

Fractal patterns in polyethylene/polyethylene oxide plasma polymers

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Abstract: The formation of nanoscale island patterns is observed when the plasma-activated flux of polyolefins is directed onto the surface of polyether plasma polymer. Nanophase separation is confirmed by AFM-IR measurements. The shape of the islands changes from ramified fractal to anisotropic dendrite depending on glassy dynamics in the underlying polyether film. AC-chip specific heat nanocalorimetry confirms that segmental dynamics in this film can be controlled by its thickness and by the discharge power.

Keywords: fractal islands, polyethylene, polyethylene oxide, AFM-IR.

1. Introduction

The formation of patterns on the surface of copolymer films has been an area of strong scientific interest for decades; however, such self-organization phenomena have been investigated predominantly in solutions or melts. Gas phase approaches have been studied to a much lesser extent, although solution-free synthesis may be advantageous, especially in terms of the implementation into existing thin film deposition technologies, which are based mainly on the use of vacuum.

It has been known that certain polymers, such as poly(ethylene oxide) (PEO) and poly(ethylene) (PE), may undergo thermal decomposition, when heated under vacuum, with the release of homologous series of volatile oligomers. The released oligomer fluxes may be further condensed on solid support with the formation of thin films. Low-temperature plasma can be also introduced to activate the oligomers and to induce the formation of cross-links in the growing films. Simultaneous plasma-assisted co-deposition of PEO and PE was demonstrated to result in the growth of micro-phase separated bi-component coatings with complex architecture [1]. Recently, we also noticed that, if the deposition is performed sequentially, PE forms remarkable islands of different shape (fractal or dendrite) on top of flat PEO. Here, we investigate the aggregation of the PE islands in dependence on the properties of underlying PEO.

2. Experimental

Sequential Plasma-Assisted Vapour Phase Deposition of PEO and PE was performed in a vacuum chamber under Ar pressure of 1 Pa. PEO and PE (Sigma-Aldrich) were loaded into two crucibles and these were installed in above an rf magnetron equipped with a graphite target. Quartz Crystal Microbalance (QCM) was used to monitor the deposition rate. A loadlock system was used to

introduce polished silicon substrates (<100> Si, ON Semiconductor, Czech Republic) into the chamber.

In the first stage, PEO was heated to the temperature of 280 °C at which thermal decomposition occurs and the discharge power was adjusted to a needed value. The substrates were introduced above the crucible after constant deposition rate has been achieved. Plasma polymer PEO film was deposited for a certain time, then the substrate was withdrawn from the chamber and heating of PEO was turned off. At the second stage, the same approach was used for PE whereas the PEO films pre-synthesized in the first stage were used as substrates. For all the experiments, PE was deposited with the constant discharge power of 5 W.

Nanoscale infrared spectroscopy (nanoIR2-FS system with a QCL laser, Anasys Instruments) was used to analyse the topography and the local chemical composition of the PE nano-islands on PEO. The AFM-IR measurements were performed in an intermittent contact regime the wavenumber range of 1850-950 cm⁻¹ (MIR region) in an intermittent contact mode. Conventional AFM (Ntegra Prima, NT-MDT) was also used to analyse the morphology of the coatings.

AC-chip specific nanocalorimetry was used to establish the dynamic glass transition temperature of PEO films similar to a procedure described elsewhere [2].

3. Results and Discussion

PEO forms continuous and smooth films when deposited onto Si substrates. The NMR and XPS analyses (not shown) evidence the high retention of the C-O-C groups which reaches 80 at. % at lower power used. The GEC analysis established the narrow distribution of molar masses for the PEO film deposited without plasma ($M_n=1.1 \times 10^3$ g/mol). The bi-modal distribution with the higher molar mass tail was obtained for the film deposited with 5 W plasma and it points to re-polymerization

processes running with activated polyethers on the surface.

PE also retains its chemical structure when deposited onto Si substrates without plasma. A similar to PEO trend in the molar mass distributions was confirmed: the narrow distribution in plasma-free films ($M_n=1.4\times 10^3$ g/mol) changes to the bi-modal distribution at 5 W plasma used.

If PE is plasma-deposited onto the surface of the PEO films, a nanoscale pattern forms instead of a continuous coating. Non-polar polyolefin molecules tend to self-organize into isolated islands of 7 nm thickness on top of the polyether coating consisting of polar C-O-C groups (Fig. 1).

