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Letters

Glass Transition of Stereoregular Poly(methyl methacrylate) at Interfaces

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The glass transition temperature (T_g) of layers of stereoregular poly(methyl methacrylate) (PMMA) spin-cast on silicon and aluminum surfaces has been investigated by ellipsometry. The interfacial specific interactions were highlighted and quantified by infrared reflection absorption spectroscopy. It was found that depending on PMMA tacticity, a strong correlation exists between the density of the polymer/surface interactions and the T_g of that polymer at the interface. Indeed, i-PMMA with a large density of interfacial interactions increases its T_g at the interface whereas s-PMMA with a lower value of bonded segments exhibits a T_g depression. It is suggested that a certain level of interfacial interactions associated with an increase of density of the layer will compensate for the increase of mobility resulting from a reduction of the entanglement density or a segregation of chain ends at an interface.

Introduction

Up to now, the real nature of the glass transition process, which is a well-known phenomenon, is still imperfectly understood even for bulk polymers. This transition has often been discussed through theories mainly based on thermodynamic¹ or entropic and kinetic^{2,3} considerations. The concept of cooperativity which considers a length scale of correlation that depends on temperature has also been widely used.^{4,5} The mobility and the dynamics of polymer chains near a surface have relevance in many fields of technological importance, such as adhesion or composites. Thus, the effects of a surface or an interface on the glass

transition temperature have been the subject of considerable interest in recent years.⁶⁻¹⁰

The investigation of the glass transition temperature (T_g) of different polymer/substrates systems has been carried out by varying the molecular weight of the polymer,⁶ the internal architecture of the layer, or the surface treatment of the substrate.⁷ Generally speaking, polymers at free surfaces or in contact with repulsive surfaces are dominated by entropic effects such as chain end segregation, confinement effects, or disentanglement, which leads to a T_g depression,^{8,9} whereas enthalpic forces at attractive surfaces increase the T_g of the bulk polymers.¹⁰

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Table 1. Characteristics of the PMMA Used in the Study^a

PMMA	tacticity (%) ^b i:h:s	M_n (10^{-3} g/mol)	M_w/M_n	T_g (°C)
i-PMMA	97:03:0	37	1.21	61
a-PMMA	7:29:64	30.5	1.19	114
s-PMMA	0:20:80	33	1.05	131

^a The tacticity has been measured by ^1H NMR. ^b The letters i, h, and s represent the content of isotactic, heterotactic, and syndiotactic triads of the polymer, respectively.

A factor that has never been envisaged is the stereoregularity of the polymer. Nevertheless, the tacticity of polymers such as poly(methyl methacrylate) (PMMA) is known to be responsible of large differences in the T_g of that polymer.¹¹ Therefore, the question is: is there any effect of the PMMA tacticity on its T_g at an interface? To answer this question, we report results of ellipsometric investigation of the T_g of thin layers of different PMMA isomers spin cast on reactive surfaces such as silicon and aluminum.

Experimental Section

The PMMA used was purchased from Polymer Source Inc.¹² Their characteristics are given in Table 1. They were synthesized by anionic polymerization to ensure well-defined tacticity, polydispersity, and molecular weight. These polymers were spin cast from chloroform solutions (1, 5, and 10 g/L) on (111) silicon surfaces. The substrates were etched in $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ solution prior to polymer deposition. Silicon wafers covered by vacuum-evaporated aluminum were also used. The spin-coated samples were studied "as deposit" but also after annealing, above T_g , for at least 3 h and cooled at a constant rate.

Infrared reflection absorption spectroscopy (IRAS) was carried out by using a Bruker IFS 66 spectrometer equipped with a Specac grazing-angle device (incidence angle 82° , polarization parallel to the incident wave plane). Grams¹³ software used for the curve-fitting of the carbonyl peak allows the determination of the absorbance due to the bonded carbonyls and the absorbance due to the free carbonyls.

