



Morphology of poly(propylene azelate) gratings prepared by nanoimprint lithography as revealed by atomic force microscopy and grazing incidence X-ray scattering



M. Soccio^{a, c}, D.R. Rueda^a, M.C. García-Gutiérrez^a, N. Alayo^b, F. Pérez-Murano^b, N. Lotti^c, A. Munari^c, T.A. Ezquerro^{a, *}

^a Instituto de Estructura de la Materia, IEM-CSIC, Serrano 119-121, 28006 Madrid, Spain

^b Instituto de Microelectrónica de Barcelona IMB-CNM (CSIC), Campus UAB 08193, Cerdanyola del Vallès (Bellaterra), Barcelona, Spain

^c Dipartimento di Ingegneria Civile, Chimica, Ambientale e dei Materiali, Università di Bologna, Via Terracini 28, 40131 Bologna, Italy

ARTICLE INFO

Article history:

Received 7 November 2014

Received in revised form

5 December 2014

Accepted 26 January 2015

Available online 31 January 2015

Keywords:

Polymer nanoconfinement

Grazing incidence X-ray scattering

Nanoimprint lithography

ABSTRACT

Nanostructured gratings of semicrystalline poly(propylene azelate) (PPAz) have been prepared over spin-coated thin films by Nanoimprint Lithography (NIL). The structure and morphology of the gratings have been investigated by combining Atomic Force Microscopy (AFM) and Grazing Incidence X-ray Scattering at small angle (GISAXS) and wide angle (GIWAXS). The results reveal that NIL affects significantly the orientation of the crystalline lamellae. PPAz gratings are more abundant in edge-on lamellae than the reference non-printed films. We attribute this effect to the PPAz preferential crystallization as flat-on lamellae on silicon surfaces either the stamp trench walls or the substrate surface. Thus, the flat-on lamellae on the trench walls appear to be edge-on lamellae in the printed sample. These results further support NIL as an appropriate procedure in order to control polymer crystal orientation.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

The control of polymer crystallization at nano and micrometer level can be a crucial issue in order to optimize functionality of polymer systems. Typical examples are the performance of organic photovoltaics cells [1] or polymer memory devices [2] among others. Nanopatterning of polymers is nowadays possible by using a great variety of techniques aiming to achieve controlled structures [3]. Nanoimprint Lithography (NIL) is a very efficient method to produce nanometer-scale resolution patterns on polymer surfaces [4]. By means of NIL, a certain pattern acts as a stamp that can be replicated by mechanical contact over a molten polymer film [5–7]. Previous studies on nanoimprinting over semicrystalline polymers using stamps with either gratings [8,9] or pillars [10] point towards the existence of two main regimes described as of low and high confinement. In the first case the thickness of the film is significantly higher than the protrusion height of the stamp and therefore the structured surface appears over a residual polymer film. In this situation polymer crystallization tends to be controlled by the

underlying continuous film. In the second case, a higher level of confinement appears when the polymer film thickness is comparable or lower than the protrusion height. In this situation little residual film persists after NIL fabrication and polymer crystallization develops in quasi non-interconnected regions. A rather similar effect appears by infiltration of a semicrystalline polymer into porous alumina membranes [11,12]. Preparation of nano-gratings by NIL in poly(vinylidene fluoride) (PVDF) films have shown that edge-on crystalline lamellae can be predominantly obtained under low confinement conditions while flat-on ones appears under higher confinement [8]. NIL studies on poly(vinylidene fluoride-trifluoro ethylene) (P(VDF-TrFE)) random copolymers indicated that confinement by NIL tends to favor the presence of edge-on lamellae over the flat-on ones [13] and that this disposition is more favorable from the point of view of the ferroelectric properties [10]. Nanoimprinting in poly(ethylene oxide) have shown also that crystallization was significantly affected by the geometric constraints imposed by the mold. These examples emphasize the relevance of investigating the effect of confinement on the crystal orientation during imprinting.

Aliphatic polyesters have attracted considerable attention recently as they combine the features of biodegradability and

* Corresponding author.

E-mail address: t.ezquerro@csic.es (T.A. Ezquerro).

biocompatibility with physical and chemical properties comparable with some of the most extensively commodity polymers [14]. Aliphatic polyesters based on 1,4-butanediol are among the most studied being probably Poly(butylene succinate) (PBS) the one which has found a great variety of applications. In particular PBS micrometer size gratings have been prepared and their potential application as structured biomimetic surfaces for tissue engineering has been discussed [15]. However, studies of crystal orientation in these types of gratings are still scarce. Aliphatic polyesters based on 1,3-propanediol can be an attractive alternative to those above mentioned specially since recently they are commercially available at low cost and in high purity [16]. Previously, we have reported on the structure and morphology of spin-coated thin films of a series of linear aliphatic polyesters $[-O-(CH_2)_3-O-CO-(CH_2)_Y-CO-]$ based on 1,3-propanediol with different length of the acid subunit ($Y = 2, 3, 4$ and 7) [17,18]. Thin spin-coated films of the aliphatic polyester with $Y = 7$, poly(propylene azelate) (PPAz) are rather stable against dewetting until thicknesses of about 15 nm and they exhibit a well-defined flat-on lamellae morphology [18]. For this reason PPAz is a good candidate as model aliphatic polyester in order to investigate the effect of NIL on the crystal orientation.

In this work we report on the structure and morphology of grating nanostructures prepared by NIL on spin-coated poly(propylene azelate) thin films. A combined study, by means of atomic force microscopy (AFM) and grazing incidence wide angle X-ray scattering (GIWAXS), reveals an enhancement of the edge-on lamellae population.

