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Communications to the Editor

Embedding of Noble Metal Nanoclusters into Polymers as a Potential Probe of the Surface Glass Transition

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Introduction. It is well-known nowadays that thin surface layers of polymers as well as polymers in a thin film configuration may have physical properties different from those of the bulk material due to interfacial interaction and effects of surface molecular motion.[1] Therefore, knowledge of the surface glass transition temperature is of both fundamental as well as practical interest. Theoretical calculations predict that the polymer surface becomes either softer[2] or harder than the bulk.[3] Experimental investigations involving different methods also produced controversial results. For example, a significant T_g depression of 20−60 K was obtained by means of the positron annihilation Doppler broadening technique with a low-energy positron beam[4] and from experiments on the basis of scanning viscoelasticity microscopy[5] on the surface of polystyrene films. In contrast, a large hardening effect was observed on polystyrene films from thermal expansion data obtained by X-ray reflectivity measurements.[6] There are different possible explanations for this controversy: the difference in the thermal history of the samples, differences in film thickness, effects of polymer−substrate interaction, or differences in depth resolution of the methods used.

In this Communication, we report the embedding of noble metal nanoclusters into a polymer as a new probe to study the dynamic properties of the polymer surface near the glass transition. Our recent TEM and AFM measurements show that evaporated noble metals initially form discontinuous layers on polymer substrates consisting of spherical clusters, whose density and size depends on the deposition parameters as well as on the particular metal−polymer combination.[7,8] The embedding process is monitored by means of X-ray photoelectron spectroscopy (XPS). The clusters are embedded into the polymer bulk upon heating the polymer above its glass transition temperature, where the polymer chains attain long-range mobility.[9] There is a driving force for embedding the metal clusters[9] since the surface tension γ_M of the metal particles exceeds the sum of the interfacial tension γ_{MP} and the polymer surface tension γ_P: $\gamma_M > \gamma_{MP} + \gamma_P$

Experimental Section. Monodisperse polystyrene (PS) and polycarbonate (PC) films with different T_g were used in the experiments. Bisphenol-A polycarbonate (BPA−PC, $M_w = 40\,000$ g/mol) and bisphenol trimethylcyclohexane polycarbonate (TMC−PC, $M_w = 30\,000$ g/mol) were provided by BAYER and monodisperse polystyrene with different M_w (4000−200000 g/mol) was obtained from Aldrich Chemical in the form of a granulate. The bulk T_g values were taken as specified by the provider or determined in our laboratory by using differential scanning calorimetry (DSC) with a heating rate of 10 K/min. Polymer films were prepared by dissolving polymer granulate in methylene dichloride and casting on a Si substrate in a Petri dish. Subsequent slow vaporization of the solvent at room temperature for 24 h yielded films of typically 0.5−2 μm thickness measured with a profilometer (Stylus DEKTAK 8000, Veeco Ins. Inc.). This thickness is sufficient to avoid influences of polymer−substrate interactions on the polymer surface dynamics. Since it was expected that the behavior of the polymer films is highly sensitive to thermal history, the films were cured under vacuum at a temperature $T = T_g(\text{bulk}) + 30$ K for 1 h and then cooled at a constant rate of 2 K/min to room temperature (room temperature) before deposition of the metals.

Copper was evaporated from a heated Mo crucible mounted in the preparation chamber of the XPS spectrometer (Omicron Full Lab) onto the polymer films at

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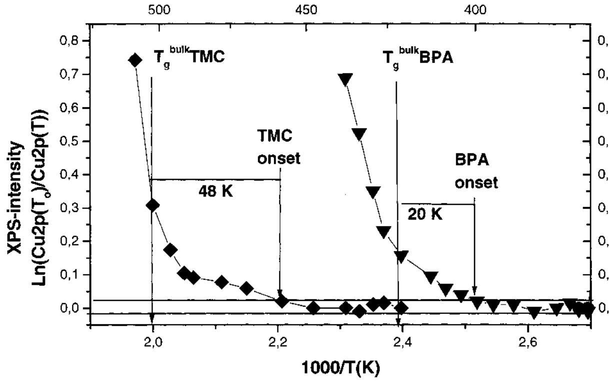

