

# Adsorption Kinetics of Ultrathin Polymer Films in the Melt Probed by Dielectric Spectroscopy and Second-Harmonic Generation

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**ABSTRACT:** We studied the adsorption kinetics of supported ultrathin films of dye-labeled polystyrene (*l*-PS) by combining dielectric spectroscopy (DS) and the interface-specific non-linear optical second harmonic generation (SHG) technique. While DS is sensitive to the fraction of mobile dye moieties (chromophores), the SHG signal probes their anisotropic



orientation. Time-resolved measurements were performed above the glass transition temperature on two different sample geometries. In one configuration, the *l*-PS layer is placed in contact with the aluminum surface, while in the other one, the deposition is done on a strongly adsorbed layer of neat PS. From the time dependence of the dielectric strength and SHG signal of the *l*-PS layer in contact with the metal, we detected two different kinetics regimes. We interpret these regimes in terms of the interplay between adsorption and orientation of the adsorbing labeling moieties. At early times, dye moieties get adsorbed adopting an orientation parallel to the surface. When adsorption proceeds to completeness, the kinetics slows down and the dye moieties progressively orient normal to the surface. Conversely, when the layer of *l*-PS layer is deposited on the strongly adsorbed layer of neat PS, both the dielectric strength and the SHG signal do not show any variation with time. This means that no adsorption takes place.

# **1. INTRODUCTION**

Polymer adsorption is relevant in different technological fields ranging from coatings to pharmaceutical applications and nanocomposite materials.<sup>1</sup> For this reason, much effort has been devoted to understanding both experimentally<sup>2</sup> and theoretically<sup>3</sup> the kinetics of adsorption of polymer layers on a solid surface. At the interface, the polymer conformation is perturbed compared to the bulk because of the interaction of the surface and geometrical constraints. As a consequence, in ultrathin polymer films (thickness <200 nm), dynamical properties such as diffusion,<sup>4</sup> crystallization kinetics,<sup>5</sup> and the glass transition<sup>6,7</sup> may substantially differ from their bulk counterpart. Hence, for a better control of the functionality of polymer layers, the understanding of surface—polymer interaction at a fundamental level is essential.

First studies of polymer adsorption were focused on predicting the adsorbed amount and the density profile at equilibrium.<sup>8</sup> However, recent studies revealed that adsorbed polymer layers may not fully equilibrate on experimental time scales.<sup>9,10</sup> Moreover, polymer adsorption on a solid surface proceeds through various regimes of different kinetics before equilibrium may be reached, after days or weeks, depending on the molecular characteristics of the polymer.<sup>11,12</sup> In particular, the conformation of each newly adsorbing chain changes with time and surface coverage: chains arriving first at the surface adsorb with a relatively flat conformation, while those arriving later adsorb with a loosely bound conformation.<sup>13-15</sup>

A number of experimental approaches such as neutron scattering,<sup>16</sup> ellipsometry,<sup>17</sup> and IR spectroscopy<sup>18</sup> have been employed to study the nature of polymer adsorption onto surfaces from dilute solutions. Recently, we investigated, by dielectric spectroscopy, the effect of annealing on the dielectric response of multilayer ultrathin films capped between aluminum electrodes.<sup>19</sup> By selectively placing a layer of dye-labeled polystyrene (PS) at different depths inside films of neat PS, we observed changes of the glass transition temperature ( $T_g$ ) with respect to the bulk exclusively when the labeled layer is placed in contact with the metal. Furthermore, for ultrathin films of neat PS we found that the variation of  $T_g$  during annealing follows the same kinetics as the thickening of the layer irreversibly adsorbed onto the solid substrate.<sup>20</sup> Deviations from bulk behavior would arise from nonequilibrium conformations of the adsorbed chains, as

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confirmed by the evolution of the distribution of relaxation times upon annealing. These studies motivated further investigations of the adsorption process in order to achieve a direct experimental observation of real-time conformational changes that occur during the formation of the adsorbed layer. For this aim, we used dielectric spectroscopy to study the segmental mobility, in conjunction with second-harmonic generation. This last technique is based on the nonlinear optical response of chromophores which are arranged in a noncentrosymmetric configuration. The SHG signal is very sensitive to any breaking of inversion symmetry in materials, induced by e.g. internal electrical or magnetic fields,<sup>21</sup> surfaces, and interfaces.<sup>22,23</sup> The symmetry at interfaces can also be broken by molecular adsorption.<sup>24</sup> The particular arrangement of the adsorbed molecules, oriented parallel or perpendicular to the interface, can in itself constitute a source of SHG signal. In our study, we have employed SHG active dye moieties, whose orientation upon adsorption is probed.

