Supporting Information for:

Remotely controlling the crystallization of thin polymer coatings

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A. Sample preparation and determination of the layer thicknesses

- **B.** Analysis of the Crystallization Kinetics
- C. Analysis of the Structural Relaxation

A. Sample preparation and determination of the layer thicknesses

Poly(ethylene terephthalate) (PET), in sheets of 250µm, M_n =38.80kg/mol and M_w/M_n =1.97, was dissolved in a trifluoroacetic acid (TFA) and chloroform mixture (5/2 ratio) and spincoated (1 min at 3000 rpm) on top of clean glass plates covered with an aluminum electrode (99% Al, pressure<10⁻⁶mbar, evaporation rate ≥ 10 nm s⁻¹, thickness ~ 50nm; contact with air, before spincoating, favors formation of a 2-3nm Al₂O₃, which enhances affinity with PET). Polystyrene, obtained from Polymer Source inc. (Mw=932kg/mol, Mw/Mn=1.2) was dissolved in toluene and spincoated (1 min at 3000 rpm) on top of the PET film. Each spincoating step was followed by annealing (20 min at 348 K, Tg_{PET}< 348 K <Tg_{PS}) and then placed in vacuum to favor solvent evaporation (> 24h at 7·10⁻⁵bar). The ~ 4mm² multilayer capacitor was completed by evaporation of the top aluminum electrode (same evaporation conditions, thus no oxide layer in contact with the PS). Thicknesses of 15-1500 nm and 10-250 nm for PET and PS respectively, were obtained in the double layer configuration and verified by ellipsometry and Atomic Force Microscopy (AFM). The final configuration, from bottom to top, can be expresses as Al/AlOx/PET/PS/Al. We could not prepare samples in the inverted geometry (Al/AlOx/PS/PET/Al) because no selective solvent would dissolve PET and not PS.

Determination of the thickness of the dielectric layers composing the multilayer by means of the total electric capacitance would impose large uncertainties. We thus preferred measuring the thickness of each single layer separately. Within experimental uncertainties, measurements by means of different techniques, such as ellipsometry, capacitance measurement and AFM provided the same value for the layer thicknesses.

B. Analysis of the Crystallization Kinetics

We show data on a series of multilayers of constant hPET (=26.5 nm) and variable hPS, and the corresponding dielectric spectra of the PET layer.



In the previous graphs, we showed the time evolution of the dielectric strength for the above-mentioned series. To ease comparison, after fitting with equation (1) of the text, we removed the contribution from adsorption and normalized the curves from 0 to 1, see Figure S1. The normalized dielectric strength thus reads as an Avrami equation, written in a KWW form

$$\Delta \varepsilon_N(t) = 1 - \exp(-t/t_{CRY})^{\beta}$$
(S1)

A straight line corresponding to a conversion of ~ 63% (1-e-1) crosses the curves at t=t_{CRY}. We assigned the value of the incubation time, t_N , to the time corresponding to the condition $\Delta \epsilon_N(t_N) = 0.015$, that is, a conversion comparable to the noise in our measurements.

In Figure S2 we show the evolution of $\Delta \epsilon_N$ at short times, the value of t_N – evaluated as the shortest time after which $\Delta \epsilon_N$ exceeds by one standard deviation the constant value characteristic of the incubation period [1] – is not affected by h_{PS} . A similar information can be extracted from the Avrami plot, see Figure S3. This type of graph also permitted to verify that the value of the Avrami exponent, β , is independent on t_N , a condition further confirmed by plotting the normalized dielectric strength as a function of t/t_{CRY} , see Figure S4. While an excellent overlapping is observed at larger values of t/t_{CRY} , the behavior at short annealing times is depending on h_{PS} , as expected by the constant t_N when plotting $\Delta \epsilon_N$ vs t. We can thus conclude that varying h_{PS} does not affect the nucleation of the underlying PET layer.

We analyzed the data sets of our measurements both via global fits to Eq 1 of the main text and via separated fits of the adsorption and crystallization components. The results of the two procedures are comparable within 5%, except for films thicker than 140 nm, where a larger discrepancy (<15%) is observed. In this thickness regime, in fact, the crystallization process is too fast and the reduction in dielectric strength due to crystallization is convoluted to that due to adsorption. In this case, we considered the "separated" fitting procedure as more reliable, because of the smaller number of free parameters per fitting run.

D. Analysis of the Structural Relaxation



Figure S5

In Figure S5 we plotted the frequency dependence of the dielectric relaxation (here the imaginary part of the dielectric function) of PET for multilayers containing layers of PS of thickness varying from 253nm to 10 nm. To ease comparison, we shifted the curves on the vertical axis. The frequency of the maximum of structural corresponds to the condition $f_{\text{max}} \tau 2\pi = 1$. f_{max} is not affected by h_{PS}, thus the relaxation time of PET is not influenced by the thickness of the PS layer.

In conclusion, as mentioned in the text, τ , t_N and β are not affected by h_{PS} , while t_{CRY} increases upon reduction of the thickness of the noncrystallazible layer. Consequently, as expected from the constant volume of the crystallizable layer, we can discard the role of nucleation and segmental mobility on the trends in $t_{CRY}(h_{PS})$.

References

[1] Sanz, A.; Nogales, A.; Ezquerra, T. A.; Macromolecules 2010, 43, 29-32