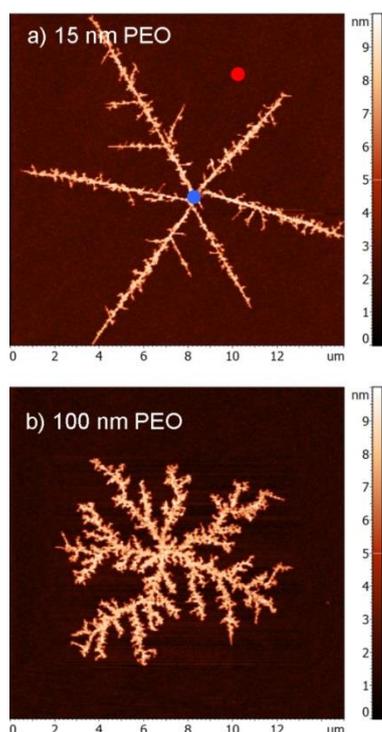


Fig. 1 Height AFM images of PE islands formed on PEO films with different thickness: a) 15 nm; b) 100 nm. Red and blue circles designate the spots for acquiring the AFM-IR spectra (see below). The deposition parameters are: PEO (the discharge power is 10 W, the QCM deposition rate is 20 Hz/min, the deposition time is 20 and 3 min, the crucible-substrate distance is 10 cm), PE (the discharge power is 5 W, the QCM deposition rate is 20 Hz/min, the deposition time is 30 min, the crucible-substrate distance is 20 cm).

Two spots were chosen on the sample belonging to the PEO film (red circle) and to the PE island on top of the PEO film (blue circle). The local chemical composition was analysed by acquiring the AFM-IR spectra (Fig. 2). Since both PEO and PE contain the methylene groups, bending vibrations of these groups at 1460 cm^{-1} were chosen to normalize the spectra. The difference between

the two spectra can be seen most clearly in the lower wavenumber region where the stretching vibrations of ethers are located. Strong absorption from the C-O-C groups is detected for the PEO film. In the case of the PE island, AFM-IR probes the entire thickness of the coating including 7 nm of PEO and 15 nm of underlying PEO. Thus, the signal from the C-O-C groups is also detected but it is attenuated as compared to the uncovered PEO film.

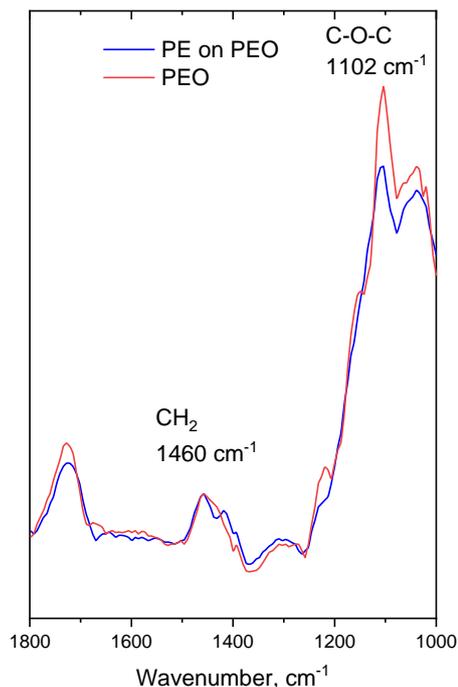


Fig. 2 AFM-IR spectra taken on 15 nm PEO and on 7 nm thick PE island grown on 15 nm PEO. The spectra are normalized to the intensity of the methylene groups at 1460 cm^{-1} present both in PE and PEO.

AFM-IR chemical mapping was applied to the PE/PEO sample (Fig. 3). The sample was scanned in the intermittent contact mode and the IR signal was monitored simultaneously either at 1102 cm^{-1} (the ether groups of PEO) or at 1460 cm^{-1} (the methylene groups present both in PE and PEO). Strong chemical contrast is obtained for the ether groups and the IR signal replicates the contours of the island. On the other hand, very weak chemical contrast is obtained from the CH_2 groups. Thus, the AFM-IR measurements confirm the phase separation between PE and PEO.

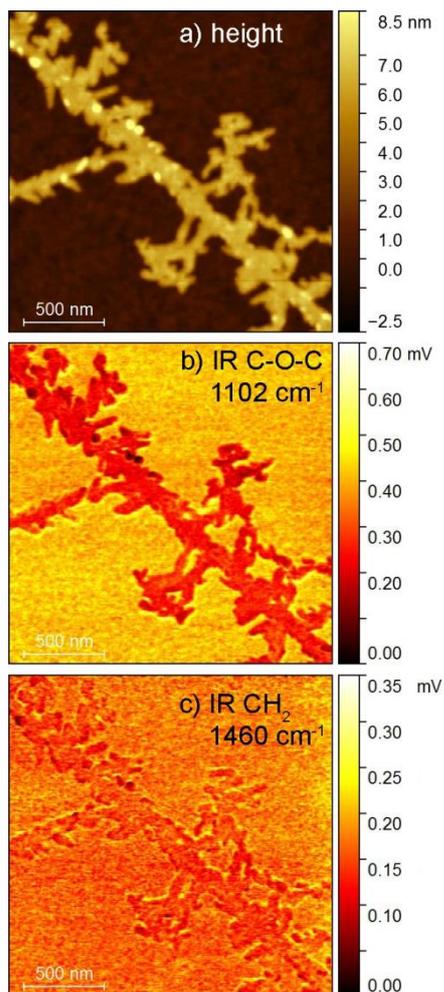


Fig. 3 AFM-IR of the PE island on top of the 15 nm PEO film: a) height image; b) IR signal at 1102 cm^{-1} corresponding to the C-O-C groups present only in PEO; c) IR signal at 1460 cm^{-1} corresponding to the CH_2 groups present both in PE and PEO.