### 2. EXPERIMENTAL SECTION

2.1. Synthesis of the Labeled Polystyrene (I-PS). 4-Aminobenzonitrille (Aldrich), 2-(methylphenylamino)ethanol (Aldrich), methacrylic anhydride (Aldrich), styrene (Sigma-Aldrich), and 2,2'-azoisobutyronitrile (AIBN) (Fluka) were used as received. The synthesis of the chromophore 4-[(E)-[4-(2-hydroxyethyl(methyl)amino)phenyl]azo]benzonitrile (CN) was carried out according to literature procedures.<sup>25</sup> The photochromic methacrylate 2-[4-[(E)-(4-cyanophenyl)azo]-N-methylanilino]ethyl 2-methacrylate (MCN) was obtained starting from azo dye (CN) and methacrylic anhydride and following the reaction elsewhere described.<sup>26</sup> The labeled polystyrene, poly(2-[4-[(E)-(4-cyanophenyl) azo]-N-methylanilino]ethyl 2-methacrylate-co-styrene), was synthesized in bulk radical polymerization in the presence of azobis(isobutyronitrile) (AIBN), used as radical initiator. The reaction was performed in an ampule, purged with nitrogen, where the styrene monomer was first mixed with the methacrylic monomer (MCN) (3% mol) and then with the AIBN initiator (0, 15% w/w). The mixture was kept at 90 °C in a nitrogen atmosphere for 72 h. After completion of the reaction, the copolymer was dissolved in benzene and purified by precipitation in methanol. Gel permeation chromatography (GPC) measurements revealed that the functionalized polystyrene (*l*-PS) had a  $M_w = 20$  kg/mol and PDI = 2.

The labeling azobenzene organic molecule (4-[(E)-[4-(2-hydroxyethyl (methyl)amino)phenyl]azo]benzonitrile) has both a strong permanent dipole moment and hyperpolarizability, which make this group a suitable dielectric label and a probe for SHG experiments.

Some experiments were conducted with atactic polystyrene ( $M_w = 97$  kg/mol, PDI = 1.01) purchased from Scientific Polymer products and used as received.

**2.2. Preparation of Ultrathin Polymer Films.** Ultrathin single layers of labeled PS (*l*-PS) were prepared by spincoating filtered solutions of the polymer in chloroform on glass slides onto which a 50 nm thick layer of aluminum was previously deposited by thermal evaporation in a high vacuum ( $p \le 10^{-6}$  mbar). After deposition, samples were annealed at 110 °C for 20 min on a hot plate in order to remove residual solvent and to reduce mechanical stresses induced by the spincoating process. Subsequently, the samples were kept under high vacuum at room temperature overnight. Exclusively for the dielectric measurements, a second aluminum layer was evaporated at high deposition rate (~10 nm/s) onto the polymer film to form a top electrode.

Bilayer films were prepared by spin-coating a layer of *l*-PS on top of a densely adsorbed layer of neat PS prepared following the experimental approach used by Guiselin.<sup>27,28</sup> The procedure consisted in depositing a thick layer of PS onto the Al substrate and annealing it at 150  $^{\circ}C$  for  ${\sim}20$  h in order to promote the formation of a strongly adsorbed layer at the metal interface.

After completion of the annealing stage, the nonadsorbed chains were washed away dipping the samples in the same good solvent used for spin-coating (chloroform). Guiselin brushes were then dried overnight in high vacuum ( $p \le 10^{-6}$  mbar) before preparing the bilayer films.

