Sequential infiltration synthesis (SIS) provides a successful route to grow inorganic materials into polymeric films by penetrating gaseous precursors into the polymer, both in order to enhance the functional properties of the polymer creating an organic–inorganic hybrid material, and to fabricate inorganic nanostructures when infiltrating in patterned polymer films or in self-assembled block copolymers. A SIS process consists in a controlled sequence of metal–organic precursor and coreactant vapor exposure cycles of the polymer films in an evacuated reactor. Here, a study of the SIS process of alumina using trimethylaluminum (TMA) and \( \text{H}_2\text{O} \) in various polymer films using in situ dynamic spectroscopic ellipsometry (SE) is reported. In situ dynamic SE enables time-resolved monitoring of the polymer swelling, which is relevant to the diffusion and retains the metal precursor into the polymer itself. Diffusion coefficients of TMA in poly(methylmethacrylate) (PMMA) are extracted, investigating the swelling of pristine PMMA films during TMA infiltration and shown to be dependent on polymer molecular weight. In situ dynamic SE allows to control the SIS process, tuning it from an atomic layer deposition – like process for long purge to a chemical vapor deposition – like process selectively confined inside the polymer films.

1. Introduction

Sequential infiltration synthesis (SIS) has been demonstrated to be a viable preparation route for hybrid inorganic–organic materials, by penetration of gaseous metal precursors into polymer films, fibers, foams, or biomaterials.\(^1\) The incorporation of inorganic materials into organic matrices offers the possibility to enhance the mechanical properties of the final composite,\(^6\) to improve its chemical etch resistance,\(^9\) to tune its optical properties,\(^1\) or its oil sorption capability for efficient extraction of oil from water.\(^3\) In particular, infiltration in lithographically patterned polymeric thin films\(^{12,13}\) or in self-assembled block copolymer (BCP) films\(^{9,14,15}\) allows the formation of inorganic nanostructures, once the polymer matrix is removed by an \( \text{O}_2 \) plasma or annealing step. Simply replicating the patterned polymer or BCP templates, metal oxide (\( \text{Al}_2\text{O}_3, \text{TiO}_2, \text{SiO}_2, \) or \( \text{ZnO}\)) and metal (\( \text{W}\)) nanoarchitectures have been directly fabricated, for applications as sub-20 nm enhanced lithographic masks\(^{16-18}\) or as active elements in advanced nanoscale electronic devices.

Typical SIS process consists of a controlled sequence of metal–organic precursor and coreactant vapor exposures of the organic samples in an atomic layer deposition (ALD) reactor, intercalating appropriate purging cycles of inert gas to remove unreacted molecules or reaction by-products. The process is quite complex involving chemical and physical reactions of the precursors among themselves and with the host matrix. In particular, diffusion of precursors throughout the infiltrated polymer films plays a fundamental role in the kinetic of the infiltration process and needs to be monitored in real time to get a comprehensive picture of the specific SIS process under investigation. In order to achieve optimal control of the infiltration process, in situ analysis techniques have been tailored to characterize how the polymer film is modified as a consequence of the infiltration process itself, achieving information on the evolution of the sample during the process.

The most studied SIS process has been the infiltration of trimethylaluminum (TMA) in combination with \( \text{H}_2\text{O} \) for the synthesis of \( \text{Al}_2\text{O}_3 \) into polymeric films, and in situ quartz crystal microbalance (QCM) measurements and in situ Fourier transform infrared (FTIR) spectroscopy\(^{12,19-21}\) have been the mostly used in situ techniques for investigating the infiltration mechanism. Both the characterization techniques demonstrated the dependence of effective infiltration on the presence of intermolecular interactions between the metal–organic precursor and some functional groups in the polymer, and the influence of process parameters as temperature, precursor exposure, purge duration, and pulse sequence. In situ QCM showed different alumina mass uptake per cycle in different polymers and allowed displaying mass uptake and loss during TMA dosing and
purging, respectively. In the case of poly(methylmethacrylate) (PMMA) films, FTIR analysis evidenced that the interaction between TMA and C=O and C=O=R moieties enables to form a reversible adduct C=O⋯Al(CH3)3 for the subsequent nucleation of Al2O3.[1,20–22] For a PS-b-PMMA BCPs made of PMMA and polystyrene (PS), TMA infiltration process discriminates PMMA with respect to PS domains where no TMA-phylic groups are available, allowing to selectively grow alumina only in PMMA volume and to create inorganic nanostructures as replicas of the BCP template.[15,24–26] Anyways, a clear and comprehensive picture of the different phenomena occurring during a SIS process is still missing.

