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Development of porous thin film polymers using metathetic etching on block copolymers



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ABSTRACT

The use of a metathetic catalytic reaction in the degradation of block copolymers is an important opportunity to develop varying porous structures using a one-pot method. In a non-solvent system, the 2nd Generation Grubbs' catalyst etches alkene containing polymers. The structural integrity of the system is maintained over relatively short time periods. This allows the degradation of the alkene component whilst maintaining the microstructure. Catalytic control leads to porous structures of varying size, density, and distribution. This method is demonstrated on backed thin films, resulting in varying porosities. Pore density and regularity is enhanced by decreasing the film thickness to improve mass transfer of the catalyst through the polymer and increase stability from the supportive backing.

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1. Introduction

The development of porous polymers is an area of growing interest due to the push from electronics and medical industries [1]. Many rely on oriented block copolymers to provide a template which can be achieved by degradation. For polymers containing carbon-carbon double bonds (C=C) ozone can be used; however, control is limited using this technique. More recently catalysis to remove unsaturated polymers has been explored.

Metathesis is the reaction of a transition metal centered catalyst acting on a C=C where an exchange of groups via a metallocyclic ring intermediate occurs. Traditionally, metathesis catalysis has been used for polymerization. More recently the reverse process, polymer degradation, has received attention [2–6]; here, the reactant is a polymer (containing a C=C) reducing in molecular weight to form the product. Recently, selectivity for an individual component in a block copolymer has been reported [7–9]. However, little attention has been paid to the resulting structures [10], and none to the controlling variables. The work here demonstrates the feasibility of producing porous thin films using metathetic etching. Furthermore, the simplicity of this technique will allow not only more polymeric choices for porous applications but also great potential for scale-up.

2. Experimental methods

A cylinder forming tri-block copolymer with a glassy continuous phase was used: polystyrene-(1,4)polybutadiene-polystyrene (SBS) (PB=26%mass, $M_n=87 \text{ kg mol}^{-1}$, PDI=1.08). The solvents (Sigma > 99%) and 2nd Generation Grubbs catalyst (Sigma) were used as received. The catalyst was stored under nitrogen.

A 10% mass solution of SBS in toluene was spin-coated onto ethanol-cleaned glass (5 mm thick, 4 cm square) to make (controlled by speed) films: $1 \pm 0.1 \mu\text{m}$ (500 rpm) and $400 \pm 50 \text{ nm}$ (3000 rpm). They were dried in a vacuum oven at room temperature and subsequently solvent annealed (tetrahydrofuran saturated nitrogen at room temperature) to vertically align the cylinders [11]. Thickness, orientation, and surface roughness were measured using Atomic Force Microscopy (AFM) (Fig. 1) before (to confirm that surface non-homogeneity was minimal) and after annealing. The latter shows morphological sizes and spacings consistent with Small Angle X-ray measurements ($d=24.3 \text{ nm}$).

A 100 mL reactor purged with nitrogen was charged with hexane (50 mL). A nitrogen purge at 1 mL min^{-1} continuously flushed the headspace throughout the reaction. The solid catalyst was added, dissolving and tinting the hexane pink. The glass mounted thin film was submerged, above a mesh separator (to protect the sample from the stir-bar).

To observe the full reaction space, a fractional factorial design (2^3) was used, resolving three variables (treatments) at two levels (Table 1). After the reaction samples were removed and rinsed in methanol to remove remaining active catalyst. Samples were then briefly returned to the vacuum oven to remove any remaining liquid prior to AFM analysis.

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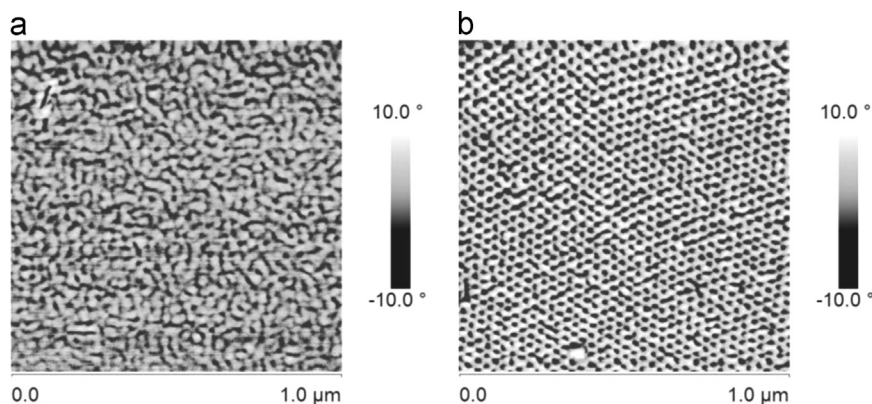


Fig. 1. AFM tapping mode phase images for a 1 μm film after (a) spin-coating (b) annealing.

