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The Gel-like Structure of Polymer in Thin Films: An Explanation of the Thickness Dependent Glass Transition?

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Summary: The understanding of the origin of the thickness (*h*) dependent glass transition temperature, $T_g(h)$, reported over the last decade for supported and freely standing thin polymer films, is still unclear. Indeed, the spin-coating process, the interfacial adsorption as well as the freezing-in of non-equilibrated chain conformations and orientations caused by fast solvent evaporation could result in partially disentangled chains which can be depicted as a gel-like structure. The effect of PMMA stereoregularity on the chain conformation and orientation and its persistence length in thin films is discussed. Moreover, striking evolutions of $T_g(h)$ by changing the nature of the solvent support the assumption of a specific organisation of the chains in thin films which can hold over thickness far above *R*g.

Keywords: conformation; orientation; PMMA; stereoregular polymers; thin films

Introduction

From many studies over the last ten years it has been observed that the glass transition temperature of thin polymer films, $T_g(h)$, differs from that of the bulk polymer, T_g(bulk). Beaucage et al. and Keddie et al[1,2] were the first who carried out extended studies of that phenomenon by using ellipsometry on polystyrene (PS) films of thickness less than 40 nm which exhibited a $T_g(h) < T_g$(bulk). Other works[3-5] have reported that the modification of the glass transition temperature is influenced by the surface treatment which leads to silanized, SiO_x or Si-H silicon surfaces. Freely standing PS films[6-7] have been used as a route to achieve thin films which are not directly influenced by the presence of a substrate during the $T_g(h)$ measurement.

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From the literature it turns out that no fully accepted theoretical concept is yet available to explain the evolution of $T_g(h)$ for thin polymer films on solid surfaces and which takes polymer-surface interactions into account. $T_g(h)$ of polymers such as PMMA, poly(2-vinyl pyridine) or poly(vinyl chloride) (PVC)[2,8-10] has also been investigated for supported thin films. These polymers are known to develop rather strong attractive interactions with the SiO_x surface (e.g. on silicon wafers). For all these polymers an increase of $T_g(h)$ with decreasing h is claimed. Therefore, a generally accepted conclusion drawn from these results, is that the evolution of $T_g(h)$ towards higher or lower temperature than the bulk T_g is directly related to the strength of the interfacial interactions. In our recent two last publications[8,10] we have emphasized exceptions to this rule which highlighted that this view is perhaps too simplistic. A restriction to enthalpic considerations neglects other possible causes for the observed $T_g(h)$ dependences in supported thin films.

In this paper, we present our most recent experimental results on $T_g(h)$ of supported thin films, studied by using ellipsometry at variable temperature. The influence of several factors such as polymer microstructure, conditions of film preparation, and chain conformation and orientation on $T_g(h)$ is addressed.

Experimental

Stereoregular PMMA used has been purchased from Polymer Source Inc., Canada. The PMMA samples containing i) 97 % isotactic triads, ii) 55% syndiotactic triads and iii) 80% syndiotactic triads are called *i*-PMMA, *a*-PMMA and *s*-PMMA, respectively. Molecular weights were 35 kg/mol and polydisperisty about 1.05. These polymers were spin cast from dilute solutions on (111) silicon wafers. The substrates were treated during at least 2 h in an UV-ozone chamber prior to polymer deposition. The desired thickness of the polymer films (20 to 150 nm) was achieved by varying the concentration of the solution (5 to 40 g/L). The spin coated samples were studied after they were annealed at T_g(bulk) + 70°C, for at least 24 h and cooled to room temperature at a constant rate.