In this work, we investigated the infiltration process of TMA and H2O in PMMA and PS films, as building blocks of PS-b-PMMA BCPs, using in situ dynamic spectroscopic ellipsometry (SE). Ellipsometry is a noninvasive optical technique that has been widely used for studies of polymer layers under several conditions[27–29] and in combination with ALD processes.[30–32] In situ dynamic SE allows the continuous acquisition of information about the changes of the thickness and refractive index n of the polymer film during infiltration, without the need of ad hoc samples, as for in situ QCM measurements, and without interrupting the process, both over subsequent cycles and during the different steps of a single cycle, on a shorter timescale than in situ FTIR spectroscopy analysis. Through in situ dynamic ellipsometric analysis of polymer infiltration, quantitative information about TMA diffusivity in pristine PMMA matrix was obtained, gaining further insight into the process kinetics, whose comprehension is required for process optimization and for extension of the SIS methodology to the synthesis of new materials and to other polymeric matrices.

2. Results and Discussion

2.1. Infiltration in PMMA and PS Films

Figure 1a shows the temporal evolution of thickness and refractive index, as extracted from dynamic SE data, for 55 nm thick PMMA and PS films during 10-SIS-cycle process, as that we used for infiltrating PS-b-PMMA BCP with perpendicular lamellae morphology reported in ref. [25]. The two polymer films exhibit completely different swelling behavior during infiltration. In the first cycle, PMMA thickness largely increases during TMA injection and exposure and subsequently decreases during the following TMA purge and H2O pulse. Correspondingly, the refractive index decreases during TMA infiltration and then increases back in the remaining part of the SIS cycle. In the second and third cycles, thickness changes are still quite large during TMA injection and exposure steps but less than that for the pristine PMMA. Starting from the fourth cycle on, a very small thickness increase is observed during each TMA exposure step. Conversely, PS film exhibits no significant swelling and refractive index changes during the whole infiltration process. The difference in the swelling behavior of PMMA and PS is a signature of the different solubility of TMA in the two polymers. The solubility of TMA in polymers containing C=O groups, as PMMA, is larger than the solubility of TMA in polymers without C=O groups, such as PS, because of the effective intermolecular interaction between TMA and C=O groups, commonly identified in a Lewis acid–base interaction.[33]

Starting from collected SE data, we argue that the initial PMMA thickness increase during first TMA exposure is due to TMA molecules diffusing in the polymer film and in small percentage forming an adduct with the carbonyl groups of PMMA. Such physisorbed state is reported to be mainly reversible,[21] consequently physisorbed molecules may diffuse out, together with nonreacted TMA molecules during sufficiently long TMA purging steps, resulting in polymer deswelling. During H2O pulsing, the physisorbed TMA is converted in alumina, fixing Al2O3 seeds inside the polymer matrix and resulting in an increase of the polymer film thickness at the
end of the first SIS cycle. In the following two cycles, TMA diffuses in a polymer matrix including still reachable and not yet saturated C=O moieties together with alumina nucleation sites created in the previous cycle. Consequently, the observed film swelling is lower than in the first cycle, with a corresponding lower thickness increase after H2O pulse. As the SIS process proceeds, PMMA thickness increase after each cycle is further reduced, suggesting a different growth mechanism associated to the reduced availability of C=O reactive sites and lowered TMA diffusivity inside the polymer.

Interestingly, a small reduction (1.3%) of the refractive index of the infiltrated PMMA film is observed during the large film swelling (50%) occurring throughout the first TMA exposure. Moreover, almost no variation of the refractive index is registered upon a 20% increment of the PMMA film thickness at the end of the 10-SIS-cycle process. These experimental results indicate that the infiltration of a large amount of aluminum-containing precursor, subsequently converted in alumina with higher refractive index than that of PMMA,[34] balances the density reduction expected as a consequence of the large volume increase. As previously discussed, the different swelling behavior of PS films during TMA infiltration, with no significant change in the refractive index, can be ascribed to the absence of reactive carbonyl moieties in PS, with the Al precursor diffusing in and out of the polymer film during each cycle. Nevertheless, a slight but gradual increment in thickness is observed over repeated SIS cycles, as summarized in Figure 1b, where the PS and PMMA thickness increases at the end of each cycle during the 10-SIS-cycle processes are reported. The initial PS thickness increase is very similar to that of ALD alumina at 90 °C[35] during the first SIS cycle. During the following cycles, the polymer thickness increase is slightly larger, suggesting the occurrence of some oxide growth inside the PS matrix.[1,36–38] The PMMA growth trend already described appears even more evident in Figure 1b, being dramatically different from PS, and showing two distinct regimes with a large thickness increase during the initial cycles followed by an almost negligible thickness increase in the subsequent cycles of the process.

