Effect of environmental humidity on the ionic transport of poly(ethylene oxide) thin films by local dielectric spectroscopy

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Supporting Information

Local dielectric spectroscopy procedure. For nDS measurements, we recorded first a nDI map using the so-called *point and shoot* protocol implemented by the AFM manufacturer (Bruker). This method allowed placing the AFM probe on specific spots of the sample's surface, depending on the nDI contrast information. Then, at each one of these spots, we recorded a tapping mode ramp. The ramp size was set to 50 nm, the trigger amplitude error was -50 mV, and the ramping rate was 1 Hz. Dynamic ramping experiments were performed before measuring each frequency point. In this way we guaranteed a reproducible tip-sample distance. Examples of the dynamic ramping curves acquired prior to nDS are presented in Figure S1 for the three different humidity conditions. Throughout all these experiments, the mechanical cantilever excitation was hold constant. With increasing humidity, we observe a decrease of about 120 mV in the free tapping amplitude from 15 %RH to 50 %RH (figure 2a-c). This correlates to a reduced tip-sample distance by ~ 5 nm. Considering this shift, the usual tip-sample distance in our nDS spectroscopy experiments was $z_0 = 50 \pm 5$ nm. At such distance, the mechanical excitation of the probe was suppressed and an AC voltage was applied to it. The AC bias amplitude was 6.8 V_{RMS} and the frequency was swept in the $1 \le f(Hz) \le 10^5$ range.



Figure S1: Tapping mode ramping curves, as captured prior to nDS at a) 15 %RH, b) 35 %RH, and 50 %RH, respectively.

nDS analysis. The phase of the probe oscillations at 2ω does not provide the nDS spectra in a straight-forward manner. The resulting nDS signal was obtained by calculating the frequency-dependent phase shift $\Delta\theta(\omega)$, defined as:

$$\Delta \theta(\omega) = \theta_{REF}(\omega) - \theta_{SAMPLE}(\omega) \tag{SI-1}$$

where $\theta_{\text{REF}}(\omega)$ is the so-called *reference phase*, and $\theta_{\text{SAMPLE}}(\omega)$ is the phase measured for the PEO sample. The reference phase was determined by performing an nDS spectrum on a material with negligible electrical losses at room temperature (PVAc thin film, h = 500 nm, $M_{\text{w}} = 240$ kg/mol). The θ_{REF} parameter depends on the electronics and the mechanical characteristics of the AFM probe. The reference measurement was verified to show a humidity independent behavior (Figure S2).



Figure S2. nDS data for PVAc measured at room temperature as a function of %RH. The circles represent 15 %RH, while the green and black lines show the results at 35% and 50 %RH.

For the physical analysis of the nDS spectra, we have to model the total system capacitance $C^*(\omega)$. Here, we used the physical model of the capacitance between the AFM probe and a thin film sample, by considering separately the contributions from the two parts of the probe: the apex of the tip and the cantilever. This model was presented by Miccio and collaborators previously.¹ They modeled the tip contribution following the results presented by Gomila and collaborators,²⁻⁴ leading to:

$$\frac{\partial C_{TIP}^{*}(\omega)}{\partial z} \propto 2\pi\varepsilon_0 \frac{R^2 (1 - \sin\theta_0)}{z_0^2 + z_0 R (1 - \sin\theta_0)} \left(1 + \frac{h}{z_0 \varepsilon_{LOC}^{*}(\omega)}\right)^{-1} \times F_{2\omega_{eTIP}^{*}}(\omega) \propto \left(1 + \frac{h}{[z_0 + R (1 - \sin\theta_0)] \varepsilon_{LOC}^{*}(\omega)}\right)^{-1}$$
(SI-2)

where $\varepsilon_0 = 8.85 \times 10^{-12}$ F m⁻¹ is the vacuum permittivity, *R* is the effective tip radius and θ_0 is the cone angle. The subscript LOC in $\varepsilon^*(\omega)$ denotes that, in general, this complex dielectric function will be related to the local properties of the material.