We used a FT-IR spectrometer (Bruker IFS-66) equipped with a mercury-cadmium-telluride (MCT) detector. Experiments were performed with a Specac specular reflectance element used in polarized reflection-absorption mode (RAIR). The incidence angle is varied from 20 to 82°. The experimental reflectivity is measured at each incidence angle and compared to the theoretic reflectivity obtained from the Kramers-Kronig equations. According to the methodology developed in reference,[11] the ratio of these two reflectivities obtained at different angles of incidence allows the calculation of the orientation of the backbone chain axis as well as the persistence length of the orientation in the thin film. Other FT-IR experiments were performed with a Specac attenuated total reflectance (ATR) device equipped with a heating cell working in the temperature range of 25 to 160 °C. The methodology was developed by O'Reilly et al[12] for their calculations of the conformational energies ΔE of bulk stereoregular PMMA. The ATR spectrum, recorded at 25 °C, was subtracted from the spectra recorded at higher temperatures. The exact methodology for the calculation of ΔE in bulk and thin films is detailed in reference.[13]

Spectroscopic ellipsometry experiments were performed by using a Sopra ES4M apparatus working in the wavelength range from 0.4 to 0.8 μm, equipped with a hot-stage allowing for a variable heating rate. The so-called kinetic ellipsometric scans were performed at a heating rate of 2 °C/min. The experimental data points allowed to identify two temperature ranges represented by two intersecting lines of different slopes.

Results and Discussion

Since the works of Karasz et al.[14] it is well known that in the bulk PMMA stereoisomers show a large difference in T_g(bulk), ranging between 40 and 130°C for *i*-PMMA and s-PMMA, respectively. It is worth noting that the origin of this discrepancy in T_g(bulk), usually related to structural parameters, is still not fully understood. As shown in Figure 1, the $T_g(h)$ of thin films of isotactic PMMA increased significantly for thickness lower than 50 nm whereas a decrease of the $T_g(h)$ was observed for the syndiotactic PMMA. The largest film thickness for which a non-zero ΔT_g value could be detected corresponds to about 8 R_g for the polymers under investigation. For all PMMA samples, $T_g(h)$ of the thinnest layers seemed to tend to the same unique value, $T_g(h)^*$, of 100 ± 5°C, independent of tacticity. It is worth mentioning that this value corresponds roughly to the bulk T_g of the atactic PMMA. For films thinner than 20 nm, microscopic full thickness holes, as observed by optical microscopy, prevented us from any accurate determination of $T_g(h)$ by ellipsometry, also complicated by light scattering effects. Therefore, no evidence can be provided that this limiting value $T_g(h)^*$ holds also for $h < 20$ nm.

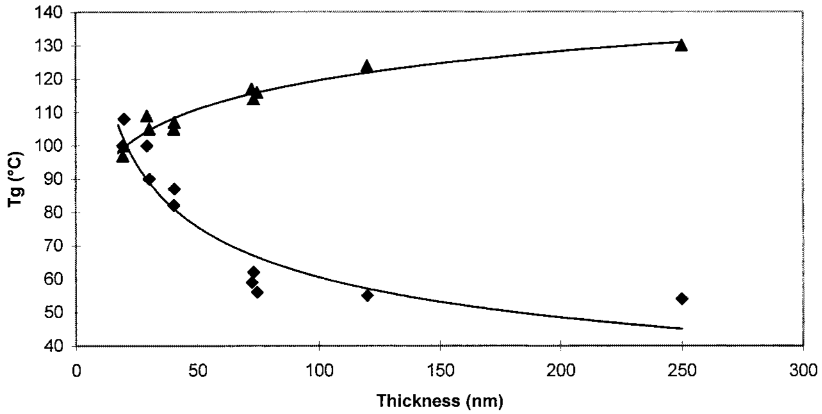

Fig. 1. Evolution of $T_g(h)$ as a function of the thickness of stereoregular PMMA thin films investigated by variable temperature ellipsometry. ▲ corresponds to *s*-PMMA and ◆ represents *i*-PMMA.

Chain Conformation and Orientation in Thin Films

The conformational energies ΔE calculated from ATR spectra on the carbonyl absorption band obtained at variable temperature are listed in Table 1. Although the carbonyl group belongs to the side-chain, its environment is modified by conformational rearrangements occurring in both, the side-chain and the backbone. It is observed that the conformational energy of PMMA thin films is always higher than its bulk value.