**2.3. Dielectric Relaxation Spectroscopy.** A high-resolution dielectric analyzer (Alpha Analyzer, Novocontrol Technologies) is used to measure the complex dielectric function  $\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$  ( $\omega$  is the angular frequency,  $\varepsilon'$  and  $\varepsilon''$  are the real and the imaginary parts of the complex dielectric function) in the frequency range from  $10^{-1}$  to  $10^6$  Hz. All measurements were performed under N<sub>2</sub> in a closed cell to prevent any possible oxidation, degradation, or moisture uptake. The thickness of the samples *h* was evaluated from the value of the real part of the sample capacitance (*C'*) outside the region of dipolar relaxation processes, using the relation for the capacitance in the geometry of parallel plates, which reads  $C' = \varepsilon_{\infty} \varepsilon_0(S/h)$ , where  $\varepsilon_{\infty}$  is dielectric constant of the polymer,  $\varepsilon_0$  is the permittivity of the vacuum (8.85 ×  $10^{-12}$  F/m), and *S* is the effective area of the capacitor (4 mm<sup>2</sup>).

The bilayer film was modeled as a series of capacitance where  $C_{tot}^*$  is given by  $1/C^*_{tot} = 1/C^*_{PS} + 1/C^*_{l-PS}$  where  $C^*_{PS}$  and  $C^*_{l-PS}$  are the complex capacitance relative to the PS and to the labeled PS, respectively. From the knowledge of the intrinsic contribution of neat PS, it was possible to extract the contribution of the labeled layer from the total response of the bilayer film.

To obtain quantitative information from the isothermal dielectric spectra, relaxation processes were analyzed using the empirical Havriliak–Negami (HN) function

$$\varepsilon^*(\omega) = \varepsilon_{\infty} + \frac{\Delta\varepsilon}{\left[1 + (i\omega\tau_{\rm HN})^{\alpha}\right]^{\beta}} \tag{1}$$

where  $\tau_{\rm HN}$  is the relaxation time,  $\alpha$  and  $\beta$  are shape parameters describing the symmetric and asymmetric broadening of the  $\alpha$ -peak, and  $\Delta \varepsilon$  is the relaxation strength. This last quantity is proportional to both the mean-square dipole moment and the density of dipoles ( $\Delta \varepsilon \sim N\langle \mu^2 \rangle$ ) and provides a measure of the amount of mobile polar chain segments involved in the structural relaxation.

**2.4. Second-Harmonic Generation.** SHG measurements were performed using a Ti:sapphire laser at a wavelength of 800 nm, emitting 100 fs short pulses with a repetition rate of 82 MHz. First, the beam was polarized by a Glann-laser polarizer mounted on a motorized rotation stage, which was alternated between s- and p-polarization. After passing a filter to exclude any 400 nm light, the beam was focused on the sample at an incidence angle of  $45^{\circ}$ . The reflected beam was filtered to exclude any 800 nm light and subsequently the SHG passed through a p-polarized analyzer. Finally, the SHG signal was collected by a photomultiplier tube cooled to  $-20 \,^{\circ}$ C to improve the signal-to-noise ratio. The resulting electrical current pulses were processed by a gated photon counter.

In the dipole approximation the optical polarization  $P(2\omega)$  at the double frequency  $\omega$  of incident light can be written as<sup>29</sup>

$$\mathbf{P}_{i}(2\omega) = \chi_{ijk}^{(2)}(2\omega:\omega,\omega)\mathbf{E}_{j}(\omega)\mathbf{E}_{k}(\omega)$$
(2)

where  $E(\omega)$  is the electric field of the incident light, *i*, *j*, and *k* are the Cartesian coordinates, and  $\chi_{ijk}^{(2)}$  is the second-order susceptibility tensor. This third-rank tensor consists of 27 elements; however, their number is considerably simplified depending on the particular symmetry of the system at study. For instance, in the case of an in-plane isotropic sample the susceptibility tensor becomes

$$\chi_{ijk}^{(2)}(2\omega:\omega,\omega) = \begin{pmatrix} 0 & 0 & 0 & \chi_{xxz} & 0\\ 0 & 0 & \chi_{yyz} & 0 & 0\\ \chi_{zxx} & \chi_{zyy} & \chi_{zzz} & 0 & 0 & 0 \end{pmatrix}$$
(3)