Time of flight-secondary ion mass spectroscopy (ToF-SIMS) depth profiles of 55 nm thick PMMA films and 55 nm thick PS films upon a 10-SIS-cycle TMA/H2O SIS process are shown in Figure 2a, b, respectively. The aluminum-related signals, corresponding to Al− and AIO− secondary ions, clearly highlight a different Al2O3 content in the two polymeric matrix. Interestingly, the infiltrated PMMA film exhibits very high Al− and AIO− signals, suggesting significant Al2O3 incorporation in the polymer film. Moreover, Al− and AIO− signals are constant throughout the entire profile, indicating a homogeneous distribution of Al2O3 in the PMMA matrix. Conversely, Al− and AIO− signals clearly demonstrate a limited but not negligible incorporation of Al2O3 in the PS matrix, consistent with the thickness increase reported in Figure 1b.

After selective removal of the infiltrated polymer matrix by O2 plasma treatment, the resulting alumina film obtained from PMMA infiltration is 26.9 nm thick and exhibits refractive index \( n = 1.47 \) at 632.8 nm with a smooth and homogeneous surface (Figure 2c). It is worth to note that the refractive index is lower than that of alumina grown by ALD at \( T < 100 °C \). Actually, a refractive index \( n = 1.54 \) was obtained for Al2O3 films grown by a conventional ALD process at 90 °C, in agreement with values reported in literature.[35,39] The low value of the refractive index corresponds to a lower density of the infiltrated Al2O3 film with respect to ALD Al2O3, being their chemical composition very similar, as reported in ref. [25]. This indicates that the film is slightly porous, with a porosity of 16%, as evaluated by using the Bruggeman effective medium approximation (EMA) for modeling the optical constants of the film, described as a physical combination of alumina deposited by ALD at 90 °C and voids.

Figure 2. ToF-SIMS depth profiles of a) 55 nm thick PMMA films and b) 55 nm thick PS films after 10-SIS-cycle TMA/H2O SIS process. FE-SEM images of alumina films resulting from 10-SIS-cycle TMA/H2O SIS process in c) 55 nm thick PMMA and d) 55 nm thick PS films after removal of polymer matrix in O2 plasma.
From infiltration of the 55 nm thick PS film, a much thinner (11.4 nm) metal oxide film was obtained compared to that from infiltrated PMMA. This Al$_2$O$_3$ film exhibits even lower refractive index ($n = 1.32$), corresponding to a larger porosity of 35%, and a completely different film morphology, as shown in Figure 2d. Interestingly, very similar PS thickness increase over 10-SIS-cycle process and similar metal oxide films after polymer removal in O$_2$ plasma were obtained, increasing the duration of the purge step from 60 up to 300 s (Section S1, Supporting Information). Data indicate that the observed Al$_2$O$_3$ growth in the PS matrix cannot be explained in terms of residual TMA precursor molecules still present in the polymer matrix after a short 60 s purging time. The negligible variation in the final thickness and morphology of the Al$_2$O$_3$ films observed by increasing the duration of the purge step suggests that the growth of alumina inside the PS film is related to the presence of some defects in the films acting as reaction sites for TMA molecules. This interpretation is supported by the almost constant Al$^+$ signal in ToF-SIMS depth profile of the infiltrated PS matrix. These results are of large interest for application of SIS in BCP films, when selective infiltrations of PMMA domains with respect to PS domains are required in order to replicate the BCP templates. Actually, they indicate that alumina grows inside the PS phase of the BCP matrix, if many SIS cycles are performed and defects are present as nucleation for the growth, independent of the purging length.

2.2. Infiltration in PMMA Films with Different Thicknesses

Figure 3a reports the thickness increase of PMMA films ($M_n = 14$ kg mol$^{-1}$) with initial thickness 100, 55, 25, and 8 nm after each SIS cycle. Independent of the PMMA initial thickness, we observed the occurrence of two growth regimes for all PMMA films. During the first three SIS cycles, large polymer thickness increase is attributed to large incorporation of metal oxide in the polymer bulk. In the second part of the process, the reduced polymer thickness increase may be due to a superposition of several processes: the change in the mechanical properties of the polymer matrix once it has been infiltrated and inorganic material has been grown inside it,$^{[14,40]}$ the reduced interaction between TMA and the polymer, being the functional moieties in PMMA largely consumed during the first infiltration cycles, or an effectively reduced incorporation of alumina, assuming that TMA diffusion in the PMMA volume is limited by previously grown alumina and corresponds to a very small subsurface infiltration or to an ALD-like growth on the surface in the second part of the infiltration process. Such trend is in agreement with data about alumina infiltrated in random copolymer films as a function of SIS cycle reported in the literature,$^{[36]}$ where the largest alumina infiltration is the result of the first SIS cycle, with a half rate reduction in the following cycles.

