



## A new method for patterning azopolymer thin film surfaces



Sh. Golghasemi Sorkhabi <sup>a, b, \*</sup>, R. Barille <sup>b</sup>, S. Ahmadi-Kandjani <sup>a</sup>, S. Zielinska <sup>c</sup>, E. Ortyl <sup>c</sup>

<sup>a</sup> Research Institute for Applied Physics and Astronomy (RIAPA), University of Tabriz, Tabriz, Iran

<sup>b</sup> University of Angers/UMR CNRS 6200, MOLTECH-Anjou, 49045 Angers, France

<sup>c</sup> Wrocław University of Technology, Faculty of Chemistry, Department of Polymer Engineering and Technology, 50-370 Wrocław, Poland

### ARTICLE INFO

#### Article history:

Received 13 January 2017

Received in revised form

28 February 2017

Accepted 3 March 2017

#### Keywords:

Surface patterning

Azopolymer

Solvent-droplet-induced-dewetting

Photo-patterning

Nano-doughnut

### ABSTRACT

We present a simple bottom-up approach via an incoherent unpolarized illumination and the choice of a solvent-droplet-induced-dewetting method to photoinduce nano doughnuts on the surface of azopolymer thin films. We demonstrate that doughnut-shaped nanostructures can be formed and tailored with a wide range of typical sizes, thus providing a rich field of applications using surface photo-patterning. Furthermore, due to the presence of highly photoactive azobenzene derivative in the material, illumination of these nanostructures by a polarized laser light shows the possibility of a further growth and reshaping opening the way for fundamental studies of size-dependent scaling laws of optical properties and possible fabrication of nano-reactor or nano-trap patterns.

© 2017 Elsevier B.V. All rights reserved.

### 1. Introduction

As a substantial base for the development of future technologies we are currently witnessing an explosion of novel ideas and strategies in nano-science with fusion of bottom-up and top-down strategies. Manipulation, conception and examination of nano-structured objects and devices in precise, sensitive and specific manners are some of the pillars of construction of new technologies for domains of photonics or nano-medicine [1]. In this regard, due to their potentials in the emerging field of controlled nanostructure formation, thin films of polymers containing azobenzene chromophores have generated significant interest with the development of nanofabrication and characterization techniques [2]. The geometrical configuration of the azo bond in azobenzene based compounds can be changed reversibly from *trans* to *cis* by irradiation with light intensity and/or polarization gradient. The photo-induced reversible *trans-cis-trans* isomerization of azobenzenes lead to spontaneous large scale macroscopic motion of polymer material leading to surface deformation of material below  $T_g$  [3]. This light induced movement has been recognized as a useful tool to enforce reversible changes in a variety of molecular systems; a

possible technology for a broad range of fundamental and applied researches [4]. The mass transport not only provides a unique opportunity for nanostructure formation but also due to the unique photophysical behavior of these materials, azopolymers nanostructures can be optimized and reshaped via controlled light field, to gain the desired behavior [5].

In order to procure and explore novel opportunities for developing new applications in material science, nano-photonics and nano-biotechnology, advancement toward smaller features is of paramount importance in nano-fabrication [6].

In this regard, over the past decade, a variety of both top-down and bottom-up fabrication approaches such as: direct-writing, nano-imprinting and self-assembly, have been used to fabricate a range of well-defined nanostructured materials with desirable physical and chemical attributes. Among these, the bottom-up self-assembly process offers the most realistic solution toward the fabrication of next-generation functional materials and devices [7]. As a potential self-assembly technique, dewetting is regarded as a suitable method for micro and nanoscale fabrication as self-organization during dewetting leads to the fabrication of a nearly equal sized collection of holes and droplets [8,9].

Several approaches have been developed for fabricating nano-structured arrays with organic molecules by controlling the dewetting [10,11]. Dewetting of polymer thin films have been explored experimentally and theoretically, although dewetting of azopolymer has not been suggested in the literature. Azopolymer

\* Corresponding author. Research Institute for Applied Physics and Astronomy (RIAPA), University of Tabriz, Tabriz, Iran.

E-mail addresses: [Shahla.golghasemi@gmail.com](mailto:Shahla.golghasemi@gmail.com), [Sh.Golghasemi@tabrizu.ac.ir](mailto:Sh.Golghasemi@tabrizu.ac.ir) (Sh.G. Sorkhabi), [S\\_ahmadi@tabrizu.ac.ir](mailto:S_ahmadi@tabrizu.ac.ir) (S. Ahmadi-Kandjani).

nanostructures are produced through irradiation with a single laser or a laser pattern. However, examples of quite rare utilization of incoherent white-light for thin film regular photo-patterning and reshaping of azopolymer nanostructures has been recently demonstrated [12].

In this work, we experimentally show a simple bottom-up approach to produce doughnut shaped nanostructures on the surface of azopolymer thin films by the choice of a solvent-droplet-induced-dewetting method and an incoherent unpolarized light illumination. Also, due to the presence of highly photoactive azobenzene derivative in the material, illumination of these nanostructures by a polarized laser light shows the possibility of a further growth and reshaping of the structures.