Spectroscopic ellipsometry experiments were performed by using a Sopra ES4M apparatus working in a wavelength range from 0.4 to 0.8 μm . It was equipped with a heating rate programmable hot-stage. The ellipsometric angles were recorded at stabilized temperatures increased by 10° increments. The fit of $\tan \phi$ and $\cos \Delta$ in this range of frequencies allows the calculation of thickness and refractive index of the layers. The so-called kinetic ellipsometric scans were performed by focusing on only one wavelength (0.75 micrometers) and with a heating rate of 1 deg/min.

Results and Discussion

IRAS has been performed to investigate the interfacial interactions taking place between the PMMA and the aluminum surface. The silicon surface rather complicates our analysis of the IRAS spectra because of a poor signal-to-noise ratio of the recorded spectra. The infrared reflectance studies of a solvent cast thin PMMA film on silicon substrate covered by vacuum-evaporated gold has shown that the carbonyl peak is located at 1740 cm^{-1} . This wavenumber is considered for that study as a reference for the free carbonyl since no specific interactions are expected for PMMA on gold.

The shift toward lower frequencies of the adsorption band of the carbonyl is assumed to be due to acid-base interactions occurring between the carbonyl and the hydroxyl groups of the alumina layer covering the

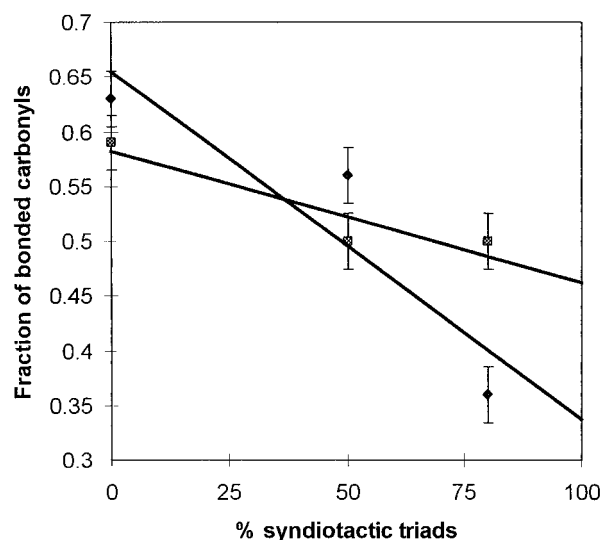


Figure 1. Fraction of bonded carbonyls, which has been calculated from the curve-fitting of the infrared carbonyl peak, plotted as a function of the percentage of syndiotactic triads in the polymer. ■ represents the values obtained from the layer spin-cast from a 5 g/L PMMA solution and ◆ represents the values obtained from the layer spin-cast from a 1 g/L solution.

aluminum surface.¹⁴ The part of the carbonyl peak ascribed to the bonded carbonyl is always located at 1730 cm^{-1} whatever the PMMA tacticity. Therefore, the nature and intensity of the specific interfacial interactions do not differ from one PMMA isomer to another. Curve-fitting analysis allows the calculation of the fraction of carbonyl groups, involved in acid-base interactions, $f_{\text{C=O}}^{\text{ab}}$, by the equation

$$f_{\text{C=O}}^{\text{ab}} = \frac{A_{\text{C=O}}^{\text{ab}}}{A_{\text{C=O}}^{\text{ab}} + \frac{\epsilon_{\text{C=O}}^{\text{ab}}}{\epsilon_{\text{C=O}}^{\text{f}}} A_{\text{C=O}}^{\text{f}}} \quad (1)$$

where $A_{\text{C=O}}^{\text{ab}}$ and $A_{\text{C=O}}^{\text{f}}$ are the peak fitted integrated intensity of the 1730 cm^{-1} peak and of 1740 cm^{-1} peak, respectively. The ratio of the molar absorption coefficients has not been found in the literature for the PMMA/aluminum system. The fraction of acid-base bonded carbonyls, reported in Figure 1, have been calculated using a ratio equal to unity, to a first approximation.¹⁵ The surface-bonded carbonyl fraction is found to decrease from isotactic to syndiotactic PMMA. Moreover, this tendency is enhanced for the lowest layer thickness because of a more direct investigation of the chains bonded to the surface. The signal provided by these interfacial polymer chains is probably partially screened by the nonadsorbed chains for the highest layer thickness. It should be noticed that the differences in the film thickness between PMMA isomer leads to variations in the calculated bonded carbonyl fraction that are within the range of experimental error ascribed to the IRAS technique. The dependence between tacticity and bonded carbonyl fraction tends to prove that the surface configuration of the adsorbed layer depends strongly on the PMMA stereoregularity. The influence of the polymer tacticity on the conformation of the adsorbed PMMA chains has been further discussed in a previous paper.¹⁶ In that work a large increase of the