The AFM measurements revealed that the PE islands may exhibit markedly different shapes. For example, the images of Fig. 1 demonstrate the PE islands deposited on the PEO films prepared at identical conditions but with different thickness. Anisotropic star-shaped dendrites are formed on ultra-thin 15 nm PEO whereas ramified fractal islands grow on thicker 100 nm PEO. Given that the chemical composition and the molar mass distribution of both PEO films are identical, we conclude that it is the difference in dynamics of segmental motion that is responsible for the observed changes. It is known that the vicinity of a rigid support imposes constraints on the mobility of molecular segments in ultra-thin polymer coatings [3]. The confinement effects are typically manifested at 10-20 nm distance from the polymer-substrate interface. Therefore, in the case of 15 nm PEO, polyolefin molecules diffuse on the more rigid surface,

the segmental mobility of which is significantly suppressed by the proximity of the Si substrate. For the 100 nm PEO coating, the influence of the substrate is diminished, the polyether macromolecules are more flexible at the free surface and their mobility sets additional barriers to the surface diffusion of incoming polyolefins. As a consequence, the PE islands grow close to a diffusion-limited aggregation (DLA) regime which is characterized by the formation of less anisotropic ramified fractal patterns [4].

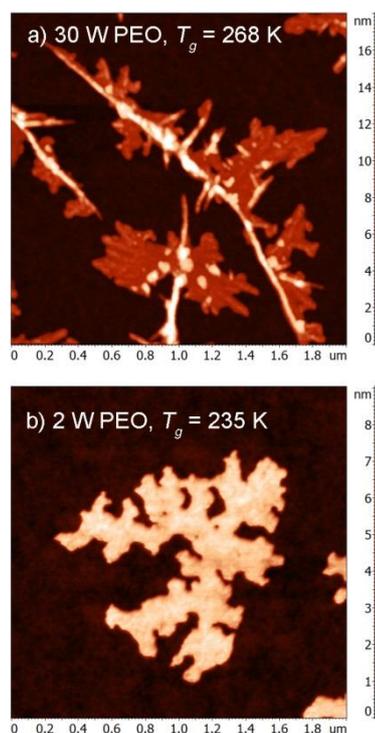


Fig. 4 Height AFM images of PE islands formed on 100 nm thick PEO films with different cross-link density controlled by the discharge power: a) 30 W; b) 2 W. The deposition parameters are: PEO (the QCM deposition rate is 20 Hz/min, the deposition time is 20 min, the crucible-substrate distance is 10 cm), PE (the discharge power is 5 W, the QCM deposition rate is 20 Hz/min, the deposition time is 30 s, the crucible-substrate distance is 10 cm). The glass transition temperature values are shown as measured at 10 Hz by AC-chip specific heat nanocalorimetry.

The flexibility of the PEO chains can be also tuned by the discharge power. Higher power leads to an increase of the plasma density and, as a result, to stronger fragmentation of the PEO oligomers. The following re-polymerization of the plasma-activated polyethers on the surface proceeds with the formation of coatings with higher cross-link density. Here, the PEO films of similar thickness were deposited using 30 W and 2 W power directly onto the chips for specific heat nanocalorimetry

measurements. The glass transition temperature T_g of the 30 W film was found to be at 268 K whereas substantially smaller $T_g = 235$ K was obtained for the 2 W film [2]. The glass transition temperature is directly related to the segmental motion in amorphous polymers, being higher for polymers with highly constrained segmental mobility. Hence, the nanocalorimetry results confirm that the surface of the 30 W sample is more rigid as compared to the 2 W sample. As an outcome of this, the PE islands grow with more anisotropic and elongated shape on the 30 W PEO film (Fig. 4) whereas polyolefins aggregate into the islands of the ramified structure on the 2 W PEO film, in a close analogy with the deposition on the thickness-dependent PEO coatings.

4. Conclusions

Plasma-activated polyolefins self-organize into two-dimensional islands when deposited on the surface of flat PEO plasma polymer. The thickness of the islands remains at about 7 nm but the shape depends drastically on the segmental mobility of underlying PEO. Less constrained PEO introduces energetic barriers to the surface diffusion and the PE islands grow with the ramified fractal structure close to the DLA regime. For highly constrained PEO, anisotropic growth of PE islands prevails and more elongated dendrite-type islands are formed. The segmental dynamics in PEO can be controlled by its thickness due to constraints imposed by the rigid substrate at the polymer/substrate interface. Alternatively, the mobility of the PEO segments can be adjusted by the discharge power supplied during the PEO deposition due to the control over the cross-link density in the resultant coatings.

5. Acknowledgements

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6. References

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