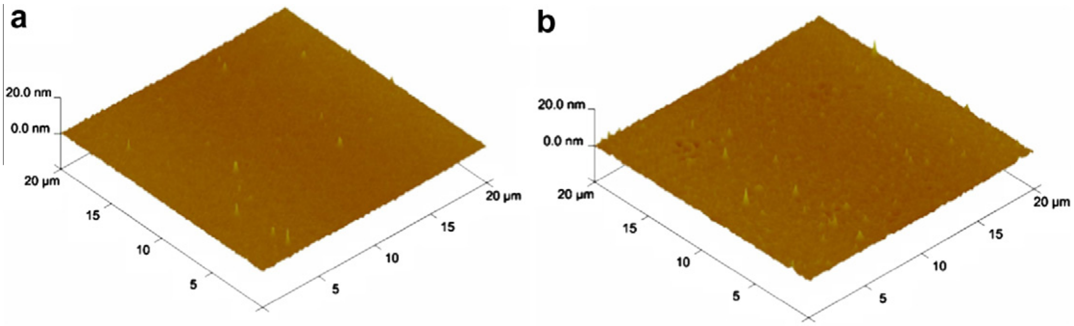


Fig. 1. Twenty by 20 μm^2 AFM pictures of the surface of a 12 nm thin hyperbranched PS film on a silicon wafer as-prepared (a) and after annealing (at 80 °C for 15 h in argon ambience) (b) with a root mean square roughness of 0.5 and 0.6 nm, respectively.

on the surface of a silicon wafer was checked in a separate experiment by different melt transition standards from Perkin Elmer (Sn, Pb, In, Zn) commonly used for calorimetry. The standards were melted to the wafer surface at appropriate temperature, then cooled, and reheated to record the melt transition and corresponding thermometer reading. By visually observing the consecutive melting points for the compounds at a ramp of 2 K/min, the temperature was checked within an accuracy of ±1 K in the temperature range (300–690 K).

All polymer films were thoroughly annealed *in situ* under defined ambience (Ar) for at least 15 h well above T_g and the boiling point of the applied solvent (linear, star-like PS at 130 °C, hb PS at 80 °C). In order to obtain fully equilibrated polymer films the measured data were continuously monitored until sample stability was reached. Immediately after annealing, the measurements for T_g determination were commenced at moderate scan rates of about 2 K/min without exposing the samples to ambient air again, preventing any water take-up or other ascendancies.

The layer thickness d and the refractive index n were fitted to the ellipsometric angles Ψ and Δ measured in the entire wavelength range applying the layer stack Si/SiO_2/polymer/ambient as optical model. The extinction coefficient k of all applied polymers was checked to be zero in the used wavelength range. Values of the optical constants of the applied substrates (Si, SiO_2) were taken from the literature [30]. A Cauchy dispersion for the wavelength dependence of the polymer refractive index n was assumed. It should be noted that changes in the optical properties of the substrate (Si) with temperature can have significant impact on the thickness accuracy of thin films [31]. Therefore, temperature dependent data from the software (Complete EASE™) [30] were used in which the optical properties of Si are stored as a function of temperature.

