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Glass Transition Temperatures of High-Density Poly(methyl methacrylate) Brushes

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Introduction. Ultrathin polymer films on a solid substrate (supported films) are extremely interesting objects both scientifically and practically. Detailed knowledge of their structure and properties is essential for the design of advanced materials such as electronic devices, lubricants, and photoresists.[1−3] The glass transition temperature (T_g) of a supported polymer film has been studied in a number recent papers,[4−16] in which T_g has been shown to strongly depend on the thickness of the film and the nature of the substrate. A free or repulsive surface can influence the polymer in contact by restricting the chain conformation and causing the segregation of chain ends or short chains from the bulk of the film. These are entropic effects and generally lower the T_g. An attractive surface, on the other hand, has enthalpic as well as entropic effects on the film, and it can make the T_g either lower or higher depending on the nature and strength of the interactions. Obviously, these surface effects are more important for thinner films than thicker ones, thus causing the dependence of T_g on film thickness.

This communication is the first report on the T_g of a series of *high-density* polymer brushes formed on a solid surface. Polymer brushes swollen by a solvent are important in many areas of science and technology, e.g., colloid stabilization, adhesion, lubricant, and rheology,[17−20] and they have been extensively studied.[21,22] Dry polymer brushes are also interesting as a kind of supported films. However, the effect of end-grafting on T_g has been studied only in a limited number of papers.[5c,11,12c] All of them dealt with low- to moderate-density brushes, and the grafting effects on T_g were rather minor or unclear. We have observed a marked increase in T_g for the ultrathin films of poly(methyl methacrylate) (PMMA) end-grafted on a silicon wafer with an extremely high, nearly constant surface density but differing chain lengths (differing film thicknesses). In what follows, we will present the relevant experimental results and show that the increase in T_g originates not only from the surface effect (of the chemically bound chain ends) but also from the characteristic bulk structure/properties of the high-density brushes.

Experimental Section. PMMA brushes on a silicon wafer were prepared by the surface-initiated atom transfer radical polymerization (ATRP),[23,24] as described previously.[21,25] Table 1 shows the characteristics of the samples. The number- and weight-average molecular weights (M_n and M_w) are the values, as determined by PMMA-calibrated gel permeation chromatography (GPC), for the free polymers that were simultaneously produced from the free (unbound) initiator added to the solution.[24a,25] There are reasons to believe that the molecular characteristics of the free polymers closely approximate those of the graft polymers.[21,25,26] Several of the free polymers were spin-cast from a toluene solution on a hydrophobically treated silicon wafer.[27] The thickness of each cast film was adjusted so as to be nearly equal to that of the corresponding brush film. The thicknesses (L_d's) of the brushes and the cast films, as determined at room temperature by spectroscopic ellipsometry (see below), are also given in Table 1.

Table 1. Characteristics of the Brushes and the Cast Films

		brush		cast film
M_n[a]	M_w/M_n[a]	L_d[b] (nm)	σ[c] (chains nm^{-2})	L_d[b] (nm)
15 000	1.10	13	0.61	
20 000	1.08	19	0.67	
24 000	1.17	30	0.88	30
44 000	1.12	40	0.63	40
75 000	1.10	64	0.60	64
96 000	1.11	90	0.66	90
154 000	1.08	142	0.65	149
177 000	1.26	172	0.68	180
182 000	1.17	151	0.59	

[a] Values for the free polymers produced in solution (see text). [b] Thickness in the dry state determined by ellipsometry. [c] Values calculated from L_d, M_n, and the bulk density of a PMMA film (1.19 g/cm^3).[28]

T_g was determined on a spectroscopic ellipsometer (M-2000U, J. A. Woolam, USA) equipped with a homemade temperature-controlled vacuum cell, designed for an incident angle of 70°. The sample was heated or cooled continuously at a constant rate of 2 °C/min. At every 20 s, the ellipsometric angles (Ψ and Δ) were recorded in a wavelength range from 380 to 1000 nm, and the temperature (T) of the sample was directly measured using a thermocouple. To avoid adsorption of contaminants like water, all measurements were made under vacuum. The heating−cooling cycle was repeated at least four times for each sample, confirming that all the cycles except for the first heating scan gave virtually the same result. This good reproducibility excludes possible dewetting or decomposition of the sample by heating. T_g was determined from the Ψ vs T diagram recorded at a wavelength of 623 nm with cooling scans (see below).