Figure 1. Change in the XPS Cu 2p(T_0)/Cu 2p(T) intensity ratio for the systems Cu/TMC−, BPA−polycarbonate as a function of the annealing temperature (heating rate 0.5 K/min, T_0 = 298 K). ln(Cu 2p(T_0)/Cu 2p(T)) is propotional to embedding depth of the Cu clusters. The solid line represents the 1σ deviation from the baseline in the glassy state.

room temperature. The deposition rate and the nominal thickness of the metal layers were monitored by a quartz crystal microbalance. The surface chemical composition of the polymers and the evaporated metal clusters as well as the embedding depth were investigated using XPS. As described in previous papers noble metals grow as spherical clusters on the polymer surface.[7,8] The size of the nanoclusters (1−4 nm) as well as the their penetration depth were determined by an indirect method based on the measurement of the ratio of two XPS lines of the same metal with different kinetic energies and respectively different attenuation lengths of the photoelectrons. This method has been described in detail previously in ref 10.

After deposition of the metal film at room temperature the samples were heated in situ with different rates (0.1−1 K/min). The samples (polymer film on Si) were fixed with graphite glue onto the Ti sample holder and the temperature was measured with a thermocouple mounted directly on the sample holder. Prior to the measurements the temperature was calibrated with a second thermocouple mounted directly onto the polymer surface and the error in the temperature measurement was determined to be smaller than 2 K. The particle embedding depth z was determined from the XPS Cu 2p(T_0)/Cu 2p(T) intensity ratio assuming a negligible contribution of cluster coalescence to the observed decrease of the intensity ratio.[7,11]

Results and Discussion. Figure 1 depicts the increase in the XPS intensity ratio Cu 2p(T_0)/Cu 2p(T) upon heating the sample at a constant rate of 0.5 K. Embedding of metal particles into BPA−PC after annealing above T_g is confirmed through the significant change in the XPS Cu 2p(T_0)/Cu 2p(T) intensity ratio in Figure 1 as well as in the ion depth profiles (Figure 2) obtained before and after annealing of the sample. The maximum in depth distribution of Cu in Figure 2 is in good agreement with the value of the embedding depth z calculated from the attenuation of the Cu 2p intensity. According to the theoretical model from ref 9 the embedding depth z as a function of time t for a single spherical particle with size 2r under condition $z < 2r$ can be described through the following equation:

$$z^3 \approx tA/(12\pi\eta) \qquad (1)$$

In eq 1, η is the viscosity in the surface region and A the Hammaker constant describing the van der Waals interaction between the metal particle and the polymer, which pulls the particle into the polymer. Figure 3 shows a typical plot of z^3 as a function of t at constant temperature T = 418 K ($\approx T_g$(BPA)), which is consistent with the linear behavior predicted by eq 1. With $A = 10^{-16}$ N m from ref 9 and using the values displayed in Figure 3 yields $\eta = 3 \times 10^{11}$ Ps which is in the right order of magnitude for a polymer above but near its glass transition.

The change in the XPS intensity ratio vs temperature and time reflects the kinetics of the embedding process, and the strong upturn in the data in Figure 1 is related to a drastic decrease of the polymer viscosity at the surface glass transition. This interpretation is obvious since embedding of the metal particles requires long-range mobility of the polymer chains and hence cannot take place below T_g. In Figure 1, there is a good correlation between the onset of metal cluster embedding as marked in the figure and the bulk polymer glass transition temperature for the two different polycarbonates. This is further supported by the results obtained for two polystyrene samples of different molecular weight and hence different T_g shown in Figure 4. These results suggest a connection between the onset of cluster embedding and the surface glass transition, $T_{g,S}$, although the two temperatures are not necessarily identical. The question where exactly to place T_{gS} is currently under investigation, but the presentation of the required extended theoretical and experimental

