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Remotely controlling the crystallization of thin polymer coatings

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Remotely controlling the crystallization of thin polymer coatings

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Abstract

We introduce a method permitting remote control of the crystallization of thin polymer films, not requiring changes in the film thickness or the interfacial chemistry. The procedure is based on the assembly of hybrid multilayers, where ultrathin films of a crystallizable polymer – poly(ethylene terephthalate), PET – are embedded in parallel with noncrystalline polymer layers – polystyrene, PS – into metallic slabs. Variation of the size of the PS film allowed tuning the crystallization rate of PET layers of constant thickness. We demonstrate that this phenomenon is ascribable to an increase in the interfacial dispersive forces that, enhancing physisorption of PET at the polymer/metal interface, causes a shortage of material at the crystal growth front.

Introduction

Polymer coatings of nanometric thickness are about to enter our everyday life in the form of protective layers, stimuli-responsive membranes, components of revolutionary flexible electronics devices, etc.¹ With respect to thin films of inorganic materials, these “soft” systems are preferred because of easier and more versatile fabrication methods and the lack of degradation within long shelf time.² Despite the tremendous literature available on this field, a full comprehension of the properties of these nanolayers has not been achieved yet. Thin polymer films, in fact, exhibit altered behavior with respect to the bulk, characterized by shifts in the phase transition temperatures and significant changes in other physical properties affecting processability, as flow, thermal expansion, mechanical stress,³⁻⁶

On this regard, similarly as for smaller molecules and liquid crystals,⁷ crystallization of polymers becomes slower upon confinement at the nanoscale level,⁸ where a severe reduction in the overall crystallization rate is commonly observed.⁹⁻¹¹ In extreme cases, below a critical thickness (usually on the order of few tens of nm) crystallization is not observed on time scales of industrial interest.¹²⁻¹³ The inhibition of crystallization upon confinement has attracted a considerable technological interest. Being able to suppress, or at least reduce, the crystallization rate would yield, for example, a tremendous increase in safety of those amorphous drugs where the crystalline form has non-negligible toxicity,¹⁴ and a neat improvement in the lifetime of polymer-based nanodevices, as coatings for optics and display applications where presence of crystals affects materials properties,⁸ e.g. opacity.

An operational parameter to evaluate the timescale of the formation of ordered structures is given by the crystallization time, t_{CRY} , a quantity, proportional to the inverse of the crystallization rate, that can be determined by monitoring the time evolution of the crystalline (or amorphous) volume fraction. In our previous work, we demonstrated that the thickness dependence of t_{CRY} can be written as the product of two terms, one related to the reduced

nucleation probability and the other taking into account the lower diffusion rate in proximity of interfacial layers.^{13, 15-17} To understand the physics behind the first term, we consider a polymer melt with homogenous nuclei density. In such case, a reduction of the thickness, h , achievable by considering thinner and thinner slabs of the above-mentioned melt, yields lower and lower probabilities to find active nuclei within a given portion of the slab. Such probability scales¹⁸ with V^{-1} , where V is the sample volume. Working at constant sample surface, as in the case of most of the studies performed, results in a proportionality of the type $t_{CRY} \sim h^{-1}$, which was verified by our previous experiments.^{13, 15} The second term can be obtained by measurements of the segmental relaxation time τ , which is related to diffusion ($\sim t_{CRY}^{-1}$) via a modified Stokes-Einstein relation,¹⁹ $t_{CRY} \sim \tau^\xi$ where ξ is the Stokes-Einstein fractional exponent. This parameter typically assumes values between 1 and 0, implying that crystallization (translational diffusion, mass transport¹⁶) becomes relatively faster than rotational dynamics as e.g. probed by measurements of glassy dynamics.²⁰ As segmental dynamics can be affected by nanoconfinement,⁴ a corresponding effect is expected also for diffusion and crystallization kinetics. Combining the contributions of nucleation and the diffusion, we got:

$$t_{CRY}(h,T) = \frac{\Lambda(T)}{h} \tau(h,T)^\xi \quad (1)$$

where Λ is a temperature dependent term related to bulk nucleation density and to the numerical value of ξ .