## 2. Experimental

Azopolymer thin films are made from a highly photoactive azobenzene derivative containing heterocyclic sulfonamide moieties (IZO-3). The details of synthesis of the used copolymer based on 2- [2- [4-[(E)-(4-[(2,6-dimethyl-pyrimidin-4yl)amino]sulfonyl)phenyl]diazenyl]phenyl](methyl) amino]ethoxy ethyl 2-methylacrylate\_ are reported elsewhere. The chemical structure of this copolymer is shown in Fig. 1 [13]. Thin films were prepared by dissolving azopolymer in THF (50 mg in 1 ml of THF) and spin-coated on a pre-cleaned glass substrate. Prepared films were let in oven overnight at 80 °C to remove any residual solvent and also for obtaining films whose surface morphology appears featureless or is not dominated by pinholes and other surface defects. The film thickness was determined by a Dektak Profilometer and was around 550–600 nm. Mean molecular weight,  $W_M$ , of polymers has been determined by Gel permeation chromatography (GPC) using Waters 917 columns, RIDK-102 detector and APEX ver. 3.1 recorder and is between 14000 and 19000 g/mol. A mobile phase was  $\gamma$ -butyrolactone and molecular weight refers to polystyrene standards ( $M_w = 16500$  g/mol,  $M_n = 11750$  g/mol).

A Mettler Toledo DSC has been used for glass transition temperature ( $T_g$ ) determination of polymers with scanning of 20 K/min. The glass transition temperature ( $T_g$ ) was 71 °C (344.5 K).

Considering the importance of surface modification and the numerous applications of azopolymer thin films, this azopolymer and its relating compounds have been the subject of studies for investigating the surface deformation through laser illumination [14–16]. However, the method chosen to create the initial patterns on the surface of azopolymer film here is solvent-droplet-induced dewetting. A 0.3  $\mu$ l droplet of solvent was dropped on the thin film surface. Upon contact the droplet spreads and covers an area of approximately 50mm<sup>2</sup> on the surface. An incoherent white light from a xenon lamp (Hamamtsu, C2177-01) was used to initiate the photoinduced mass transport in the film. To illuminate the sample by a polarized light, a horizontally linearly polarized beam from a DPSS laser operating at a wavelength of  $\lambda = 473$  nm was used. In the next steps a quarter/half wave plate was used to control and change the polarization and direction of the polarization of the laser beam. The thin film topography was studied with an atomic-force microscope (AFM, Veeco Instruments Inc) in the contact mode.

## 3. Result and discussion

We tested several common solvents as hexane, cyclohexane, toluene, chloroform, dichloromethane, dimethyl sulfoxide (DMSO), 1–4 dioxane and acetone. Finally n-Heptan was chosen for the optimal pattern on the surface in term of available structures. In a first experiment, a 0.3  $\mu$ l droplet of the selected solvent (n-Heptan) was dropped off on the surface of the azopolymer thin film. A droplet of this volume covers an area of approximately 50mm<sup>2</sup> on

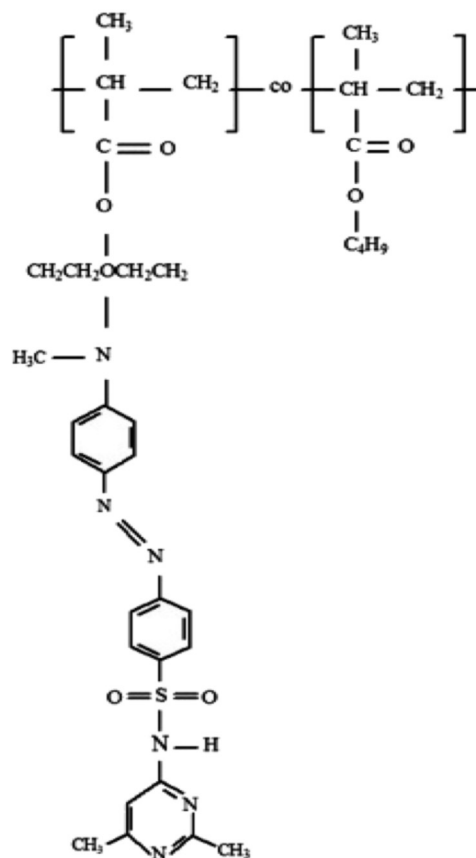


Fig. 1. Chemical structure of azopolymer.

the surface. n-Heptan has a medium boiling point of 98 °C and an evaporation rate of 2.80 (Butyl acetate:1). Owing to the low solubility of azopolymer in the solvent (n-Heptan), dewetted films appear completely flat and undisturbed to the naked eye and does not exhibit any changes in the absorption spectra (Fig. 2). The glass transition temperature of the polymer decreases below the room temperature due to absorption of the solvent into the polymer matrix, increasing the free volume of the polymer and resulting in an enhancement of the polymer molecules' mobility. These molecules are now able to reorganize freely which in turn leads to the rupture and dewetting of the thin film (hole formation) [17]. A small quantity of solvent entering in the azopolymer thin film is not sufficient to induce enough chain mobility. The glassy state is maintained and because the polymer is neither removed nor evaporated, the dissolved polymer can only be redistributed. The hole formation is due to migration of the polymer from the center of the hole to the perimeter during solvent evaporation [18].

The location of holes appears random but can be controlled with initial changes of the film topography [19] or by dewetting on already prepared patterned surfaces as we demonstrate later.

The mean length scale of the period between nearest nano-holes created by solvent-droplet-induced dewetting on the surface of azopolymer thin film was calculated via statistical processing of obtained AFM image (Fig. 3). We found an average value  $\lambda_f$  of  $2.5 \pm 0.1$   $\mu$ m which is in good agreement with the theoretical results of 2.17  $\mu$ m, given by Ref. [11]:

$$\lambda_f = \left( \frac{M_e \gamma_s}{|S|} \right)^{1/3} \frac{h_0^{7/6}}{M^{1/2}} \quad (1)$$

Download English Version:

<https://daneshyari.com/en/article/5442862>

Download Persian Version:

<https://daneshyari.com/article/5442862>

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