Table 1. Conformational energies ΔE of bulk and thin films of stereoregular PMMA calculated for temperatures $T > T_g$ from the carbonyl peak observed by infrared measurements. The values in round brackets are taken from reference.[12]

Thickness (nm)	ΔE: *i*-PMMA (cal/mol)	ΔE: *s*-PMMA (cal/mol)
25	1729 ± 304	2733 ± 320
45	1711 ± 221	2023 ± 114
75	1506 ± 252	1657 ± 280
PMMA (bulk)	471 ± 95 (680 ± 20)	879 ± 64 (1227 ± 115)

This trend was ascribed to an increase of the population of trans conformers in a thin film. Moreover, the increase of ΔE was found to be higher for *s*-PMMA than for *i*-PMMA, in agreement with our results obtained from ATR measurements. This can be taken as evidence for more pronounced conformational rearrangements occurring in thin films compared to the bulk of these polymers. Moreover, rearrangements are more relevant in *s*-PMMA films compared to *i*-PMMA films. *s*-PMMA seems to be more sensitive to confinement effects or/and to interfacial interactions.

This increase in trans conformation of polymer in contact with surfaces has already been reported for PMMA adsorbed on alumina powder[15] and ascribed to the strong interactions involved in this system. However, Brulet et al.[16] also claimed that the persistence length of PS is significantly increased in ultrathin supported film which is consistent with an increase of the population of trans conformers. In the former case adsorption effects seem to be predominant on the modifications of conformation of polymer chains, whereas in the latter case, other effects such as confinement or fast drying might be responsible for the conformational rearrangements. As shown in Table 1, conformational modifications are more pronounced for low thickness but it is difficult to draw from these results any conclusion on the relevance of layer models. This model is based on the intuitive assumption that the chains directly in contact with the surface are highly perturbed in their conformation and mobility, whereas the other are in their unperturbed bulk-like state. Another model accounts for a distortion of the chains directly connected to the interface but with the possibility of a thickness persistence of the perturbation by a mechanism which has to be elucidated.

In order to partially answer to this question, RAIR experiments were conducted at different incidence angles which allow the determination of the average chain orientation in the thin films by using the infrared absorbtion peak $\upsilon_a(CH_2)$ at 2916 cm^{-1}. This vibration mode is parallel to the chain backbone axis. The average orientation angle $<\varphi>$ in a 22 nm film is 48° and 52° for *i*-PMMA and *s*-PMMA, respectively. These angles are not far from 54.7° which represents the isotropic angle corresponding to the totally randomly oriented chains. However, if the layer model drawn in reference[11] is used, the orientation of the layer close to the silicon surface can be obtained, as well as the persistence length of the orientation.

The results given in Table 2 show that the orientation of the chain backbone axis differs with the PMMA tacticity. As claimed in a previous paper,[17] the *i*-PMMA chains are predominately oriented parallel to the surface whereas the *s*-PMMA chains are mainly oblique with respect to the surface plane. This is due to the stereospecific preferential adsorption of isotactic sequences at the surface of silica.[18] The calculated orientation persistence length provides fruitful information on the structure of the thin film since this length is in the order of magnitude of the radius of gyration of the PMMA chains. The idea of a perturbed layer of thickness equivalent to only one chain dimension is consistent with many fundamental works.[19] However, this result is enable to explain why the $T_g(h)$ can be modified for thickness ranging from 8 to 10 times R_g. Therefore, some influence of the conditions of preparation of the thin film cannot be ruled out either.

Table 2. Orientation and persistence length in thin films of stereoregular PMMA determined form RAIR experiments.