Results and Discussion. Figure 1 shows a typical $\Psi - T$ plot for the cooling scan. Since the characteristic angleΨ is approximately linear to L_d in the studied ranges of film thickness and refractive index,[29] T_g may be determined as the temperature at which the two straight lines representing the glassy and rubbery regions, respectively, intersect with each other, as indicated in the figure. The T_g determined in this way is estimated to be accurate within 1 °C, in all cases.

Figure 2 shows the plot of the T_g's of the brushes and the cast films. Remarkable is the difference in the T_g behavior between these two types of ultrathin films. As already noted, the molecular characteristics of the polymer forming each cast film are closely similar to those of the polymer forming the brush of (nearly) the same thickness, and therefore the T_g difference cannot be ascribed to differences in molecular characteristics such as chain length, chain length distribution, and

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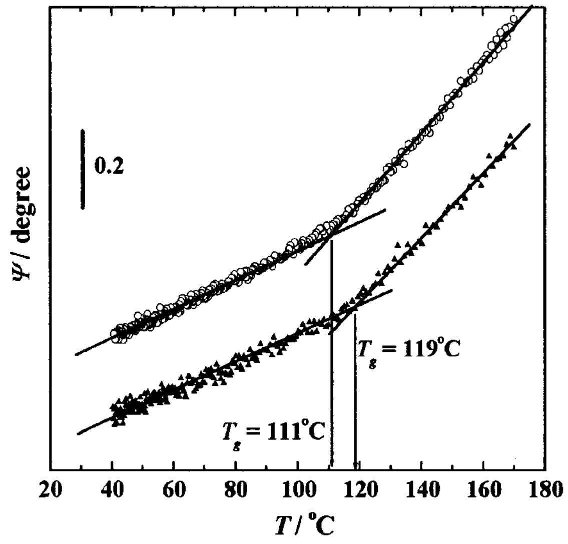

Figure 1. Typical $\Psi - T$ plots in the cooling scan. The solid triangles and open circles represent the data for the brush (L_d = 64 nm) and the cast film (L_d = 64 nm), respectively. The solid lines are the best fits for the rubbery- and glassy-region data.

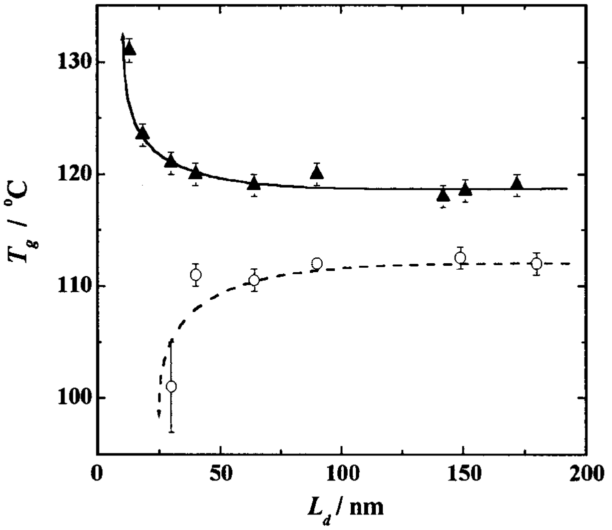

Figure 2. Plots of T_g vs L_d. The solid triangles and open circles represent the data for the brushes and the cast films, respectively. The solid and broken lines are a guide to eyes.

stereoregularities. It may totally be ascribed to the effects of grafting, i.e., chemically binding one of the chain ends on the substrate surface.