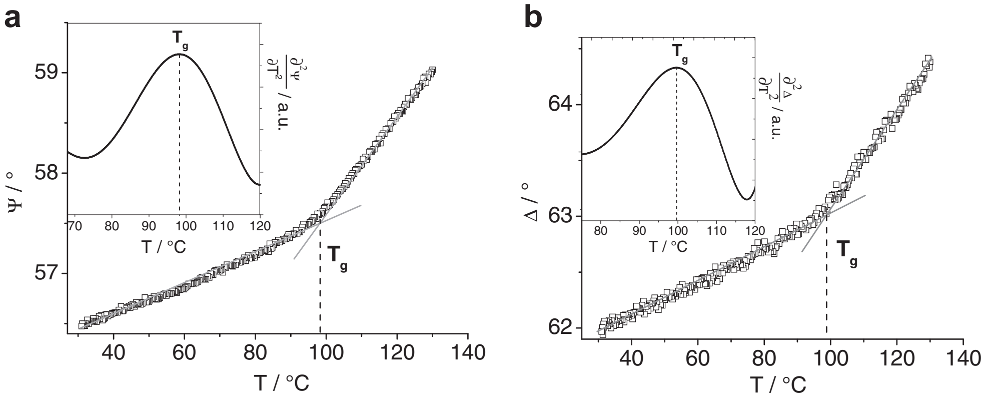


Fig. 2. Ellipsometric angles ψ(a) and Δ(b) as function of temperature for a 118 nm thin linear PS film at a wavelength λ of 700 nm. The gray lines are a guide to the eye to illustrate the two linear regimes (glassy and rubbery) whose intersection point indicates the glass transition temperature T_g. The insets show the second derivatives of the interpolated data, the respective maxima indicate T_g.

The temperature position of the discontinuity (commonly referred to as "kink") in either $\psi(T)$ or $\Delta(T)$ (Fig. 2) and $d(T)$ or $n(T)$, respectively is known to occur at the ellipsometric glass transition temperature. For improved accuracy [27], the extrema of the interpolated curves of the second derivatives $\partial\psi^2/\partial T^2$ and $\partial\Delta^2/\partial T^2$ (or $\partial d^2/\partial T^2$, $\partial n^2/\partial T^2$) were used to determine T_g.

Interpolation was done by applying a 9th order polynomial fit.

To check the reproducibility of our results several heating and cooling cycles were carried out on the samples after annealing and the data was recorded as shown in Fig. 3. As can be seen in the aforementioned figure, good reproducibility of results is ascertained and the T_g values obtained consistently lie within an experimental accuracy of ±2 K.

3. Results and discussion

Systematically varied polystyrene samples with linear, star-like and hyperbranched topologies were investigated in terms of glass transition temperature in confined geometry of thin films. All ellipsometric measurements show a clear discontinuity ("kink") in the investigated temperature dependency of the layer thickness due to the transition from the glassy to the rubbery state, also referred as to glass transition temperature T_g (Fig. 4).

Fig. 5 summarizes the experimental results for all three polymer topologies (linear, star-like and hyperbranched). Within the experimental accuracy of ±2 K no altered T_g for thin linear PS films with a molecular weight of 27,500 $\mathrm{g\,mol^{-1}}$ is ascertained down to 26 nm. Thinner PS films were not stable due to dewetting phenomenon and hence not investigated in this study.

Beside the linear PS samples two star-like PS counterparts with different molecular weights (41,200 $\mathrm{g\,mol^{-1}}$ and 749,000 $\mathrm{g\,mol^{-1}}$) were investigated. The lower molecular weight star-like sample shows a maximum T_g depression of about 3 K at 11 nm, whereas the higher molecular weight equivalent shows a depression of about 2 K at 10 nm. Therefore it can be concluded that no significant molecular weight effect on T_g in dependence of layer thick-

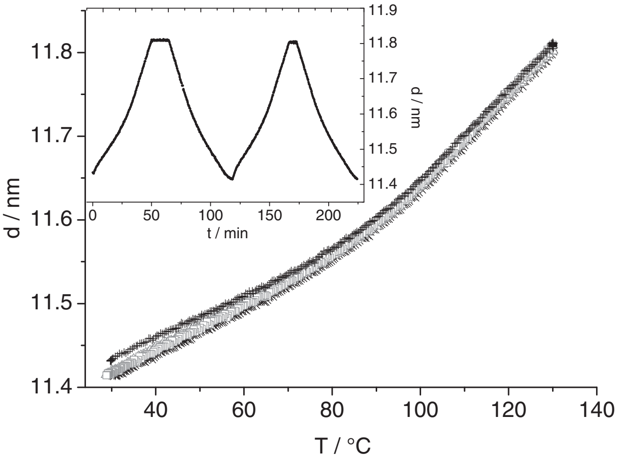


Fig. 3. Film thickness d of a 11 nm thin star-like PS sample during several heating and cooling cycles. In the inset the corresponding time dependency of d is plotted. The coincidence of the curves proves the good reproducibility of the measurements.