In Figure 3b, we plot the PMMA thickness increase (right axis) as measured by in situ SE at end of the 10-SIS-cycle process as a function of initial PMMA film thickness. We observe that the final infiltrated PMMA thickness increment grows linearly with the starting PMMA thickness. Further, considering the thickness of alumina obtained for the full 10-SIS-cycle process as a function of the initial PMMA thickness, we observe that the alumina thickness increases almost linearly but with different rates with respect to PMMA thickness increment. The incorporated amount of alumina as a percentage of PMMA initial thickness decreases. We can argue that the film results only partially infiltrated as PMMA thickness increases. According to ToF-SIMS analysis (Section S2, Supporting Information), alumina is incorporated throughout the entire film depth, with a concentration that is fairly constant up to interface with the substrate, irrespective of the film thickness. Collected data suggest that TMA molecules diffuse throughout the entire film during the SIS process, leading to a homogeneous Al$_2$O$_3$ growth within the volume of the polymer film. Yet, the intensity of the Al$^+$ and AlO$^-$ signals slightly decreases with the thickness of the polymeric film. This is associated to a concomitant increase of the C$_1$ signal, suggesting that the fraction of Al$_2$O$_3$ in the volume of PMMA film is slightly reduced when increasing the thickness of the polymer film.

In any case, the alumina to PMMA initial thickness ratio remains larger than that reported in ref. [12], where the calculated ratio for reaction-limited growth inside the polymer is 0.22. We assume that the oxide incorporated in the polymer film during the 10-SIS-cycle process is due to both TMA...
molecules physisorbed to functional PMMA groups and non-reacted TMA molecules still present inside the polymer after purging and reacting with H₂O. In the next paragraph, we analyze the swelling of pristine PMMA films as a function of TMA dose and purging time during the first SIS cycle, and we demonstrate that the proposed picture of the infiltration process is fully supported by in situ dynamic SE analysis.

2.3. Evolution of PMMA Film during the First SIS Cycle

In situ SE analysis of SIS process enables real-time monitoring of thickness evolution of the PMMA films, providing clear evidence of polymer film modification occurring during the first SIS cycle as a consequence of film exposure to TMA and H₂O molecules. The complex phenomena occurring during the first SIS cycle are extremely interesting, and their comprehension is absolutely necessary because nucleation of Al₂O₃ seeds is often used for the subsequent infiltration of precursors that do not present good solubility in PMMA. In particular, TMA exposure phase is characterized by two main process parameters, the TMA dosing, depending in our reactor by the TMA pulse length, and the exposure duration, that can be tuned to allow complete diffusion of the penetrant molecules inside very thick polymer films. Effects of these process parameters on the PMMA film thickness evolution have to be systematically monitored to get information on TMA precursor diffusion and reaction with the host matrix.

For a fixed TMA pulse length (0.025 s) and TMA exposure duration (60 s) as those used in the 10-SIS-cycle process, we investigated TMA infiltration in PMMA films with thicknesses ranging from 4 to 100 nm, and with two different molecular weights, corresponding to \( M_n = 14 \text{ kg mol}^{-1} \) and \( M_n = 3.9 \text{ kg mol}^{-1} \), respectively. Figure 4a reports the PMMA film thickness evolution recorded during the TMA exposure phase for the various PMMA films with different initial thicknesses. Interestingly, regardless of the initial film thickness or the PMMA molecular weight value, all the samples exhibit the same general behavior, undergoing a significant thickness increase when exposed to TMA and reaching a maximum level during the exposure step.

Such maximum level is reached faster for thinner samples, since the TMA molecules diffuse over a considerably shorter path. Indeed, it is well known that the timescale of a diffusion process in a layer is extremely influenced by the layer thickness itself, with a dependency \( \propto L^2 \). Moreover, a further increase in thickness is observed in the second part of TMA exposure phase for thinner films, as a consequence of the initial fast sorption of TMA molecules and polymer matrix relaxation, as described below. It is also worth to note that the thickness increase of the thinnest films can be affected by interface effects due to interaction of TMA molecules with the substrate, that can lead to even

![Figure 4](image-url)
higher swelling ratio.\(^{[42]}\) Finally, the maximum level is reached more quickly in the PMMA films with lower molecular weight, indicating that TMA molecules benefit from a higher diffusivity in polymers with lower molecular weight.