Examining the behavior of the cast films, all of them but the thinnest one with L_d = 30 nm have a nearly constant T_g. The T_g of the bulk PMMA is known to depend on molecular weight like[31]

$$T_g = 386 - 353/(M_n/100)^{2/3} \quad (1)$$

Comparison of Figure 2 and eq 1 suggests that the exceptionally low T_g value of the thinnest film (M_n = 24 000) cannot totally be ascribed to the molecular weight effect. The interfacial effect should also be responsible for the low T_g. In fact, this effect on T_g is known to be important for L_d smaller than about 50 nm, typically.[5b]

In this range of L_d (<50 nm), where cast films suffer a significant T_g depression, the T_g of the brushes steeply increases with decreasing L_d. Similar observations have been reported for films cast on such interacting surfaces that strongly reduce the mobility of the chains.[5b,c,6b,8,12c] Obviously, end-grafting restricts the mobility of the chains, making the T_g higher. This effect predominates over the free surface effect, causing T_g depression in our system. One may expect, however, that the effect of end-grafting on chain mobility would become less and less significant as the chain length increases, and in the limit of long chain, the T_g of the graft film would become equal to that of the cast film and hence that of the bulk polymer, since all surface effects on the overall T_g of films should be unimportant in the long chain limit. Figure 2 shows that this is *not* the case. As L_d increases over about 50 nm, T_g of the brushes reaches an almost constant value of about 119 °C, which is about 8 K higher than that of the corresponding cast films. The figure strongly suggests that this difference in T_g between the brushes and cast films would be retained in the long chain limit.

Then what is the reason for this marked increase in the T_g of the long enough brushes? It should be ascribed to the particular structure/chain conformation in high-density brushes. The studied PMMA brushes have a surface density σ of about 0.7 chains/nm^2. We previously showed[21a,b] that these high-density brushes swollen in a good solvent give a $L_e/L_{c,w}$ ratio as large as 0.8−0.9, where L_e and $L_{c,w}$ are the equilibrium thickness of the swollen brush and the weight-average contour length of the chain in the all-trans conformation, respectively. Namely, these swollen brushes are characterized by a high degree of quasi-nematic order with the chains extended nearly to their full lengths, independent of chain length. Such an anisotropic structure does exist in the dry state, where $L_d/L_{c,w}$ ratio reaches as large as 0.35 on average (cf. Table 1). Since the size of the unperturbed chain end-grafted on a repulsive surface is proportional to the square-root of chain length,[32] this large value of L_d (= 0.35 × chain length) means that the chains are still highly extended in the dry state as compared with their unperturbed dimensions. This must be the reason for the T_g increment in the high-density brushes. In fact, for the previously studied low- to moderate-density brushes with $\sigma \leq 0.1$ chains/nm^2, no T_g increment has been observed at large L_d[5c,12c] or at any L_d.[11] Mechanistic details of the T_g increment in anisotropic films remain to be studied.

Conclusions. The T_g of high-density PMMA brushes with an approximately constant surface density as high as 0.7 chains/nm^2 was studied as a function of film thickness L_d, which is proportional to the M_n of the graft chains. For $L_d \leq 50$ nm, T_g increases sharply with decreasing L_d, due to the restricted mobility of the end-grafted chains, i.e., a surface effect. For L_d larger than about 50 nm, T_g showed a constant value of about 119 °C, which is about 8 °C higher than the T_g of the corresponding cast film or, equivalently, that of bulk PMMA. This T_g increment in the long brushes is ascribed to the anisotropic structure of the graft films, in which the graft chains are highly extended along the film thickness direction for a steric reason arising from the high graft density.

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(26) Tacticity of the free polymer and graft chains was estimated by the ^{1}H NMR measurement.

(27) To adjust the surface characteristics of the substrate more closely to that of the substrate for the brush film, a silicon wafer was subjected to ultrasonification in a mixture of dimethyldichlorosilane and toluene (1:3, by volume) for 30 min, followed by ultrasonification in isopropyl alcohol for 15 min, and then dried. After this treatment, the water contact angle was around 100°.

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