Eq 1 indicates that, for relatively thick films, the crystallization time increases upon confinement, with h^{-1} . A larger increment in t_{CRY} is expected for those systems, as poly(ethylene terephthalate) (PET) and poly(L-lactic acid) (PLLA), where segmental dynamics slows down upon confinement. Such contribution is observed in correspondence of the onset of slower interfacial dynamics, h^* ($\approx 20 \text{ nm}^{21}$).

Fitting experimental data of thin films of PLLA to Eq1, however, yields values of $\xi = 2.7$, while for PET the increase in t_{CRY} with thickness for $h < 20 \text{ nm}$ is particularly sharp, hinting at values

of $\xi \gg 1$, see Figure 1. Such exotic condition would correspond to a hindered mobility regime, where mass transport is less efficient than what predicted by the Stokes-Einstein relation in bulk. We hypothesized that this phenomenon could be due to the presence of adsorbed chains at the polymer/substrate interphase, whose conformations would inhibit translational diffusion. This argument is supported by several experimental observations. First, PET forms adsorbed layers thicker than PLLA, which is in line with the larger increase in t_{CRY} upon confinement of the former system.^{13, 15} Second, experiments with chains of PEO show that, if a thick adsorbed layer is present,²²⁻²³ crystal growth is inhibited even in the presence of preexisting crystals.

Figure 1 Thickness dependence of the crystallization time of thin films of poly(ethylene terephthalate)¹³ (top panel) and poly(L-lactic acid)¹⁵ (lower panel), in isothermal conditions. The shaded area indicates the thickness region where crystallization was not observed in PET up to 2 days of annealing at 373 K. Fits of the experimental data to eq1 with $\xi = 1$ (continuous green lines) and $\xi = 2.7$ (dashed blue line) are also given.

With these ideas in mind, we hypothesized that it could be possible to control the crystallization kinetics of a sufficiently thin polymer film of constant thickness ($h < h^*$) by varying the value of ξ , that is, by adequately processing the nanosystem to induce a different adsorption degree.

A trivial way to achieve this goal would be holding the thin film for different annealing times above its glass transition temperature, T_g , to promote thickening of the interfacial adsorbed layer. However, because adsorption usually occurs at timescales much shorter than those of crystallization,^{13, 15, 22} such procedure cannot provide a precise control on the crystallization kinetics.

Based on recent work on polymer multilayers,²⁴ we considered a different processing strategy. Here, we introduce a method permitting to tune crystallization rate of ultrathin polymer films without affecting film thickness or interfacial chemistry (same polymer layer / supporting substrate pair). This result is achieved by following recent work on the impact of nanoconfinement on interfacial interactions.²⁴ As a proof of concept, we fabricated hybrid multilayers of the type Al/PET/PS/Al, and investigated the impact of a screening non-crystallizable layer of polystyrene (PS), separating PET from aluminum (Al) – adsorbing wall. Varying the thickness of the PS capping layer, we could adjust the amplitude of the dispersive forces acting at the interface between crystallizable layer and supporting substrate, and, hence, control the number of molecules irreversibly adsorbed. As the latter set of molecules do not take part to the crystallization process, we were able to tune the crystallization rate of the crystallizable layer, without altering its thickness.

Materials and Methods

Experiments Poly(ethylene terephthalate) ($M_n = 38800 \text{ g mol}^{-1}$, $M_w/M_n = 1.97$) was dissolved in a trifluoroacetic acid/chloroform mixture and spincoated on top of an aluminum electrode, covered by a native layer of Al oxide ($h_{\text{AlOx}} = 3 \text{ nm}$, as evaluated by ellipsometry), previously thermally evaporated onto clean glass plates. Solutions of polystyrene ($M_w=932\text{kg/mol}$, $M_w/M_n=1.2$) in toluene (non-solvent for PET) were spincoated on top of the PET films. 4 mm^2 nanocapacitors were finally obtained upon evaporation of a patterned top electrode. The

thicknesses of single layers of PET ($14 \text{ nm} < h_{\text{PET}} < 1000 \text{ nm}$) and PS ($10 \text{ nm} < h_{\text{PS}} < 250 \text{ nm}$) were independently determined via ellipsometry and atomic force microscopy, further experimental details can be found in the Supporting Information. PS form sharp interfaces with PET (width $< 1 \text{ nm}$, even after prolonged annealing at 481 K)²⁵, which permits neglecting the effect of interdiffusion.