The time evolution of polymeric film swelling \(\varepsilon(t)\), is defined as

\[
\varepsilon(t) = \frac{l(t) - L}{L}
\]

(1)

where \(L\) and \(l(t)\) are the initial thickness and the thickness of the polymer film at time \(t\), respectively, providing information about the kinetics of the diffusive process of the infiltrating molecules inside the polymeric matrix.\(^{[43]}\) For instance, by measuring the dilation of a glassy polyimide thin film caused by the sorption of CO\(_2\) molecules at low pressure, Wessling et al.\(^{[43]}\) observed a swelling curve following the exactly same evolution of the sorption curves obtained by mass-uptake measurements.

The initial thickness increase shows a time dependency \(\propto t^{1/2}\) and is attributed to the diffusion of penetrant molecules following a Fickian behavior. This first sorption of molecules can produce a stress into the polymeric matrix, leading to a slow relaxation of the glassy film. As a consequence of this structural relaxation of the polymeric matrix, more molecules can diffuse and be sorbed into the film, causing a slower second increase of mass and thickness of the polymer film.\(^{[44]}\)

Following this approach, the thickness increase of PMMA films in Figure 4a was analyzed, having in mind that the infiltration process of TMA in PMMA is affected by the fact that TMA molecules fast react to functional groups in the polymer. Figure 4b reports the normalized swelling \(\varepsilon(t)/\varepsilon_{\text{max}}\) as a function of \(t^{1/2}/L\) for the various PMMA films. The value \(\varepsilon_{\text{max}}\) corresponds to the maximum swelling reached during the precursor exposure.

The linear dependence of \(\varepsilon(t)/\varepsilon_{\text{max}}\) versus \(t^{1/2}/L\) during the initial stages of the swelling process is in perfect agreement with Equation (2), that approximates the evolution of the swelling \(\varepsilon(t)\) for small \(\tau\) (Section S3, Supporting Information), when the infiltration process is dominated by a Fickian diffusion behavior for the precursor molecules infiltrating the polymer.\(^{[41]}\)

\[
\varepsilon(t) \sim 4\varepsilon_{\text{max}} \frac{D}{\pi} \left[\frac{L^2}{t}\right]
\]

(2)

where \(D\) is the “effective” diffusion coefficient of the precursor molecules in the specific polymer matrix, being precursor diffusion reduced by the reaction of a portion of the precursor molecules when entering the polymer film.\(^{[5]}\) From the trends of \(\varepsilon(t)/\varepsilon_{\text{max}}\) with respect to \(t^{1/2}/L\) in Figure 4b, it is clearly possible to distinguish two separate groups of curves corresponding to the different PMMA molecular weights.

They both follow a linear trend for \(\varepsilon(t)/\varepsilon_{\text{max}}\) values up to 0.7, proving that the infiltration is governed by a Fickian diffusion stage in the beginning of the TMA exposure phase. By considering the Fickian part of the curves, the effective diffusion coefficients of TMA molecules inside PMMA samples were calculated using Equation (2) through a linear fitting of the experimental data. The corresponding effective diffusion coefficient are \(D_{3.0} = 4.5 \times 10^{-12}\) cm\(^2\) s\(^{-1}\) and \(D_{1.4} = 1.2 \times 10^{-12}\) cm\(^2\) s\(^{-1}\) for PMMA films with \(M_n = 3.9\) kg mol\(^{-1}\) and \(M_n = 14\) kg mol\(^{-1}\), respectively. These values confirm that TMA molecules diffuse faster in PMMA samples with lower molecular weight. Interestingly, assuming TMA molecule mean diameter \(d = 0.5\) nm, the extracted \(D\) values are in excellent agreement with diffusivity data available in the literature,\(^{[45]}\) showing that diffusion coefficients of organic vapors and gases in PMMA at 90 °C scale as a function of the penetrant molecule mean diameter \(d\).

Similarly, the effect of TMA dosing on the thickness increase of 100 nm thick PMMA films was monitored by in situ dynamic SE (Figure 4c). The thickness increase as a consequence of TMA injection and exposure depends on TMA dosing, varying linearly from 40% to a maximum of 60% of the initial thickness when increasing TMA pulse from 0.02 to 0.04 s. Data indicate that TMA concentration within the polymer matrix depends on the TMA pressure in the reactor and can be tuned by properly adjusting the duration of the TMA pulse. Actually, we expect that, further increasing the TMA pulse and consequently the partial pressure of TMA in the reaction chamber, a saturation value for the swelling of the polymeric film would be achieved, consistent with experimental data available in the literature about mass uptake with multiple TMA pulses.\(^{[12,19]}\)

Figure 4d reports the normalized swelling \(\varepsilon(t)/\varepsilon_{\text{max}}\) as a function of \(t^{1/2}/L\) for increasing TMA dosage. All the curves exhibit the same linear behavior during the initial stages of the process, irrespective of the TMA dosing. Experimental data indicate that the TMA infiltration is characterized by an initial Fickian diffusion regime with almost the same effective diffusion constant that is independent on the TMA dosing in the range of values explored in this work.