Polymer	Thickness (nm)	Orientation (°/Surface)	Persistence length (nm)
i-PMMA	22	16	8.7
s-PMMA	26	68	10.1

Influence of the Solvent

We have also investigated, by combining DSC and thermogravimetric analysis (TGA), the solvent induced glass transition of bulk *i*-PMMA and *s*-PMMA. Similar studies were already performed by Chow and by Vrentas and Vrentas.[20,21] At a given temperature, e.g., 20 °C, i.e., room temperature, the critical solvent fraction, $\phi_{c,}$ at which the system becomes glassy, is 0.25 and 0.30 for the *i*-PMMA and *s*-PMMA, respectively. This factor alone cannot account for the different behavior of these two stereoisomers in thin layers, that has been reported previously. However, if T_g of the polymer/solvent blend is normalized by T_g of the pure bulk polymer, T_g(bulk) and plotted as a function of the solvent volume fraction, ϕ, this so normalized value exhibited a constant decrease for *i*-PMMA with increase of solvent content, whereas it tended to level off for $\phi > 0.4$ *for s*-PMMA as shown in Figure 2.

The evolution of the polymer microstructure dependent $T_g(h)$ may be related to the spin-coating deposition mode. Reiter and de Gennes[22] have recently proposed a scenario which attempts to describe the processes which take place during thin film formation by spin-coating. In that paper, the authors suggested that at a given solvent concentration ψ_c the system freezes which could yield a so-called transient network providing unexpected thermal expansion properties to the thin films. This ϕ_c -value is related to the thermodynamic polymer solvent interaction parameter, χ, of the solvent as claimed by Leibler et al.[23] Therefore, this parameter might be assumed to be a relevant factor affecting $T_g(h)$. The solvent induced T_g studied by DSC on bulk stereoregular PMMA/chloroform systems has highlighted an unexpected behavior of the syndiotactic isomer. Indeed, T_g of s-PMMA is higher than of *i*-PMMA for high solvent content. This result might be explained by the formation of some kind of physical network where the chains can be connected through the solvent in a so-called gel-like structure. Many works have shown that s-PMMA can self-aggregate[24,25] in some solvents (THF, acetone), even at low polymer concentrations, but no indications can be found for such association in chloroform. However, to our knowledge, no studies were carried out at high concentrations of stereoregular PMMA to know if this system could achieve a gel-like state. Moreover, the freezing-in effect induced by the fast evaporation of the solvent could be an additional factor leading to the formation of a gel-like structure. Actually, the occurrence of such a structure near a surface was already mentioned by Overney et al.[26] who suggested that, based on AFM measurements, disentanglement at interfaces may happen. Sanyal et al.[27] suggested that part of the chain could be physically grafted to the substrate and that the rest is in a coiled configuration such as in mushroom configuration. However, they did not give further arguments for explaining the physical meaning of their intriguing results.

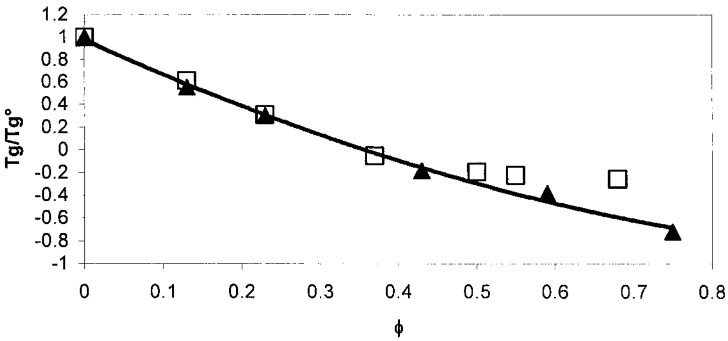

Fig. 2. Evolution of the normalized T_g of stereoregular PMMA with the fraction, ϕ, of solvent contained, as determined by DSC. The triangles and the squares correspond to *i*-PMMA and *s*-PMMA, respectively.

