European Polymer Journal 75 (2016) 234–242

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Macromolecular Nanotechnology

Poly(ethylene oxide)-block-polystyrene thin films morphology controlled by drying conditions and substrate topography

Jacek Jenczyk *, Emerson Coy, Stefan Jurga

NanoBioMedical Centre, Adam Mickiewicz University, Umultowska 85, 61-614 Poznań, Poland

ARTICLE INFO

Article history:
Received 5 November 2015
Received in revised form 22 December 2015
Accepted 23 December 2015
Available online 24 December 2015

Keywords:
Diblock copolymers
Polymer films
Self-assembling phenomenon
Atomic force microscopy
Polymer single crystal

ABSTRACT

Thin polymer films made of polystyrene-b-poly(ethylene oxide) (PS-PEO) diblock copolymer were deposited via spin-coating technique on thermally reconstructed sapphire substrates in order to obtain self-assembled polymer matrices characterized by long range domain ordering. This approach, under specific solvent vapor annealing conditions, enabled us to fabricate polymer films exhibiting quasi long-range crystalline organization of hexagonally packed PEO cylinders aligned perpendicularly with respect to the substrate surface. In order to find an optimal conditions for thin film fabrication, the influence of moisture annealing process on polymer films morphology was examined. Different drying conditions revealed semicrystalline nature of poly(ethylene oxide) block. Consequently, apart from regular amorphous layers, various crystalline forms were also observed, including dendritic crystals, densely branched structures and square shaped single crystals. Presented data show how strongly the polymer film morphology depends on annealing conditions.

1. Introduction

Block copolymers belong to a group of self-assembling materials which are believed to play an important role in future microelectronics and nanolithography [1–6]. Their ability to form various micro domain topologies is a consequence of a thermodynamically driven phase separation which is a manifestation of a delicate balance between entropic and enthalpic contribution to the overall free energy of the system. Depending on relative volume fraction of a particular block and the temperature, there have been number of copolymer morphologies observed both using experimental techniques [7,8] and relying on computer simulations [9–12]: starting from relatively simple lamellar structures, passing through hexagonally packed cylinders, cubically ordered spheres and ending with remarkable gyroidal architecture. This structural diversity was theoretically predicted and thoroughly described more than three decades ago [13] by means of Flory–Huggins Theory of polymers. In consequence a phase diagram for a simple two block copolymer (A-b-B) system was obtained and has been also proven experimentally [14]. Periodic nature of self-assembled polymers together with a nanoscale dimensions of their domains draw an attention of scientists and engineers due to the fact that copolymers can potentially open new areas for nanolithography. Taking into consideration limitations of conventional photolithographic methods there is a need of searching for an alternative techniques which enable one to break the limit of 30 nm feature size [15]. Although, there are exceptionally precise top-down nanopattern generation methods available, such as electron-beam and scanning-probe

---

* Corresponding author.
E-mail address: jacjen@amu.edu.pl (J. Jenczyk).

http://dx.doi.org/10.1016/j.eurpolymj.2015.12.020
0014-3057/© 2015 Elsevier Ltd. All rights reserved.

nanolithographies, their major disadvantage is that they are extremely time consuming and hence applicable exclusively for small area purposes. Therefore, nowadays a lot of effort is made to utilize the bottom-up processes based on thin polymer film self-assembling onto crystalline substrates [16,17]. Despite of relatively easy control over the morphology type and domain dimensions, the major drawbacks of copolymeric matrices remain the lack of long range domain order and substantial number of defects present. In order to overcome these issues several different approaches have been proposed [18–24]. One of the most common is the method of domain ordering induced via substrate topography. In most cases it requires an initial surface preparation and that can be very demanding and time consuming. Nevertheless, there is a relatively simple approach described by Park et al. [25] where authors exploit the phenomenon of sapphire surface reconstruction [15] which leads to "saw tooth" pattern formation spreading macroscopically over the whole crystal surface. This fully anisotropic motif introduces an ordering effect on the domain topology of a thin film deposited on the surface and enables to produce large areas of perfectly organized copolymer matrices. Although, the reconstructed substrate plays an essential role, equally important are annealing conditions which can substantially affect both domain ordering and morphology of polymer film made of block copolymer. This refers especially to copolymers consisting of at least one semicrystalline block which under certain conditions can effectively form cristallites having various shapes and sizes. Despite of a wide range of studies devoted to polymer single crystals, which have been conducted in the past decades, the problem of crystal growth dynamics and an abundance of morphological motifs formed via polymer crystallization remain an interesting issues [26], especially in the developing area of ultra-thin polymer films technologies. Early works of Lotz et al. [27], who were pioneers in the field of copolymer single crystals, introduced three-layer sandwich model of monocrystalline structures. It appears that thermodynamically, the most stable state is represented by crystalline middle layer (lamella) with fully amorphous base and top layers covering crystalline lamella surfaces from both sides as it is presented schematically on Fig. 1. These copolymer crystals can develop from melt via self-seeding process which relies on thermodynamically stable remnants of pre-existing crystals acting as crystallization nuclei [26]. Therefore, due to entirely random initial orientation of those seeds the relative positions of developed crystals usually do not correlate.