Continuing the monitoring of the thickness evolution of the PMMA films during the purging step in the first SIS cycle after TMA exposure, a significant decrease of PMMA film thickness is observed (Figure 5a), as the reactor is vacuum pumped and then crossed by a 100 sccm N\(_2\) flow for 60 s. Thickness evolution as a function of time follows an exponential trend \(e^{-\tau/t}\) where \(\tau\) is assumed to be the effective time constant of the desorption process.

Figure 5b reports \(\tau\) values extracted from curves in Figure 5a, as function of the PMMA film thickness. A progressive increase of \(\tau\) values is observed when increasing PMMA film thickness. Interestingly, similar \(\tau\) values were measured for polymer films with approximately the same thickness, independent of the PMMA molecular weight. During the purging phase, outdiffusion of nonreacted TMA molecules and desorption and loss of a fraction of TMA molecules that are reversibly physisorbed to C=O groups are expected to occur, producing the shrinking of the polymer matrix. Moreover, the polymer film is subjected to internal stresses that can further contribute to the observed decrease of the film thickness. Therefore, competing processes with different characteristic times occur simultaneously during the desorption process.

The \(\tau\) values extracted from SE monitoring of the deswelling process are much shorter than those evaluated from FTIR analysis. Actually, \(\tau\) values of the order of tens of minutes are obtained monitoring C=O absorbance peak intensity variation upon increasing purging time, as reported by Biswas et al.\(^{[20,21]}\) Biswas et al. assigned the temporal evolution of C=O absorption intensity to desorption of physisorbed TMA from the
reversible adducts \( \text{C}=\text{O} - \cdots \text{Al(CH}_3\text{)_3} \) formed during TMA exposure phase. It is worth noting that the timescale of FTIR investigation is different with respect to that of SE analysis. By in situ dynamic SE, the polymer deswelling process is monitored during removal of TMA vapor from the reactor and purging in \( \text{N}_2 \) flow. Conversely, even in the case of the shortest purge step of \( 35 \) s, the first FTIR spectrum was obtained as the average over a \( 320 \) s long measurement.\(^{[20,21]} \) Therefore, we argue that the observed thickness evolution is mainly associated to the outdiffusion of nonreacted TMA molecules from the PMMA films.

According to the experimental data, the outdiffusion process is significantly slower than that of the infiltration of TMA molecules in pristine PMMA matrix. Moreover, the outdiffusion time constants are clearly dependent on the thickness of the polymer film and almost independent of the molecular weight, different from what is observed during TMA exposure and infiltration. This behavior can be attributed to the fact that the infiltrated polymeric matrix is significantly different compared to the pristine PMMA matrix. Considering the process occurring in unperturbed PMMA matrix, structural relaxation characteristic times are expected to be independent of the polymer film thickness, since they are expected to be strictly related to the elastic properties of the polymer matrix. On the contrary, shorter \( \tau \) values for deswelling were evaluated for thinner PMMA films during purging phase. We could argue that the polymer matrix is modified by the TMA infiltration, in larger extent for thinner films, and that the observed deswelling depends on the specific history of polymer systems during the infiltration process.

Figure 5c depicts the thickness evolution during the purging step in the case of \( 100 \) nm thick PMMA films infiltrated increasing input TMA doses by increasing the TMA pulse duration. From fitting of the experimental data, the time constant of the deswelling process was obtained. Figure 5d reports the \( \tau \) values as a function of the duration of the TMA pulse. Interestingly, the time constant of the exponential thickness decrease is inversely proportional to the TMA dose, i.e., the deswelling process is faster for larger TMA doses, that is, for larger sorption-induced polymer dilation.

To get more information about the residual TMA molecules present in the polymer at the end of the purging step, the PMMA shrinking occurring upon \( \text{H}_2\text{O} \) injection in the chamber was investigated in details. The reaction of TMA molecules with \( \text{H}_2\text{O} \) inside the polymer is extremely fast with an almost instantaneous decrease of the PMMA film thickness.
upon H₂O pulse. This result is perfectly consistent with data on H₂O molecule diffusion in a PMMA matrix. The PMMA thickness shrinking upon H₂O infiltration and reaction was observed to be in relation with the metal oxide incorporated in the polymer film. For instance, the 100 nm thick PMMA films infiltrated with different TMA pulses showed very similar shrinking as a consequence of H₂O pulse.