2. Experimental

2.1. Materials and spin-coated films

PPAz was synthesized by using the two-stage polycondensation procedure as previously reported [16]. PPAz was obtained with a molecular weight of $M_n = 36,000$ g/mol and a polydispersity degree of 2.5. It is characterized by both a low melting and glass transition temperature ($T_m = 49$ °C, $T_g = -56$ °C). PPAz is a semicrystalline polymer as other aliphatic polyesters of the same family [16]. Thin polymer films were prepared in a clean room class 100 by spin-coating a polymer solution in chloroform (30 mg/mL) on silicon wafers(100) (Wafer World Inc.). 0.1 mL of solution was dropped by a syringe on a square (2×2 cm²) silicon substrate. A rotation speed of 3000 rpm was reached after a 0.1 s acceleration period and maintained for 1 min. Polymer films of 302 ± 20 nm in thickness, as measured by spectrophotometry (Nanospec 6100), can be typically obtained under these conditions.

2.2. Preparation of polymer gratings by Nanoimprint Lithography, NIL

A grating (2×2 mm²) with a pitch of $L_s = 200$ nm, line width $D_s = 96$ nm and height line $H_s = 140$ nm was fabricated on mesa-type silicon stamp as previously described [19,20]. For this geometry the thickness of the spin-coated polymer film is about twice the depth of the stamp trenches. The stamp was silanized with trichloro-(1H,1H,2H,2H-perfluorooctyl)silane in order to avoid sticking of the polymer. This stamp was used to imprint spin-coated films of PPAz by means of a thermal nanoimprint system (Obducat 4 inch from Obducat). First, a temperature of 80 °C was reached in the absence of pressure. Second, a pressure of 40 atm was applied for 5 min. Third, the temperature was reduced to room temperature keeping the pressure. Fourth, pressure was removed and the stamp was detached from the polymer nanostructure. The morphological characterization of the stamps, size of lines and trenches, was performed by Scanning Electron Microscopy (SEM) (Leo 1530,

Zeiss). The depth of the stamp trenches was estimated by AFM (Dimension 3100, Bruker) in tapping mode.

2.3. Atomic force microscopy, AFM

Topography and phase images of the NIL polymer gratings were acquired by an atomic force microscope (Nanoscope V, Bruker) in tapping mode. Images were collected at room temperature. Data were analyzed with NanoScope Analysis 1.10 software.

2.4. Grazing incidence X-ray scattering, GIXS

The PPAz grating was investigated by grazing incidence at both small and wide angles X-ray scattering, (GISAXS and GIWAXS respectively) by using synchrotron radiation, in the BW4 beamline at HASYLAB (DESY, Hamburg, Germany). The sample alignment procedures are the same for GISAXS and GIWAXS experiments differing only in the sample-to-detector distance used. A detailed description of the experimental set up has been previously reported [13,21–23]. An X-ray wavelength of $\lambda = 0.13808$ nm with a beam size ($H \times V$) of 40×20 μm^2 was used in our experiments. A MarCCD detector of 2048×2048 pixels with a resolution of 79.1 μm per pixel was used. Sample-to-detector distances of 2.325 m and 0.106 m were used for GISAXS and GIWAXS, respectively. A silver behenate standard was used for calibration. The GISAXS pattern of the PPAz-grating was recorded by assuring the incoming X-ray beam is parallel to the lines of the grating and using an incidence angle, α_i of 0.4°. For GIWAXS experiments different incidence angles between 0.2° and 0.4° were used being the grating aligned both parallel and perpendicular to the X-ray beam. For the sake of comparison a non-printed area of PPAz film, outside the grating but in the same film was also investigated. Acquisition times of 30 s for the GISAXS and of 60 s for GIWAXS were typical.

3. Results and discussion

Fig. 1a shows the morphology of the stamp as obtained by SEM. Fig. 1b,c and d show the morphology of the PPAz grating as revealed by AFM images in phase (Fig. 1b) and in height with two different magnifications. The polymer grating obtained corresponds to the negative pattern of the silicon grating used as stamp. It shows a similar pitch ($L = 200$ nm) and a line width for the raised structures of about 104 nm. For semicrystalline polymers it has been proven that AFM phase images can be more effective than height images in revealing the characteristic lamellar morphology of semicrystalline polymers [9,24]. Fig. 2 shows both the AFM height and phase images at higher magnification. A height profile revealing the cross section of lines is also provided. The average height of the polymer lines is of about 120 nm which is smaller than that one of the stamp. This indicates that a residual film of about 180 nm remains underneath the grating. Looking at the images of Fig. 1 it is clear that the polymer lines present a great amount of defects which reduce line continuity to lengths smaller than about 5 μm . The observed defects mainly consist on missing line pieces producing broken lines. This can be attributed to the semicrystalline nature of the PPAz polymer which induces mechanical failure upon stamp detachment.

It is remarkable that the AFM phase image (Fig. 2a) reveals some characteristic motives, brighter ones, which can be assigned to PPAz crystalline lamellae [18]. At a first glance these crystalline lamellae seem to adopt a preferential edge-on disposition in relation to the substrate but do not exhibit a preferential orientation in relation to the main axis of the lines. It is important to emphasize that AFM phase images are revealing the morphology of the outer sample surface. Moreover, the morphology of the non-imprinted

Download English Version:

<https://daneshyari.com/en/article/5180261>

Download Persian Version:

<https://daneshyari.com/article/5180261>

[Daneshyari.com](https://daneshyari.com)