Polyethylene oxide (PEO) is well known example of semi-crystalline polymer which is able to form square-shaped single crystals with monoclinic unit cell and bounded by four (120) planes according to electron diffraction experiment [28,29]. Surprisingly, the PEO can exhibit the same feature even as a part of block copolymer system where different polymer species are chemically anchored at its one end [30,31]. Selective area electron diffraction data have demonstrated that PEO blocks crystallize with a monoclinic structure identical to that of homo-PEO [32]. Sandwich model scenario of PS-PEO copolymer single crystal growth assumes that the PEO block is incorporated into a crystal lattice in a chain-folded fashion while the second amorphous PS block is left out either in the basal or it the top space.

Numerous of experimental studies have proven that crystal growth dynamics and the eventually formed crystalline structures substantially depend on annealing conditions [26,28,32–36]. The same concerns domain morphologies [21,37–42]. Depending on (i) temperature, (ii) cooling rate, (iii) vapor pressure, (iv) type of a solvent used, (v) any specific interactions between the polymer and the substrate, (vi) polymer film thickness and of course (vii) type of the polymer used, one can expect various forms of structures emerging. Generally, for relatively thick films ($d \gg 100$ nm) there are usually regular

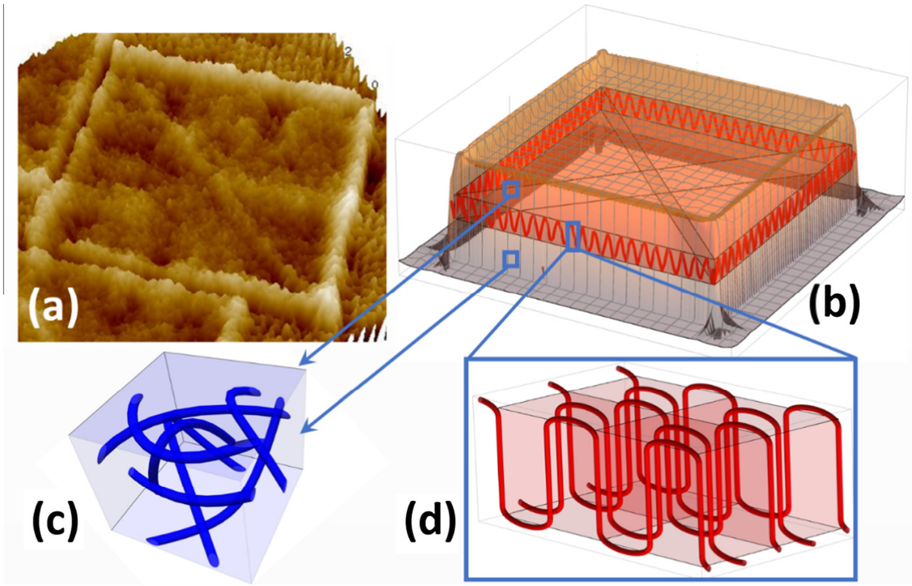

Fig. 1. (a) 3D projection of AFM topographical scan for PS-PEO monocrystal, (b) 3D model of square shaped monocrystal structure and its "sandwich"-like crossection, (c) amorphous PS base and top, (d) PEO crystalline unit cells with chain-folded arrangement.