After O₂ plasma treatment to remove the polymer matrix, the resulting alumina films have similar thicknesses, ranging from 14.2 to 17.8 nm for TMA pulse length from 0.02 up to 0.04 s, and very similar refractive index (n = 1.47 at 632.8 nm). Therefore, the larger polymer swelling as a consequence of higher TMA partial pressure in the reactor chamber has a minimal impact on the final amount of incorporated alumina, because of very fast outdiffusion of nonreacted TMA during N₂ purging, whereas similar shrinking after reaction with H₂O corresponds to similarly infiltrated alumina.

Finally, the effect of the purging time on the final amount of TMA trapped in the PMMA film was investigated by increasing the duration of the purge step from 60 to 500 s. Figure 6a reports the time evolution of the PMMA film thickness during the first SIS cycle for 100 nm thick PMMA films. The TMA pulse is 0.025 s. When applying a very long N₂ purge (500 s), the PMMA film deswells back to a thickness value that represents a sort of limiting value. The final thickness of the PMMA film upon a 500 s long purge step is about 8% larger than the initial thickness and, after infiltration with H₂O molecules, it further reduces to about 5%. We can consider this small polymer thickness increase as associated to the incorporation in the polymer film of alumina grown from TMA molecules chemically reacted with PMMA functional groups, since almost all physisorbed TMA molecules were desorbed away during this very long purge step. FTIR studies demonstrated that the amount of chemisorbed TMA molecules corresponds to a small fraction of the infiltrated and physisorbed TMA molecules.

Looking at the morphology of the film after removal or the polymer matrix (Figure 6b), we observed that the film is not continuous and with a high level of porosity. Reducing the purge length after TMA exposure to 60 s, the deswelling curve shows that TMA desorption is abruptly interrupted by injection of H₂O that reacts to form alumina, resulting in a continuous 14.4 nm thick but still porous film (Figure 6c). The film morphology and the timescale of our observation suggest that we are looking at a film resulting from infiltrated alumina grown by the reaction between a fraction of physisorbed TMA molecules on functional groups in PMMA and H₂O. Data clearly indicate that the thickness of the Al₂O₃ film can be modulated by properly adjusting the process parameters in order to control the amount of TMA molecules effectively inside the polymer film. Then, we further reduced the purging time...
(to 45 s) in order to incorporate more alumina in the polymer film. The correspondent curve in Figure 6a shows an effective larger swelling at the end of both the purging step when H₂O is injected in the reactor, and the completed SIS cycle, resulting in an alumina film with similar morphology (Figure 6d) and with same refractive index, but significantly thicker (23.4 nm) than the one obtained with 60 s purge (14.4 nm). Therefore, the largest swelling ratio between the end of the purging step and the end of SIS cycle, in addition to the final thickness, is an evidence of the largest alumina incorporated in the polymer film.

3. Conclusion

PMMA and PS thin films with different thicknesses have been infiltrated using a SIS process based on TMA and H₂O precursors. The infiltration process was monitored by in situ dynamic SE and investigated in relation to the resulting alumina films after removal of the polymer matrix by O₂ plasma. Different swelling behaviors of the two polymers were observed, evidencing the larger solubility of TMA in PMMA with respect to PS. The resulting Al₂O₃ film was thicker and denser in the case of infiltrated PMMA with respect to PS film. PMMA thickness increase after 10-SIS-cycle process, as a function of initial polymer film thickness, was related to the final alumina properties. Intracycle investigations of swelling and deswelling during TMA exposure and subsequent purging allowed obtaining useful information on the SIS process. TMA infiltration in PMMA follows a Fickian diffusion behavior with diffusion constant dependent on the PMMA molecular weight. TMA desorption similarly follows the same diffusion behavior but with a slower rate with respect to indiffusion in pristine polymer, as the polymer has been modified by TMA interaction. Changing the purging length after TMA exposure resulted in different swellings of the PMMA films and yielded in alumina films with different morphologies and porosities. In this respect, in situ dynamic SE offers the possibility to gain time-resolved insight in the infiltration process both in terms of the inorganic material amount retained in the polymer film and of diffusion and sorption or entrapping processes of precursor inside the polymer.