**Figure 1.** Evolution of the dielectric strength,  $\Delta \varepsilon$ , upon annealing time. Open symbols correspond to a single layer of *l*-PS, 30 nm thick, deposited on aluminum; half-filled symbols correspond to a 30 nm film *l*-PS deposited on a strongly absorbed layer of neat PS. The inset on the top illustrates the contribution due to reorganization of chain segments adsorbed before the measurement is started (red line); see text.

where the *x*, *y* are the coordinates in the plane of incidence and *z* is the coordinate normal to the plane. For this particular susceptibility tensor there are only three independent elements:  $\chi_{zxx} = \chi_{zyy} \neq 0$ ,  $\chi_{xxz} = \chi_{yyz} \neq 0$ , and  $\chi_{zzz} \neq 0$ . These tensor elements can be addressed depending on the choice of polarizer—analyzer combination. More specifically, for incident light polarization oriented perpendicular to the plane of incidence (S<sub>IN</sub>-polarization) and SHG polarization along the plane of incidence (P<sub>OUT</sub>-polarization) the  $\chi_{zyy}$  component is addressed. This component is attributable to molecules oriented in the plane of the sample as indicated by the *y* indices. Similarly, the P<sub>IN</sub>—P<sub>OUT</sub> polarizer analyzer combination can be related to the  $\chi_{zxxx}$   $\chi_{zzz}$  and  $\chi_{xxz}$  components. Because the  $\chi_{zzz}$  component is attributable to molecules oriented perpendicular to the plane of the sample, the ratio of SHG intensity measured in the P<sub>IN</sub>—P<sub>OUT</sub> versus S<sub>IN</sub>—P<sub>OUT</sub> combinations constitutes a measure for the out-of-plane anisotropy of the sample.

# 3. RESULTS

Investigation of polymer adsorption via dielectric spectroscopy was performed by monitoring changes in the structural ( $\alpha$ -) relaxation process in real-time and isothermal conditions. The  $\alpha$ -process is the dielectric signature of the dynamic glass transition and appears as a peak of strength  $\Delta \varepsilon$  in the frequency dependence of the imaginary part ( $\varepsilon''$ ) of the complex dielectric function. The dielectric strength  $\Delta \varepsilon$ , at a given temperature, is related to the mean-square dipole moment and provides a measure of the volume fraction of molecules relaxing on the time and length scale of the glass transition.<sup>30</sup> Figure 1 shows the annealing time dependence of  $\Delta \varepsilon$  at 125 °C for a single layer film of *l*-PS deposited on aluminum as well as for a layer of *l*-PS deposited on top of a strongly adsorbed layer of neat PS (see sketches of the two systems in Figure 1).

For the single layer film of *l*-PS in direct contact with the aluminum substrate, we observe a drop of  $\Delta\varepsilon$  up to ~35% of its starting value after 10<sup>5</sup> s of annealing. This reduction takes place through different regimes that are clearly distinguishable on a logarithmic scale via the presence of two crossovers, at  $\approx$ 700 s  $(t_{\rm on})$  and at  $\approx$ 1.5  $\times$  10<sup>5</sup> s  $(t_{\rm off})$ . The decay rate of  $\Delta\varepsilon$  is constant at short times,  $t < t_{\rm on}$ , during which some chain segments



**Figure 2.** Values of  $\rho(t)$  of the SHG signal (blue) and the  $-\Delta \varepsilon_{\text{high}}$  data points (red), plotted as a function of time for an *l*-PS film deposited on Al (top panel) and an *l*-PS film deposited onto an strongly adsorbed layer of neat PS (bottom panel).

adsorbed during spin-coating, preannealing step, and before reaching the set-point temperature (125 °C) reorganize.<sup>20</sup> These segments form an incomplete adsorbed layer which is responsible for the lower dielectric strength as compared to the bulk ( $\Delta \varepsilon_{\text{bulk}} = 1.2$ ) at the start of the measurement.