The cantilever contribution can be written as:

$$\frac{\partial \mathcal{C}_{CANT}^{*}(\omega)}{\partial z} \propto \frac{\varepsilon_0 W \zeta}{T} \left[\left(1 + \frac{h}{T \varepsilon_{AVG}^{*}(\omega)} \right)^{-1} - \frac{T}{L \sin \alpha} \left(1 + \frac{h}{T \varepsilon_{AVG}^{*}(\omega)} \right)^{-1} \right]$$
(SI-3)

where W is the cantilever width, L is the cantilever length, α is the cantilever angle, T is the cone length, and ξ accounts for the border effects. The subscript AVG in $\varepsilon^*(\omega)$ indicates that it refers to an average film property as the cantilever contribution is supposed to be non-local. The total frequency-dependent probe–sample electrical force ($F_{2\omega}^*$, eqn 1 in the main manuscript) can be evaluated from the sum of eqn (SI-2) and eqn (SI-3). The phase shift measured by nDS, relates to these equations as:

$$\Delta \theta (\omega) = \tan^{-1} \left\{ \frac{lm \left[\frac{\partial C^*(\omega)}{\partial z} \right]}{Re \left[\frac{\partial C^*(\omega)}{\partial z} \right]} \right\}$$
(SI-4)

In this work, the values used for the geometrical characteristics of the probe with the exception of the tip radius were those provided by the probe manufacturer. The effective tip radius, which is important for the tip apex contribution, was determined for each particular probe by the calibration procedure described as follows. The AFM sample stage was heated up to 333 K, and nDS measurements were carried out on a PVAc thin film (the same used for $\theta_{\text{REF}}(\omega)$). In The resulting $\Delta\theta(\omega)$ signal was modeled using eqn (SI-2) to (SI-4). We used the Havriliak– Negami function with fixed parameters for describing the dielectric function of PVAc $\varepsilon_{PVAc}^{*}(\omega)$ ⁵. Finally, we found the value of *R* in eqn(SI-2) that provided the most appropriate description of the PVAc nDS data. The so-obtained value was fixed and used for the subsequent analysis of the nDS experiments on the PEO films. Here, the *R* value was 18 ± 2 nm.

Maxwell-Wagner-Sillars (MWS) relaxation. For an heterogenous material composed by a 2-layer structure, the MWS relaxation follows a Debye-like process: ⁶

$$\varepsilon_{2L-MWS}^{*}(\omega) = \varepsilon_{\infty} + \frac{\Delta \varepsilon_{MWS}}{1 + i\omega/\omega_{MWS}}$$
(SI-5)

where ε_{∞} is the permittivity at the high frequency limit, $\Delta \varepsilon_{MWS}$ is the relaxation strength, and ω_{MWS} relates to the timescale of the relaxation process. The interfacial polarization builds up at the interface between the two layers/phases. In PEO, the crystalline phase is in principle non-conducting. Thus, it is described by a frequency independent dielectric constant ε_c , and occupies a certain volume fraction φ . The amorphous phase, in this study, is conductive and it is described by its intrinsic conductivity σ and the dielectric constant ε_a . Following this idea, the parameters in eqn. (SI-5) relate to the material properties as:⁶

$$\varepsilon_{\infty} = \frac{\varepsilon_c \varepsilon_a}{\varepsilon_c (1 - \varphi) + \varepsilon_a \varphi}$$
(SI-6)

$$\Delta \varepsilon_{MWS} = \frac{\varepsilon_c}{\varphi} \left[1 - \frac{\varepsilon_a}{\frac{\varepsilon_c}{\varphi} (1 - \varphi) + \varepsilon_a} \right]$$
(SI-7)

$$\omega_{MWS} = \frac{\sigma\varphi}{\varepsilon_0 [\varepsilon_c (1 - \varphi) + \varepsilon_a \varphi]}$$
(SI-8)

Following this simple approach to model the nDS data, we did not account properly for experimental data, as previously reported⁵. To obtain a good description, the MWS relaxation has to be modeled as a superposition of distinct Debye-like relaxations ($\varepsilon_{MWS}^{*}(\omega)$) following a Gaussian distribution of conductivities $g(\log_{10} \sigma)_{:5}$

$$\varepsilon_{PEO-MWS}^{*}(\omega) = \int_{0}^{\infty} \varepsilon_{2L-MWS}^{*}(\omega) g(\log_{10} \sigma) d(\log_{10} \sigma)$$
(SI-9)

References

- 1. L. A. Miccio, M. M. Kummali, G. A. Schwartz, Á. Alegría and J. Colmenero, *Ultramicroscopy*, 2014, **146**, 55-61.
- 2. G. Gomila, J. Toset and L. Fumagalli, *Journal of Applied Physics*, 2008, **104**, 024315.
- 3. L. Fumagalli, G. Ferrari, M. Sampietro and G. Gomila, *Nano Letters*, 2009, **9**, 1604-1608.
- 4. L. Fumagalli, G. Gramse, D. Esteban-Ferrer, M. A. Edwards and G. Gomila, *Applied Physics Letters*, 2010, **96**, 183107.
- 5. D. E. Martínez-Tong, L. A. Miccio and A. Alegria, *Soft Matter*, 2017, **13**, 5597-5603.
- 6. F. Kremer and A. Schönhals, *Broadband Dielectric Spectroscopy*, Springer, 2003.