The complex dielectric permittivity, $\varepsilon^* = \varepsilon' - i\varepsilon''$, was measured in isothermal conditions over a broad frequency range ($0.5 \text{ Hz} - 1 \text{ MHz}$) by continuous frequency sweeps (for $t > 50 \text{ h}$) via a high-resolution dielectric analyzer. Thickness of the adsorbed layer was independently measured via atomic force microscopy and ellipsometry. To extract the thickness of the adsorbed layer, $h_{\text{ads}}^{\text{PET}}$, in the multilayer geometry, we annealed the sample at 373 K for 20 min , a time larger than the characteristic adsorption time ($< 1 \text{ min}$), but smaller than t_{CRY} . Al was removed by pouring a few drops of a dilute solution of NaOH onto the upper metallic layer, the samples were then soaked in chloroform for 30 min to remove PS, and then in trifluoroacetic acid to wash out the unadsorbed PET chains. The adsorbed amount was obtained from $h_{\text{ads}}^{\text{PET}}$ via a standard procedure, described elsewhere.^{24, 26}

Determination of the crystallization time t_{CRY} Cold crystallization (devitrification of an amorphous system) was monitored via broadband dielectric spectroscopy (BDS) at 373 K , where the dielectric response of PET is dominated by an intense peak in ε'' centered around $f^{\text{max}} \approx 10 \text{ kHz}$, commonly labeled as α - and attributed to the dynamic glass transition. The link between the intensity of the α -peak, $\Delta\varepsilon$, that is the contribution of orientational polarization to the glassy dynamics, and the density of mobile dipole moments, allows following the crystallization kinetics via the conversion of the amorphous fraction. At 373 K the weaker dispersion of PS ($\Delta\varepsilon_{\text{PS}}/\Delta\varepsilon_{\text{PET}} < 0.07$) is out of the experimentally accessible frequency window, $\log(f_{\text{PET}}^{\text{max}}/f_{\text{PS}}^{\text{max}}) \approx 7$, which permits a straightforward treatment of the experimental data. The

neat response of PET was extracted from the total signal of the double layer (the two single layers were considered as capacitors in series²⁷⁻²⁸) and analyzed in terms of the empirical Havriliak-Negami function.²⁹

Figure 2 Isothermal crystallization time (373K) for layers of 23 nm thick layers of PET embedded into two Al slabs, in parallel with layers of PS of different thickness, h_{PS} . The dashed line indicated the expected value of t_{CRY} if only finite size effects were considered.

During annealing we observed a drop in the dielectric strength of the α -peak, implying a reduction in the number of mobile segments. Prior to this phenomenon, a broader peak, indicated as α' -, emerged at lower frequencies.³⁰ Ezquerro and coworkers demonstrated that the reduction in dielectric strength of the α -peak does not follow the time evolution of the total crystalline content, because of the failure of a simple two-phase model in the presence of the complex molecular architecture of semi-crystalline polymers.³¹⁻³² However, simultaneous measurements of dielectric relaxation and X-ray scattering by Fukao et al verified that for PET the increase in crystalline volume fraction can be promptly monitored by following the drop in

the sum of the intensities of the α - and the α' -processes (for sake of clarity, indicated here as the dielectric strength of PET) .³⁰ In the case of thin films, we showed that irreversible chain adsorption is a concurrent source of immobilization and straightforwardly analyzed the reduction in dielectric strength as:¹³

$$\Delta\epsilon(t)/\Delta\epsilon(t_0) = 1 - \chi \left[1 - \exp\left(-t/t_{CRY}\right)^\beta \right] - \delta \log(t/t_0) \quad (2)$$

where χ indicates the drop in dielectric strength upon crystallization, δ is a parameter proportional to the amount of dipole moments immobilized upon adsorption, t_0 indicates the onset of the measurement (set to 1 s for all samples) and β is the Avrami exponent.³³