The process of conformational reorganizations that occurs in this layer appears as a linear background in the plot  $\Delta \varepsilon$  vs log(t); see the red line in the inset of Figure 1. New adsorbing segments at 125 °C diffuse through the interfacial layer and after  $t_{on}$  (first crossover) start to get adsorbed. At  $t_{off}$  (second crossover), the reduction rate of  $\Delta \varepsilon(t)$  slows down, indicating a decrease of the adsorption kinetics. The presence of such two crossovers in  $\Delta \varepsilon(t)$  was first spotted in a previous dielectric study on polymer adsorption and is discussed elsewhere.<sup>20</sup> Unlike the single layer in contact with the aluminum substrate, the dielectric strength for the film of *l*-PS deposited onto the layer of strongly adsorbed PS shows a linear decrease as a function of log(t) for all times. Moreover, in this case the value of  $\Delta \varepsilon$  at the start of the measurement is the same as the bulk value, indicating that no adsorption takes place before the set-point temperature is reached.

Subtraction of the linear background (see above) from the measured dielectric strength for both systems allows obtaining the neat contribution corresponding to the adsorption of new segments, defined as  $\Delta \varepsilon_{\text{high}}$ . To visualize the adsorption kinetics in a more intuitive fashion, we plotted  $-\Delta \varepsilon_{\text{high}}$ , which represents a quantity proportional to the thickness of the adsorbed layer at the interface (see Figure 2).<sup>20</sup> For the single layer system, we observe a crossover from a power law regime at early times  $t < t_{\text{off}}$  to a logarithmic regime for  $t > t_{\text{off}}$ . This is in agreement with predictions from Monte Carlo studies on polymer adsorption.<sup>31</sup> Differently, the dielectric strength of the *l*-PS in the bilayer configuration, plotted in this way, shows essentially no variation with time.

In an attempt to gain more insight into changes of segmental conformation in the adsorbed layer, we performed time-resolved second-harmonic generation (SHG) experiments. The sample configurations were the same as previously investigated via dielectric spectroscopy. The SHG measurements were carried out by recording the in- and out-of-plane orientation specific signals from the interface. Analysis of the data was done by plotting the ratio  $\rho(t)$  between these in- and out-of-plane signals, i.e., the ratio of SHG intensity measured in the  $P_{IN}-P_{OUT}$  versus  $S_{IN}-P_{OUT}$  combinations, as a function of time. This ratio is sensitive to the changes of orientation upon adsorption:  $\rho(t)$  increases with a more perpendicular alignment of the probe moieties with respect to the surface. For the single layer system in contact with aluminum,  $\rho(t)$  shows a global reduction of about 50% at the end of the adsorption process. We observe that the decay of  $\rho(t)$  clearly stops at a time similar to  $t_{off}$  after which  $\rho(t)$  increases slightly until the end of the experiment. On the contrary,  $\rho(t)$  of the *l*-PS film in contact with the layer of strongly adsorbed PS remains constant, even after 20 h of annealing.

Hence, when the contact is established between *l*-PS and the metal, both  $-\Delta\varepsilon_{\rm high}$  and  $\rho(t)$  vary significantly with time in a manner which is correlated, while it is not the case for the contact between the *l*-PS and the layer of neat PS for which no variation occurs during the whole experiment.

#### 4. DISCUSSION

Immobilization of the labeled segments leads to a decrease of the mean square dipole moment  $\langle \mu^2 \rangle$  per unit volume and thus to a reduction of the dielectric strength,  $\Delta \varepsilon$ , as displayed in Figure 1 for the single layer on aluminum. Consequently, the increase of  $-\Delta \varepsilon_{\rm high}$  observed for this layer between  $t_{\rm on}$  and  $t_{\rm off}$  can be interpreted in terms of formation of an adsorbed layer containing segments which are adsorbed via the binding of the labeling dye moieties to the metal surface (see Figure 2).<sup>30</sup> Simultaneously, a decrease of the ratio  $\rho(t)$  is observed, implying that the labeling dye moieties tend to orient in a plane parallel to the surface while adsorbing. At this initial stage, the parallel orientation is allowed because the surface coverage is low (few segments are adsorbed) and large bare patches are available for adsorption.