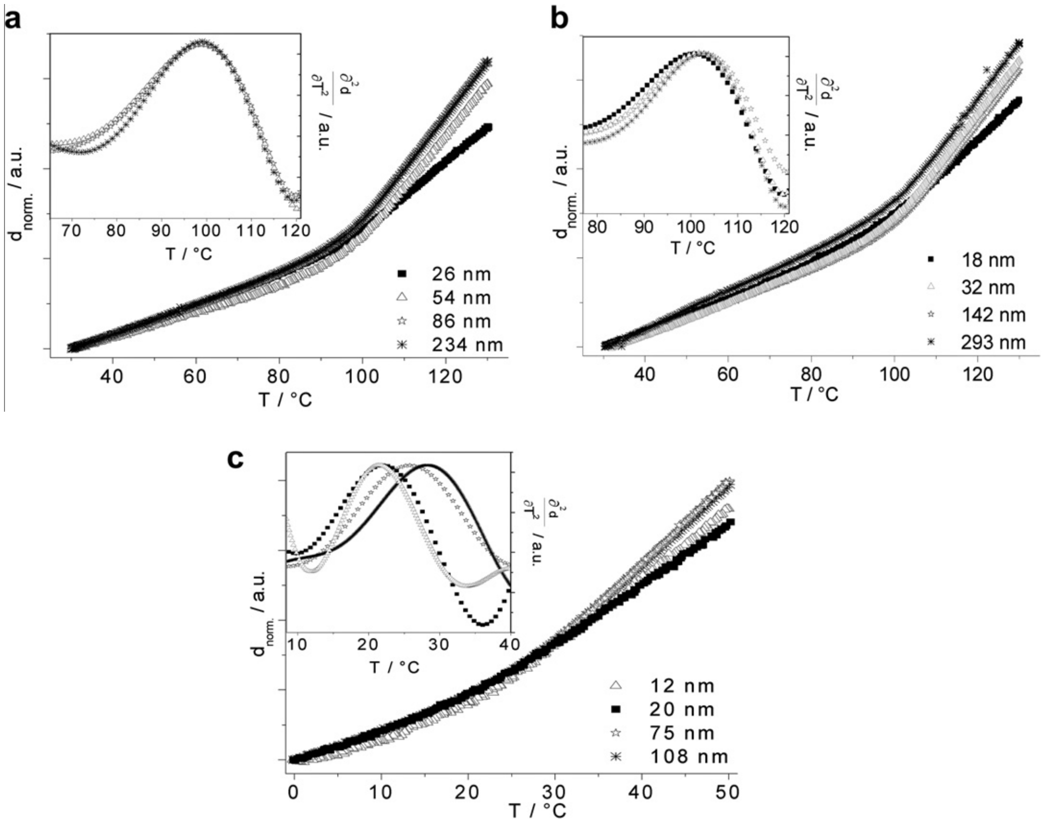


Fig. 4. Temperature dependency of normalized thickness $d_{norm.}$ (d/d_0) for all investigated topologies: linear (a), star-like (319,000 g/mol) (b) and hyperbranched (c) PS. The inset shows the corresponding second derivative of the interpolated *d(T)*-curve. For reasons of clarity only four representative measurement curves are shown for each topology.

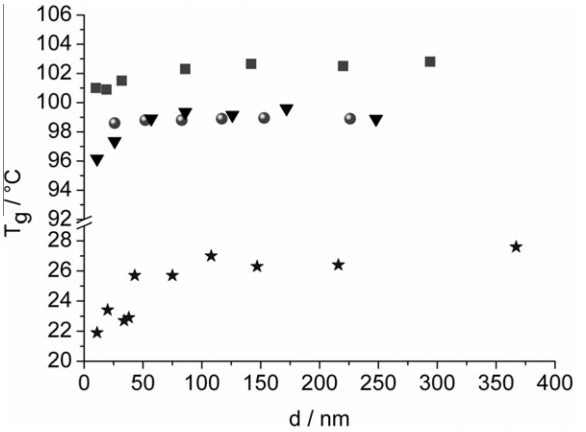


Fig. 5. T_g as a function of film thickness for different PS topologies (hyperbranched PS (stars); linear PS (circles); star-like PS with a molecular weight of 41,200 gmol^{-1} (triangles) and with a molecular weight of 749,000 gmol^{-1} (squares).

ness could be determined within the experimental accuracy. The offset of the bulk T_g of about 4 K, which was examined by ellipsometry for the thickest samples and coincides with the calorimetric bulk T_g (Table 1), is attributed to the well known molecular weight dependence of the bulk T_g [32].