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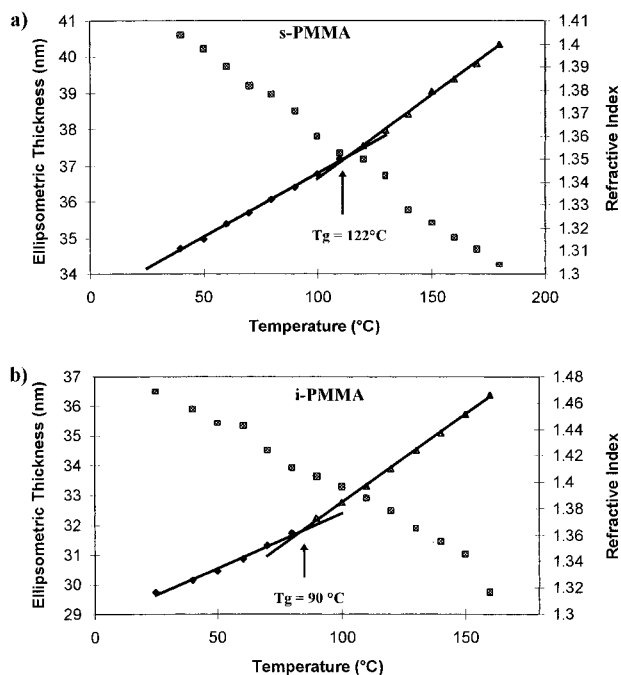


Figure 2. Ellipsometric thickness and the refractive index calculated from spectroscopic ellipsometry by fitting the recorded $\cos \Delta$ and $\tan \psi$ ellipsometric angles at different constant temperatures. The upper curve (a) corresponds to the annealed s-PMMA layer and the lower one (b) to the annealed i-PMMA layer.

conformational energy of the PMMA layer on aluminum has been calculated. This result accounts for an increase in the interfacial trans conformation, which is likely to be induced by the strong interfacial interactions. The change in interfacial conformation is also assumed to lead to a change in the arrangement and packing density of the chains at the interface.

As shown in Figure 2, the first ellipsometric experiments were carried out in spectroscopic mode at different given temperatures to determine the ellipsometric thickness and refractive index of the layers. As already observed by Keddie et al.¹⁰ the line-shape of the ellipsometric angle versus temperature was not reproducible for the as-spun samples, namely, without annealing. This is especially true for the a- and s-PMMA whereas i-PMMA exhibits roughly the same profile of the curve before and after annealing. Indeed, this isomer seems to be less sensitive to the thermal and mechanical (since spin-coating generates high elongational strain) history of the layer. In Figure 3 we show that the slope of the curve of the ellipsometric thickness of annealed PMMA layers versus temperature changes at T_g on a silicon substrate. The change in refractive index at T_g is less obvious since the scatter is larger. The calculated thermal expansion coefficients given in Table 2 are equal to $1.9 \times 10^{-4} \text{ K}^{-1}$ for the different tactic PMMA layers below T_g . In contrast, above T_g the values become tacticity dependent and range from $3.6 \times 10^{-4} \text{ K}^{-1}$ for the s-PMMA to $5.2 \times 10^{-4} \text{ K}^{-1}$ for the i-PMMA. These values are below the thermal expansion coefficients of the amorphous atactic bulk PMMA, which are 2.2 and $5.7 \times 10^{-4} \text{ K}^{-1}$ below and above T_g , respectively. Differences in the packing of the chains at the interface between isotactic and syndiotactic PMMA can explain the low value of the thermal expansivity of the s-PMMA at the interface.