The time evolution of the dielectric strength corresponds to a power law regime  $-\Delta\varepsilon_{\rm high}\sim t^{0.3}$ . Interestingly, the power law growth yields an exponent of 0.30  $\pm$  0.05, which is significantly lower than 0.5 as one would expect for diffusion-limited processes. This value is in line with earlier neutron reflectivity studies and Monte Carlo simulations and can be attributed to a screening effect due to the segments that were adsorbed before the setpoint temperature was reached (see above).<sup>31,32</sup>

The segmental adsorption mechanism provided here brings insight into other studies assessing the conformation of the whole chain. Indeed, the orientation of the dye moieties parallel to the surface could correspond to a flattened chain configuration, as expected from the literature.<sup>15,33</sup>

After a certain time, we observe a transition of the adsorption kinetics, as detected by DS. The time region (see Figure 2, hatched area, around  $t_{\text{off}}$ ) where we identify a transition between a power law regime and a slower logarithmic growth of  $-\Delta \varepsilon_{\text{high}}$  represents the beginning of a second stage of adsorption. This transition corresponds to a minimum of  $\rho(t)$  as determined by SHG, followed by an increase upon annealing.

During the second stage more segments are adsorbed at the surface, leading to a further increase of  $-\Delta\varepsilon_{\rm high}$ . However, the presence of chains with some adsorbed segments constitutes a barrier for further adsorption, and very few bare patches are available for new adsorption events.<sup>34</sup> As a result, the kinetics of adsorption slows down significantly.

At the transition (around  $t_{\text{off}}$ ), the population of dye moieties is split between some of them that were adsorbed during the first stage with an orientation parallel to the surface and the rest of it, with isotropic orientation. The increase of  $\rho(t)$  observed after  $t_{\text{off}}$ indicates that new moieties, which pertained to the isotropic population, gradually adopt an average orientation normal to the surface. The change in orientation is a consequence of the lack of space accessible for adsorption. Although at this stage the surface is nearly saturated and the penetration through the adsorbed layer is unfavorable, a labeled segment arriving from the inner part of the film still has a certain probability to find a "hole" generated by conformational fluctuations in the structure.<sup>35</sup> In this condition, the adsorption is achievable only if the new penetrating labeling moieties adopt an orientation normal to the surface.

It is possible that the perpendicular orientation of the adsorbing units observed during this latest stage of adsorption corresponds to the formation of loops and tails characterizing the conformations of adsorbed homopolymer chains at high surface coverage.<sup>15,33</sup>

Results on the bilayer system further corroborate our hypothesis. As stated in the Experimental Section, the bilayer film is composed of a 30 nm thick film of PS-l spin-coated on the top of an 8 nm layer of strongly adsorbed PS. We expect that this strongly adsorbed PS significantly retards the diffusion of the labeled segments and prevents their adsorption onto the Al surface. In fact, as shown in a recent work,<sup>36</sup> the presence of a complete adsorbed layer of PS at the metallic interface leads to a decrease of the diffusion coefficient of the labeled PS chains by 2-3 orders of magnitude as compared to the bulk value. Concomitantly, the dielectric strength as plotted in Figure 2 shows no time evolution, indicating that the time needed by the labeled segments to diffuse through the dense adsorbed layer of PS is longer than the experimental time window, and no adsorption takes place. We show with the SHG curve Figure 2b that in this case no preferential orientation occurs; in fact,  $\rho(t)$ remains constant during the whole experiment.

Hence, the changes of orientation observed for the single layer in contact with the aluminum are not found in the case where adsorption is inhibited by the strongly adsorbed PS layer. These results highlight the complementary role of second harmonic generation technique and dielectric spectroscopy in assessing the mechanisms of the adsorption process.

We do not discount the possibility that the preannealing protocol that we used for the samples is not enough to reach the equilibrium; however, this would not change the qualitative features of the responses of the two systems and their striking differences.