4. Experimental Section

**Polymer Film Preparation:** PMMA (Mₙ = 14 kg mol⁻¹, polydispersity index (PDI) = 1.2 and Mₘ = 3.9 kg mol⁻¹, PDI = 1.2) and PS (Mₙ = 13 kg mol⁻¹, PDI = 1.1) thin films of different thicknesses (from 8 to 100 nm) were prepared by adjusting the concentration of polymer–toluene solutions. The polymeric films were deposited by spin coating on top of a (100) Si substrate, cleaned in Piranha solution (H₂SO₄/H₂O₂, 3/1 vol ratio) at 80 °C for 40 min in order to increase the hydroxyl groups surface density. Then, the samples were rinsed with 2-propanol in ultrasonic bath and N₂ dried. Subsequently, the films were thermally annealed at 290 °C for 900 s in N₂ atmosphere by means of a rapid thermal process (RTP) to promote the grafting of the polymer chains to the substrate surface.[46–48] After RTP, a subset of samples was sonicated in toluene, in order to remove the nongrafted polymer fraction, obtaining very thin films.

**SIS Process:** The samples were then loaded in a cross flow commercial reactor for atomic layer deposition (Savannah 200, Ultratech Cambridge NanoTech Inc.), thermalized at 90 °C for 30 min under 100 sccm N₂ flow at a 0.6 Torr chamber pressure, before starting the infiltration process. TMA and H₂O were used as metal precursor and oxidant, respectively. The SIS cycle consisted of subsequent precursor pulses each followed by an exposure step during which the ALD chamber was isolated from the pumping line and the sample was immersed in the precursor vapor. Purging intervals under 100 sccm N₂ flow between TMA and H₂O pulse/exposure steps were performed. In the 10-SIS-cycle process, each cycle was made of 0.025 s TMA pulse/60 s exposure/60 s purge, followed by 0.015 s H₂O pulse/60 s exposure/180 s purge. After SIS process, the samples were washed in O₂ plasma (40 W, 525 Torr for 10 min), that removed the polymer matrix, leaving alumina films on the Si substrate.

**In Situ Dynamic SE:** The SIS process was monitored via a rotating compensator ellipsometer equipped with a Xe lamp (M-2000F, J. A. Woollam Co. Inc.). Two quartz windows installed on the ALD reactor lid allowed sending the incident light beam onto the sample and then detecting the reflected light beam at 70° fixed angle with respect to the substrate plane normal. Ellipsometric data were collected over the wavelength range from 250 to 1000 nm throughout the entire SIS process time, with an acquisition time of 2.5 s. Short acquisition times were required for dynamic measurements as the polymer films changed continuously during the SIS sequence precursor pulse/exposure/purge. In particular, the polymer modifications as the TMA or H₂O was injected in the ALD chamber were very fast, therefore, the acquisition time was reduced to 1.6 s when monitoring the single first infiltration cycle in pristine PMMA. Data were analyzed to determine the film thickness and refractive index using the EASE software package 2.3 version (J.A. Woollam Co. Inc.), by fitting the ellipsometric data using a film stack model composed of a Cauchy layer model for the polymer film on 2 nm thick SiO₂ on the silicon substrate.[49] Ex situ experimental Ψ and Δ spectra of final alumina layers, after O₂ plasma, were collected by the same ellipsometer at fixed 75° incidence angle and modeled using the Bruggeman EMA, to take into account film porosity and roughness, considering the alumina films resulting from polymer infiltration as a physical combination of alumina deposited by ALD at 90 °C and voids.

**Morphological and Chemical Investigation:** The structural morphology of infiltrated polymer films after the O₂ plasma step was characterized by field emission scanning electron microscopy (FE-SEM, SUPRA 40, Zeiss) using an in-lens detector and an acceleration voltage of 15 kV.

Tof-SIMS depth profiling was performed in a dual beam IONTOF IV instrument operating in negative mode. Sputtering was accomplished using Cs⁺ ions at 1 keV and rastering over a 200 × 200 μm² area. Analysis was performed using Cs⁺ ions at 25 keV and rastering over a 50 × 50 μm² area. To remove any signal variation due to fluctuation in the Cs⁺ ion current, data were normalized on the ³⁰Si⁻ signal in the silicon substrate.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

**Acknowledgements**

The authors would like to acknowledge Jacopo Frascaroli, Tommaso Giammaria, and Fabio Zanenga (CNR, Italy) and Michele Laus (UniPO, Italy) for fruitful discussions, Katia Sparnacci (UniPO, Italy) for technical assistance. This research was partially supported by the European Union’s Horizon 2020 research and innovation program under Grant Agreement No. 688072 “IONS4SET.” The paper was written through contributions of all authors.

**Conflict of Interest**

The authors declare no conflict of interest.
Keywords

in situ dynamic spectroscopic ellipsometry, inorganic–organic hybrid nanostructures, poly(methylmethacrylate), polystyrene, trimethylaluminum diffusion

Received: July 6, 2018
Revised: July 23, 2018
Published online: August 14, 2018