For the hyperbranched PS sample a maximum T_g deviation of about 5 K was found for the thinnest film (11 nm) analyzed (Fig. 5).

Taking into account the results found in this study and an experimental accuracy of about ±2 K we deduce that the polymer topology only marginally influences the glass transition in geometrical confinement.

A vast number of controversial results on the glass transition of linear PS exist in literature [6,18–23,33]. However, in many recent articles no altered bulk glass transition is reported [12,13,16,33,34]. There are several known experimental and preparative ascendancies that may lead to pronounced deviations in the glass transition of polymers. For example the presence of plasticizers, metastable states by means of residual stresses, thermal history, degradation, experimental ambience and chemical side reactions, to name but a few [6,35].

On the other hand, Raegen et al. recently reported on PS samples annealed at 423 K that the glass transition in thin films is not altered due to the selection of ambiance (air, nitrogen and vacuum) during annealing [23]. In this case, the samples were annealed in the respective ambient for only 1 h. Perlich et al. again showed that proper annealing procedures are crucial to remove all solvent residues applied for film preparation. Even annealing of PS films at 160 °C (well above T_g) for 8 h was not sufficient to remove all solvent traces [36]. It is obvious, that solvent traces in thin films may act as plasticizer and possibly mimic confinement effects.

On this account, a proper annealing procedure (temperature well above T_g for at least 15 h in inert and humidity-free atmosphere (*e.g.* Ar), as applied in our studies) is absolutely mandatory.

Another crucial point in this regard is that during film preparation or heat-treatment a polymer film may rupture triggered by inhomogeneities (nucleated dewetting). However, an influence of this phenomenon on the measured values is to our best knowledge not known. In Fig. 6 this aspect and its influence on the obtained T_g is shown. No changes in the shape of the measured curves (neither in *Ψ(T)* and *Δ(T)* nor *d(T)* and *n(T)*) were observed for a ruptured thin PS film in comparison to an analogous homogenous PS film which could have revealed that dewetting has taken place. However, the ellipsometrically determined T_g is about 6 K below the T_g determined for an analogous homogenous PS film. This implies that the fact that the film was ruptured can only be revealed using microscopic techniques like AFM or light microscopy. In that case the film was homogeneous after preparation and started to break during heat-treatment. This example shows that it is essential to carry out the measurements on homogeneous polymer films to avoid artefactual mechanisms that could mimic confinement effects. On this account, all studied films were thoroughly checked to get reliable results.

The reasons for a depressed T_g are controversially discussed in literature [1–5]. Reiter suggested that the shift

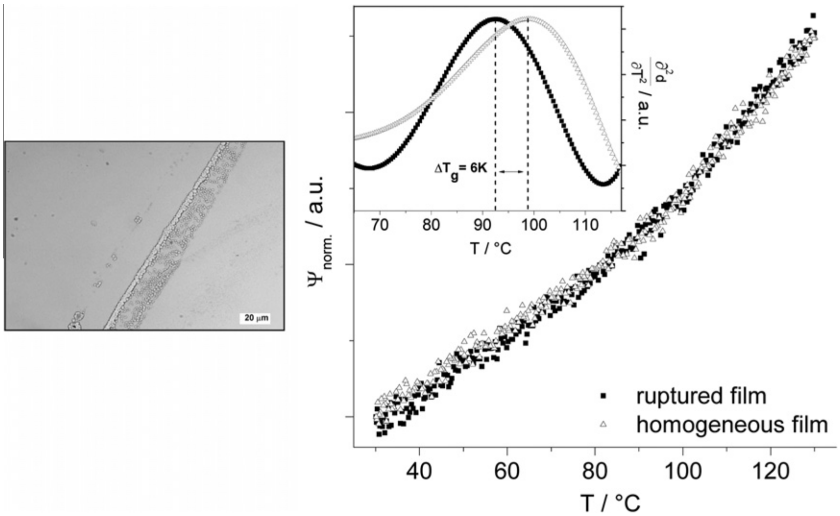


Fig. 6. Optical microscope image of a ruptured linear PS film (*left*) and the comparison of the ellipsometrical angle *Ψ* as function of temperature for the aforementioned ruptured and a respective homogenous thin (25 nm for both) PS film (*right*). The inset shows the corresponding second derivative of both curves.