To explore more in depth the kinetics of polymer adsorption, we studied labeled polystyrene films of different molecular weights as well as nonlabeled systems. As previously shown, the adsorption can be described by a characteristic time  $t_{\rm on} < t_{\rm ads} < t_{\rm off}$ .<sup>20</sup> Recently, we highlighted that properties of ultrathin films are related to the conformation of the adsorbed interfacial chains, which can be described via the ratio between the annealing time and the time scale of adsorption,  $t^* = t_{\rm ANN}/t_{\rm ads}$ . If the annealing time is much shorter than, equal to, or much higher than  $t_{\rm ads}$ , different regimes are expected as confirmed by this study for the system where adsorption occurs. For  $t^* \ll 1$  ( $t_{\rm ANN} \ll t_{\rm on}$ ) and  $t^* \gg 1$  ( $t_{\rm ANN} \gg t_{\rm off}$ ) polymer properties are invariant with respect to the annealing time, but the conformations of interfacial chains are different. On the contrary, for  $t^* \sim 1$  ( $t_{\rm on} < t < t_{\rm off}$ ) the



**Figure 3.** Ratio between the characteristic adsorption time,  $t_{ads}$ , and the structural relaxation time,  $\tau_{ca}$ , for *l*-PS 20 kg/mol used in this work (blue hexagons), labeled PS 820 kg/mol (green diamonds),<sup>19</sup> PS 97 kg/mol (red squares),<sup>20</sup> PS 160 kg/mol (black circle).<sup>20</sup>

conformations within the interfacial layer change continuously with the annealing time as well as the physical properties. By taking advantage of the capability of dielectric spectroscopy to provide direct information on the structural relaxation time  $\tau_{\alpha}$ we determined the ratio  $t_{\rm ads}/\tau_{\alpha}$  for neat and labeled polystyrene samples as a function of temperature. In agreement with a previous work,  $t_{ads}/\tau_{\alpha}$  is constant over the temperature range investigated, implying that both processes, adsorption and the dynamic glass transition, have the same activation energy (see Figure 3). For films of the labeled PS used in this study, the ratio  $\log(t_{ads}/\tau_{\alpha}) \cong 7$  implies that a measure of  $t_{ads}$  at  $T_g$  (100 s) would require annealing times of the order of 30 years. Hence, values of  $t_{\rm ads}$  at temperatures next to  $T_{\rm g}$  can be deduced from the temperature dependence of  $\tau_{\alpha}$ , a more easily accessible measurable quantity. It is noteworthy that the nature of the surface interaction can strongly impact the ratio  $\log(t_{ads}/\tau_{\alpha})$  and thus the kinetics of the adsorption process. This observation will be studied in more detail in a further work.

# **5. CONCLUSIONS**

We studied the adsorption kinetics of ultrathin polymer films of labeled PS supported on aluminum substrates and on a strongly adsorbed layer of neat PS, by combining dielectric spectroscopy (DS) and the surface-induced nonlinear optical second harmonic generation technique (SHG).

Dielectric spectroscopy, which is sensitive to molecular dynamics, allowed us to monitor the adsorption kinetics via the time dependence of the dielectric strength, a quantity proportional to the amount of mobile segments involved in the structural relaxation process. Immobilization of labeled segments during adsorption causes a reduction of the dielectric strength and by following its evolution upon annealing we were able to distinguish the different stages of the adsorption process.

At the same time, second-harmonic generation experiments yielded information on the average orientation of labeling dye moieties during adsorption, which provided insight into the mechanisms of the process itself. The SHG signal was generated from the adsorbed dye moieties, with both parallel and perpendicular orientation to the interface. By taking the ratio between the two signals, we could determine changes in the average orientation with respect to the surface normal.

Results on the *l*-PS in contact with the Al revealed a two-stage process during which we observed a strong correlation between the kinetics of adsorption and variations in the orientation of labeling moieties. At the beginning of the adsorption process (first stage), the binding of the labeled segments on the surface promotes an alignment of the labeling dye moieties parallel to it. At the end of the process (high surface coverage, second stage), adsorption develops via an alignment of the dye moieties normal to the surface. On the contrary, measurements on the *l*-PS deposited on a strongly adsorbed layer of neat PS did not display any change with time, implying that in this case no adsorption takes place at the metal surface.

Our results demonstrated the usefulness of second-harmonic generation technique as a complementary tool to dielectric spectroscopy in assessing the mechanisms of segmental adsorption. Since SHG is uniquely appropriate to probe the orientation of adsorbed dye moieties at the metal surface, we are currently expanding our approach to other systems.

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