The ellipsometric angles of ultrathin layers cast from 1 g/L PMMA solutions have been recorded on aluminum. To calculate the layer thickness, the refractive index has

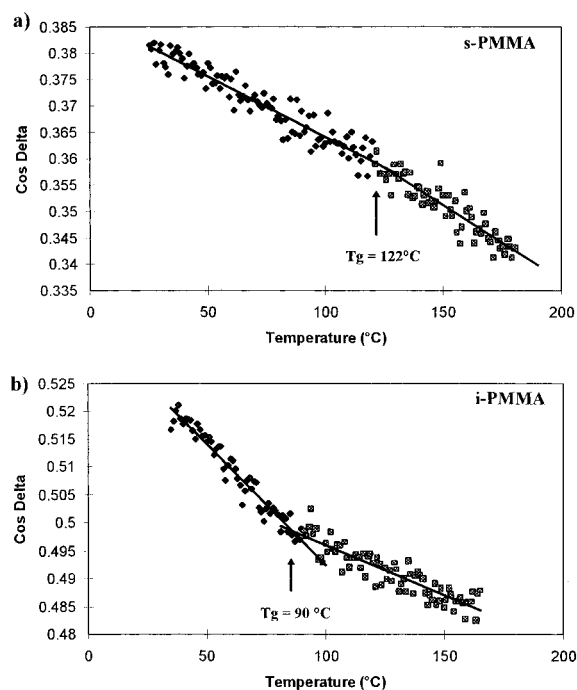


Figure 3. Kinetic ellipsometric scan corresponds to the recorded phase shift $\cos \Delta$ versus temperature at a heating rate of 1 deg/min. The upper curve (a) corresponds to the s-PMMA layer and the lower curve (b) to the i-PMMA layer.

been fixed to the value corresponding to the bulk refractive index of each PMMA isomer. This assumption made on the refractive index provides a good accuracy in the fitted spectra and especially the best reproducibility of the obtained values. The results clearly show an increase of the thickness of the layers with the increase of the PMMA syndiotacticity.¹⁶ Since an assumption has been made on the refractive index of the layer the increase in the calculated film thickness with PMMA syndiotacticity can also be envisaged as a variation in the effective refractive index of the layer. The density of the layer, which is known to be related to the refractive index by the Lorentz-Lorentz equation is, therefore, likely to be different for an i-PMMA layer or for a- or s-PMMA. This observation supports the assumption of a packing of the chain at the interface, which heavily depends on the PMMA tacticity.

The glass transition temperature can be observed in Figure 2 at about 90°C for the i-PMMA and 120°C for the s-PMMA layer. However, for more accuracy in the T_g determination, a kinetic ellipsometric scan must be envisaged. Figure 3 shows that the T_g of the PMMA layers can be detected directly from the curve of the phase shift $\cos \Delta$ versus temperature. Thus, the T_g of a layer of 35 nm on a silicon wafer is 90°C for the i-PMMA (Figure 3a) and 122 and 120°C for the a- and s-PMMA (Figure 3b), respectively. The measurements made on layers of lower thickness, namely, 20 nm, provides T_g values of 100, 125, and 110°C for the i-, a-, and s-PMMA, respectively. By decreasing the film thickness, we observe an increase on the T_g of the isotactic isomer, a slight increase of the T_g of the atactic isomer, and a depression of the T_g of the syndiotactic isomer. The T_g values recorded on the aluminum surface are in the same range as those obtained on the silicon surface as shown in Table 2.