Fluorescence experiments carried out by Chang and Morawetz[28] and more recently by Chen et al.[29] on freeze-dried solutions suggest that chain interpenetration is negligible for dilute solutions, $c < 1/[\eta]$, then increases with concentration, but seems to encounter a strong resistance for further interpenetration at concentrations above c^*. c^* is the critical concentration separating the dilute from the semi-dilute regime. Moreover, these authors reported that local conformations of PMMA chains can be related to the degree of chain entanglement which was tuned by freeze extraction from various solvents. In parallel to what happens during freeze-drying, Sauer et al.[30] suggested that the chains collapse in a less entangled state and are frozen-in in this state due to rapid solvent removal. However, very recently Bernazzani et al.[31] claimed that the modifications of T_g in thin films cannot be due to the reduced entanglement concentration. However, these experiments were not conducted with stereoregular polymers which might have a significant influence on the possibility of reentanglement.

Toluene is used for spin casting of PS thin films[1-5] but no results on the influence of the nature and the quality of the solvent on $T_g(h)$ have been reported so far. Table 3 shows $T_g(h)$ measured for stereoregular PMMA thin films spin coated from chloroform and tetrahydrofuran (THF) solutions. It is worth mentioning that these two solvents possess physico-chemical parameters such as vapour pressure, molar volume or surface tension that are rather similar. These two solvents also provide smooth films with a roughness, R_a, as measured by atomic force microscopy (AFM) of the same order of magnitude, namely about 0.3 nm. None the less, these two solvents yield large differences in $T_g(h)$ for a film thickness of 25 nm as shown in Table 3. The T_g(h) of *s*-PMMA film is found to be lower than the T_g(bulk) independent of the solvent whereas for *i*-PMMA chloroform is the only solvent which provided a $T_g(h)$ value higher than T_g(bulk).

Table 3. Comparison of $T_g(h)$ (°C) obtained by variable temperature ellipsometry for stereoregular PMMA thin films spin-coated from chloroform and THF solutions. The heating rate was 2 °C/min.

Polymer	Solvent	T_g(25 nm)	T_g(45 nm)	T_g(bulk)
i-PMMA	chloroform	104 ± 4	86 ± 3	52 ± 2
	THF	52 ± 5	53 ± 3	52 ± 2
s-PMMA	chloroform	98 ± 3	108 ± 2	125 ± 2
	THF	101 ± 5	114 ± 4	125 ± 2

These results indicate that THF leads to a lower thickness dependence of the T_g of PMMA than chloroform, especially for the isotactic isomer. It should be mentioned that the competition for the surface adsorption sites between PMMA and the solvent depends strongly on the acido-basic character of the solvent, as shown by Fowkes et al.[32] Thus, an acidic surface such as native silica interacts preferentially with PMMA in the PMMA/chloroform solution, while the solvent (THF) is preferentially attracted by the substrate for PMMA/THF solutions. It is therefore not clear whether the thermodynamic quality of the solvent or its acido-basic character dominates on the measured $T_g(h)$. The possible formation of a gel-like structure according to the nature of the solvent might be figured out by future complementary experiments.

Conclusion

We have presented a study of different factors influencing $T_g(h)$ of supported thin polymer films. The polymer microstructure is a relevant parameter for the study of the influence of entropic contributions to $T_g(h)$. The difference in the bulk T_g reported for PMMA stereoisomers was found to vanish for films of about 20 nm thickness. Changes in the chain conformation and orientation of PMMA appear to be the driving force imposing the sign of ΔT_g for polymer isomers. Freezing-in of non-equilibrated chain conformations caused by the spin-coating process is assumed to result in chain disentanglement (segregated chains) along with local conformational rearrangements. The ability to form a so-called gel-like structure at a given step of the evaporation process may also cause a particular chain dynamics in thin films depending on the microstructure of the polymer. In the future, similar studies should be performed on other polymer microstructures (stereoregular PS, copolymers) and for different thin film geometry (freely standing films) to confirm the general validity of our results and tentative conclusions.

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