Determination of the effective Hamaker constant We considered the multilayer system Al(1)/AlOx(2)/PET(3)/PS(4)/Al(5), where the numbers in parenthesis indicate the bottom-up order of the layers. While for sake of simplicity we will refer in the rest of the text as the PET/Al interface, here we explicitly took into account the presence of an oxide layer between Al and PET. The effective Hamaker constant³⁴ of the forces acting at the PET/Al interface is given by

$$A_{eff} = A_{234} - \frac{\sqrt{A_{21}A_{343}}}{(1 + h_{AlOx}/h_{PET})^3} - \frac{\sqrt{A_{541}A_{323}}}{(1 + h_{PS}/h_{PET})^3} + \frac{\sqrt{A_{545}A_{121}}}{(1 + h_{AlOx}/h_{PET} + h_{PS}/h_{PET})^3} \quad (3)$$

where A_{XYZ} is the nonretarded Hamaker constant for media X and Z interacting across medium Y, that can be calculated³⁴ from A_{XX} , A_{YY} and A_{ZZ} (with A_{jj} the Hamaker constant of a system where two similar media act across a vacuum) as $A_{132} \approx \left(\sqrt{A_{11}} - \sqrt{A_{33}}\right)\left(\sqrt{A_{22}} - \sqrt{A_{33}}\right)$. We used $A_{Al} = 40 \times 10^{-20} \text{J}$ ³⁴, $A_{Al_2O_3} = 16.75 \times 10^{-20} \text{J}$ ³⁵, $A_{PET} = 6.2 \times 10^{-20} \text{J}$ ³⁵ and $A_{PS} = 7.9 \times 10^{-20} \text{J}$ ³⁴. Simavilla et al²⁴ demonstrated that correction for retardation effects to eq 3 are not necessary in this kind of analysis.

Results and discussion

We prepared several multilayers Al/PET/PS/Al and investigated the crystallization kinetics at constant thickness of the PET layer, h_{PET} , while varying that of the PS layers, h_{PS} . Increasing h_{PS} is expected to reduce the interfacial interactions between Al and PET²⁴ and, hence, the number of PET chains adsorbed onto Al per unit surface, Γ_{PET} . Based on our hypothesis, the latter phenomenon should speed up the crystallization kinetics, that is, an increase in h_{PS} corresponds to a reduction in t_{CRY} .

Here, we first qualitatively present the results of our work and we later discuss them in term of the changes in dispersive forces in multilayers.

Results in Figure 2 show that we have been successfully able to tune the crystallization time, t_{CRY} , of a 23-nm-thick film of PET by simply placing PS capping layers of different thickness. To understand the origin of this phenomenon, we considered experiments over a larger range of h_{PET} and h_{PS} values, see Figure 3. Regardless of the thickness of the capping PS layers, when plotted as a function of the inverse thickness of the crystallizable layer t_{CRY} shows two distinct regimes connected via a smooth transition.

Figure 3 Isothermal crystallization time (373K) for layers of PET of thickness h_{PET} embedded into two Al slabs, in parallel with layers of PS of thickness h_{PS} . The dashed line indicated the expected value of t_{CRY} if only finite size effects were considered.

Above thicknesses on the order of $h_{\text{PET}}^* \approx 20 - 30$ nm, the changes in crystallization time are those typical of the nucleation limited regime, where only finite size effects are relevant $t_{\text{CRY}} \sim h_{\text{PET}}^{-1}$.¹³ In such regime, the thickness of the capping PS layer has no effect on the crystallization kinetics of PET.

For all the data series, regardless of the value of h_{PS} , a further reduction in thickness is accompanied by an increase in t_{CRY} , which, for $h < h_{\text{PET}}^*$, exceed the trend of thicker films based on nucleation effects. In this regime, at constant thickness of the crystallizable layer, an increase in h_{PS} corresponded to a reduction of t_{CRY} capable to scale down, but not to suppress, the confinement effects.