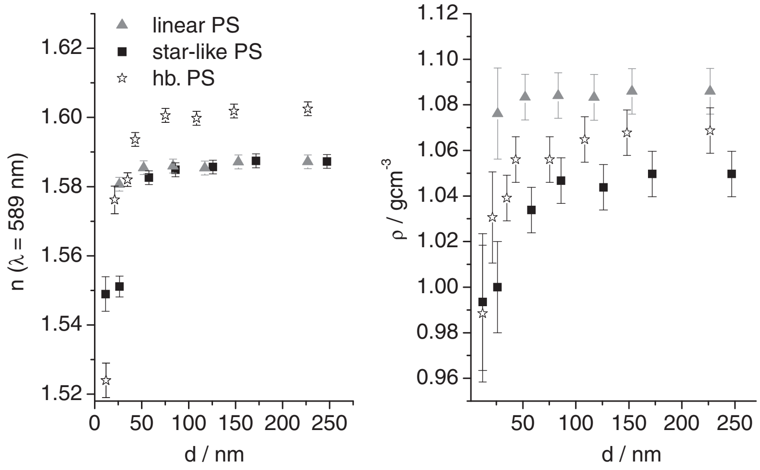


Fig. 7. Refractive index *n* (*left*) and corresponding film density *ρ* (*right*) in dependence of film thickness *d* for different PS topologies (linear, star-like (M_w: 41,200 gmol^{-1}) and hyperbranched) determined by ellipsometry.

of T_g to lower values is due to a decrease in density of thin PS films [37]. On the basis of the latter assumption the film density ρ at room temperature is calculated using the ellipsometrically determined refractive index n ($\lambda = 589$ nm) and the well-known Lorentz–Lorenz equation [38]:

$$\frac{1}{\rho} = \frac{n^2+2}{n^2-2} \cdot \frac{R_M}{M} \qquad (1)$$

where R_M is the theoretical molar refraction (at $\lambda = 589$ nm) of the polymer calculated according to the tabulated values [39]; M is the molar mass of the repeating unit. Fig. 7 summarizes the results of this evaluation for all investigated PS topologies.

A maximum decrease in film density of about 7 % and 5% could be determined for the thinnest hyperbranched (12 nm) and star-like (12 nm) PS films, respectively. However, down to 26 nm no deviation from bulk density was found for linear PS samples. Taking into consideration an experimental accuracy of up to ±3% the analyzed density aberration is not significant.

Wallace and co-workers have performed neutron reflectivity measurements to determine the density of thin (down to 6.5 nm) linear PS samples [40]. Their results coincide with the results found here; within the experimental accuracy of up to ±4% no significant altered bulk density was found.

4. Conclusion

The glass transition in confined geometry of systematically varied PS topologies (linear, star-like and hyperbranched) was investigated for the first time by means of spectroscopic *vis*-ellipsometry. In order to get robust results all studied PS samples were thoroughly annealed well above T_g for at least 15 h in inert ambience. For all PS topologies, no or only a marginal T_g depression in the order hb PS (5 K) > star-like PS (3 K) > linear PS (0 K) was determined for the thinnest films analyzed.

This T_g depression is accompanied by an altered film density in dependence of film thickness. A maximum decreased density of 5% for star-like and 4% for hyperbranched PS films as thin as about 12 nm was found. For thin (~26 nm) linear PS films no deviation from the bulk density was obtained similar to Wallace et al. [40].

In regard of these results and the experimental accuracy we assume that the polymer topology only barely influences the glass transition and film density, in the confinement of thin films.

Acknowledgments

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