Comparing the values obtained for the PMMA layers to those obtained by DSC for the bulk polymers highlights significant differences. Thus, since the T_g of i-PMMA increases of about 30 to 40° at the interface, the transition of s-PMMA occurs at 10 to 20° below its bulk T_g . The

Table 2. Values of the Glass Transition Temperature Measured by Differential Scanning Calorimetry for the Bulk PMMA^a

PMMA	T_g of bulk PMMA (°C)	T_g (°C) of the layer			thermal expansivity on Si h^{-1} (d h /d T) (K ⁻¹)
		on Si $h \approx 35$ nm	on Si $h \approx 20$ nm	on Al $h \approx 40$ nm	
i-PMMA	61	90 ± 3	100 ± 2	100 ± 4	$T < T_g$: 1.9×10^{-4} $T > T_g$: 5.2×10^{-4}
a-PMMA	114	122 ± 3	125 ± 3	128 ± 4	$T < T_g$: 1.8×10^{-4} $T > T_g$: 4.2×10^{-4}
s-PMMA	131	120 ± 5	110 ± 4	122 ± 5	$T < T_g$: 1.9×10^{-4} $T > T_g$: 3.6×10^{-4}

^a T_g values are measured by kinetic scan ellipsometry for the annealed layers of different thickness on silicon and aluminum. The thermal expansion coefficients are calculated from spectroscopic ellipsometric experiments performed on annealed layers spin-cast on silicon wafers.

increase of T_g of the a-PMMA at the silicon surface is in good agreement with data published by other authors for the same atactic polymer/substrate system.¹⁰

The main result shown in this paper is that the T_g of PMMA at an attracting surface strongly depends on PMMA tacticity. This result is rather surprising since no differences in the nature of the interfacial interactions are expected for the chemically identical PMMA isomers. Indeed, the nature of the polymer–substrate interactions should affect the mobility in thin polymer films.⁷ However, our IRAS measurements have shown that the density of interfacial interactions decreases with PMMA syndiotacticity in an amount that can reach 30% for the thinnest layers. Therefore, the enthalpic effect resulting from the density of interactions differs according to the polymer stereoregularity and may then restrict the chain mobility at the interface to an extent that depends on the polymer tacticity. The increase of the conformational energy, which has been discussed in a previous paper,¹⁶ accounts for enthalpic effects that are assumed to play a role in the change of T_g at the interface. Those interfacial conformational rearrangements shall lead to an increase of the density of the i- and a-PMMA layers as compared to the density of the s-PMMA layer. Presumably, the density gradient that occurs in the polymer at an interface¹⁷ propagates in a larger extent with an increase in the PMMA isotacticity.

Those considerations can be put forward to explain the increase of T_g which has been observed for the i- and a-PMMA, but the depression of T_g recorded for the s-PMMA layer is still an open question. An increase in the molecular mobility has been observed in confined systems.¹⁸ Although we study thin films, the thickness of our layers is far greater than the radius of gyration of

the PMMA chain preventing any confinement assumption. The interface between the air and the polymer has often been suggested to be the place of significant entropic effects such as disentanglement¹⁹ or chain end segregation.²⁰ Therefore, the free surface of glassy polymer generally exhibits depressed T_g .²¹ In the case of i- and a-PMMA the effects of the free surface are assumed to be totally outweighed by the high density of interfacial interactions. On the contrary, s-PMMA is likely to be very sensitive to the entropic effects such as chain end segregation or disentanglement occurring at an interface. Actually, that isomer seems to be unable to balance entropic effects probably due to the free surface by a sufficient density of interfacial interactions at the polymer/substrate interface. The dominant effect of the entropic forces that are likely to take place at the polymer/air interface would explain the T_g depression found for the s-PMMA at the silicon and aluminum surface.

Conclusion

This study points out, for the first time to our knowledge, that the polymer stereoregularity strongly influences the glass transition temperature of PMMA in the vicinity of an attractive surface. We also clearly demonstrate that the strong specific interfacial interactions determine the T_g at the interface. It is not so much the nature of the interaction but the number of side groups involved in interfacial interactions along the chain that is assumed to be a significant parameter of the interfacial chain mobility. Chain rearrangement and also density changes at interface induced by acid–base interactions can explain that the modification in the chain mobility is propagated far from the strict geometrical interface, namely, in the total layer thickness. The modification of the interplay between enthalpic and entropic forces at a surface can act in a different way with the polymer tacticity. Indeed, the T_g of i- and a-PMMA at a surface is dominated by interfacial enthalpic effects whereas the T_g of s-PMMA is assumed to be dominated by interfacial entropic effects.

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