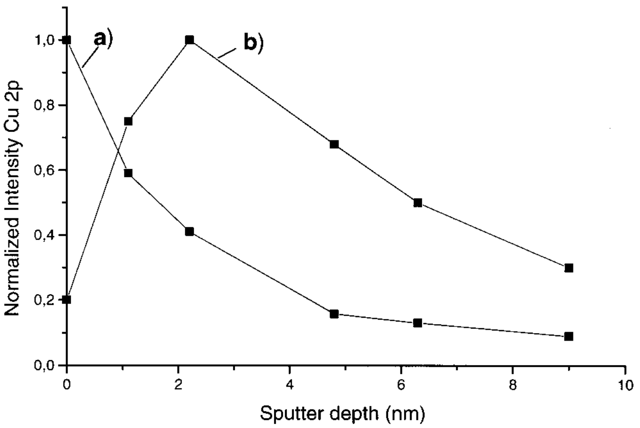

Figure 2. Depth profile of a 0.1 nm Cu deposit on BPA−polycarbonate (a) at room temperature and (b) after thermal annealing at 180 °C.

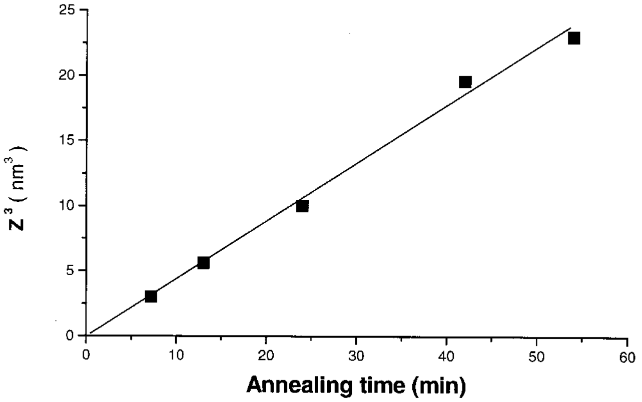

Figure 3. Dependence of the embedding depth z of Cu clusters in BPA-polycarbonate on annealing time at the temperature $T = T_{g,bulk}$ (418 K).

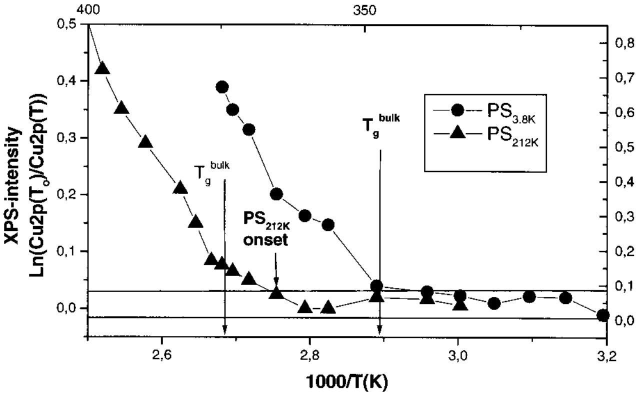

Figure 4. Correlation between the onset of Cu cluster embedding and the bulk glass transition temperature for polystyrene with two different molecular weight.

investigation is far beyond the scope of the current communication and will be published elsewhere.

The large differences between the onset temperature of metal cluster embedding and the bulk polymer glass transitions already suggest a substantial depression of the surface glass transition temperature for the polycarbonates and the higher M_w polystyrene. Thus, our results obtained by the novel method reported here and involving samples of equal history for bulk and surface T_g measurements lend support to the view that the molecular motion is enhanced near the surface due to the additional degrees of freedom. Earlier reports on a T_g increase at the surface should by examined critically.

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