This effect, not predicted by any current theory, is remarkable. The crystallization time of a 26.5 nm thick film of PET in the multilayer configuration, see Figure 2, is $16 \cdot 10^3$ s when $h_{\text{PS}} = 10$ nm, $11 \cdot 10^3$ s for $h_{\text{PS}} = 50$ nm and drops to $5 \cdot 10^3$ s if $h_{\text{PS}} = 250$ nm; for comparison, films of the same thickness in direct contact with two Al layers¹³ (a condition virtually occurring for $h_{\text{PS}} \rightarrow 0$, if short-range forces are neglected) do not crystallize within 55 h, that is $t_{\text{cry}} \gg 200 \cdot 10^3$ s, while much thicker films ($h_{\text{PET}} \gg 1$ μm) crystallize within 10 min.

The experimental trends in Figures 1 and 2 do, hence, imply that the interfacial interactions between PET and Al decreases upon increase of the thickness of the PS layer. In such case, in fact, the number of chains of PET irreversibly adsorbed onto Al would decrease.

Figure 4 Properties of multilayers with constant h_{PET} (26.5 nm) and variable h_{PS} . **a)** Direct proportionality between the crystallization time and the thickness of the layer of PET irreversibly adsorbed on aluminum. **b)** Correlation between increase in Hamaker (ΔA) constant with respect to 250 nm thick PS films (dashed line) and the thickness of the layer of PET irreversibly adsorbed on aluminum (green circles); **c)** segmental relaxation time and **d)** nucleation time as a function of h_{PS} .

We tested whether our findings could be ascribed to the taming effect of interfacial interactions recently described by Simavilla et al.,²⁴ predicting a reduction in adsorbed PET amount upon increase of the thickness of the PS layer. The idea is based on the expected impact of h_{PS} on the effective Hamaker constant, A_{eff} ,³⁴ of these hybrid system. The latter parameter quantifies the dispersion forces acting across PET between the two aluminum layers, originating from the interaction of fluctuating dipoles across different materials. Based on this reasoning, it is possible to correlate the value of the Hamaker constant with the depth of the intermolecular potential between PET and Al and, hence, to the number of chains adsorbed.

Figure 5 Proportionality between the adsorbed amount and the apparent Stokes-Einstein exponent of thin films of PET present in multilayers with constant h_{PET} (26.5 nm) and variable h_{PS} .

In our multilayers, the effective Hamaker constant at the Al/PET interface is always negative, which implies that the multilayer are stable against desorption regardless of the thickness of the PS capping layer. A_{eff} becomes less negative upon increase of h_{PS} , corresponding to smaller Al/PET interfacial interactions and thus smaller adsorbed amount. We experimentally validated this point by verifying that the number of PET chains adsorbed per unit surface, Γ_{PET} , scales with A_{eff} , see Figure 4.b. In particular, we proved that at constant thickness of PET ($h_{\text{PET}} = 26.5$ nm), a reduction of h_{PS} from large values (> 100 nm) to 15 nm provides an increment in long-range forces corresponding to an energy gain of $0.7 k_{\text{B}}T$, sufficient to ensure irreversible chain adsorption.²⁴ In particular the amount of PET chains adsorbed on Al increases by more than a factor 2 upon reduction of the PS capping layer.

Based on Eq 1, the crystallization time is affected by three parameters, τ , Λ and ξ respectively related to molecular mobility, nucleation rate and the decoupling between translational and rotational diffusion. In the following paragraphs we discuss on how h_{PS} and interfacial forces could affect these three terms. In figure 4c we plotted the value of the segmental relaxation time of multilayers with constant h_{PET} (26.5 nm) and variable h_{PS} . No significant change is observed within experimental errors. This result was expected, because varying the thickness of the PS capping layer corresponds to a very small increase in the forces acting at the PET/Al interface, quantifiable as disjoining pressure would be the order of 10^{-4} atm. Several orders of magnitude larger values (typically 0.1 GPa) are, instead, necessary to affect segmental dynamics.³⁶⁻³⁸ Similar arguments can be considered for the nucleation, because the variation in surface tension at the PET/PS interface is on the same order of magnitude of the disjoining pressure.³⁹⁻⁴⁰ These considerations are in agreement with the experimental results shown in figure 4d where the nucleation time, t_N , of multilayers with constant h_{PET} (26.5 nm), estimated as the onset of the changes in dielectric signal upon crystallization,⁴¹ is h_{PS} -invariant. This trend is also in line with the measured values of t_{CRY} in the nucleation-limited regime ($h_{PET} > 20-30$ nm) where data from multilayers containing films of PS of different thickness do perfectly overlap.

Differently than for the two previous terms, the value of the Stokes-Einstein exponent, obtained by fitting the experimental data in Figure 3 to Eq 1, is significantly affected by the thickness of the capping layer. ξ increases from 2.5, a value comparable to that found for single layers of PLLA, see Figure 1, to 5.5 when h_{PS} is reduced from 140 to 10 nm. This trend implies that ξ grows with Γ_{PET} , see Figure 5, which verifies our hypothesis.

The perturbation in crystallization kinetics rate observed in our multilayers upon reduction of the noncrystallizable layer is, consequently, totally imputable to an increase in interfacial potential between crystallizable layer and the supporting Al interface which induces an increase in adsorbed amount.

The increase in the number of adsorbed chains, at constant thickness of PET layer, implies a lower monomer density in the core of the film, that is, a shortage of crystallizable material. Consequently, at constant h_{PET} , increasing h_{PS} results in smaller neat driving forces for crystal growth,⁴² causing an increase in t_{CRY} . To further prove the validity of the hypothesis on the depletion of crystallizable material, we verified that the crystalline volume fraction reached at the end of the crystallization process ($\sim\chi$, see Eq 2) increases with h_{PS} , see Figure 6. Such results can be further parametrized by estimating the overall growth rate G_{TOT} ($\sim t_{CRY}^{-1}$) of a film of PET modeled as the sum of two chains populations, adsorbed vs nonadsorbed. Considering that the growth rate of the adsorbed chains is negligible¹³ with respect to that of the other molecules, G , we get $G_{TOT}/G \sim 1 - \Gamma_{PET}/m_{PET}$, where $m_{PET}(\sim h_{PET})$ is the total mass of the PET chains per unit area. In the case of experiments where the value of h_{PET} is kept constant, we find the scaling $t_{CRY} \sim \Gamma_{PET}$, which is verified by the data in Figure 4a.

FIG 6 Impact of the thickness of PS on χ (see Eq 1), the amount of dipole moments immobilized at the end of the crystallization process for films of PET of constant thickness (26.5 nm). Larger χ values correspond to larger crystalline contents. We observe a reduction in χ upon reduction in h_{PS} , that is, for multilayers with more negative effective Hamaker constants.

With these considerations in mind, we propose that, upon increase of the amount of chains adsorbed at the interfaces, the formation of ordered structures slows down due to the lesser availability of mobile chain at the growth front. During our experiments such a condition is always fulfilled, because the formation of an equilibrated adsorbed layer of PET onto Al is achieved before the onset of crystallization.¹³

Because Γ_{PET} smoothly increases at smaller h_{PS} , we expect that the shortage-induced reduction in growth rate would manifest around a critical thickness h^* decreasing with the size of the screening layer, in line with the evidence in Figure 2. Finally, we remark that we could successfully explain the complex phenomenology affecting the crystallization of the PET layers by simply considering the changes in the number of PET chains irreversibly adsorbed on the Al substrate, and by neglecting any possible perturbation in the molecular conformations at the PET/PS interface. While we cannot exclude that a modification of the polymer/polymer interface could take place by varying h_{PS} , the results of our experiments clearly indicate that the effect of such perturbations on the crystallization of the PET should be qualitatively similar to those described for the PET/Al interface or, eventually, negligible.

Conclusion

We verified that adequately capping a crystallizable film can be used to tune its crystallization kinetics. This process is mediated by a change in the amount of crystalline chains irreversibly adsorbed onto the supporting substrate, which induces a shortage of mobile chains at the crystal growth front. This phenomenon corresponds to a virtual increase in the Stokes-Einstein exponent, indicating less efficient mass transport. The method we introduced permitted us to achieve remote control of the crystallization kinetics of thin polymer films without changing the size of the crystallizable layer or the interfacial chemistry. Importantly, these effects are related to a perturbation in the amplitude of the interfacial interactions, that can be promptly

determined before fabricating the multilayers, which ensures an efficient control of the processing conditions.⁴³

Supporting information available Sample preparation and determination of the layer thicknesses, determination of the effective Hamaker constant, analysis of the crystallization kinetics, of the structural relaxation,

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