Table 1

The fractional factorial experiments for thin films using solution etching method (with a combination of high (*H*) and low (*L*) levels for each treatment).

Sample	Treatments		
	Film thickness (nm)	Reaction time (min \pm 0.02)	Catalyst (g \pm 0.0002)
1 ^a	1000 (\pm 100)	60	0.005
2	1000 (\pm 100)	60	0.0005
3	1000 (\pm 100)	1	0.0005
4	1000 (\pm 100)	1	0.005
5	400 (\pm 50)	1	0.005
6	400 (\pm 50)	1	0.0005
7	400 (\pm 50)	60	0.0005
8 ^a	400 (\pm 50)	60	0.005

^a These samples could not be analyzed.

Characterization: AFM (Veeco Dimension 3100 Scanning Probe Microscope) with μmasch tips (8 nm diameter, 325 kHz frequency, 46 N/m spring constant) and image (tapping mode) scan sizes of 1 μm at a scan speed of 2 Hz with 512 points/line were used.

3. Results and discussion

Both polymers have limited (Hildebrand) solubility in hexane (PS: 13.0, PB: 4.84 $\text{MPa}^{1/2}$). Control tests with hexane (no catalyst) were run. These samples start in vertical alignment (Fig. 1b) and slowly convert to horizontal orientation with exposure over time. No voids were observed.

In the presence of voids, tapping mode shows the light-colored PS matrix with dark regions, which have a different phase angle than that for PB. The identification of these dark regions as voids has been corroborated by filtration of polyethylene oxide, silver, and silica nanoparticle solutions (this relation has been previously reported with a selection of tests on free-standing films [10]). The size of the pores has been validated using particle size and image analysis. In assessing pore diameter, insufficiently round pores were approximated appropriately resulting in an increased standard deviation. The pore size distributions are expected to be log-normal, and have been modeled as such.

The influence of catalyst concentration on the degradation of the block copolymer thin films was considered. Two thicker films at low reaction time in hexane are compared: Sample 3 (Table 1) at low catalyst concentration to Sample 4's high one. Sample 3 (Fig. 2a) exhibits voids slightly smaller than the expected size (18.0 ± 9.9 nm), as dictated by the block copolymer composition.

These voids show some regularity; however they deviate in shape. When catalyst concentration was increased ten-fold (Sample 4) an insignificantly larger pore size (19.7 ± 10.5 nm) was observed with similar irregularity and a higher density of pores (148 pores μm^{-2} to 95 for Sample 3). Comparable thinner films show a more pronounced difference than their thicker film counterparts. The higher concentration of catalyst used in Sample 5 results in pores (21.0 ± 6.8 nm) with excellent roundness, compared to Sample 6 with a lower concentration of catalyst (19.8 ± 9.4 nm) (Fig. 2b). Increased pore density is observed in Sample 5 (176 pores μm^{-2}) as compared Sample 6 (140).

Samples subjected to a higher catalyst loading (Samples 4 and 5) result in larger pores over a short reaction time than those with less catalyst (Samples 3 and 6). This, and an improvement in pore circularity, was clear for thinner films. However, these increases are relatively small considering the order of magnitude increase in catalyst. Film thickness plays an important role, highlighted by better porosity observed in thinner samples. This is observed in a comparison of both Samples 3 and 6 and Samples 4 and 5. An increase in thickness results in a decrease in pore size and density.

This effect is stronger than either of the other two tested (catalyst concentration and reaction time) on influence pore diameter; whereas, pore density was equally controlled by film thickness and catalyst concentration. Mass transfer through the polymer limits the catalyst, therefore, thinner films are more rapidly penetrated and degraded by the catalyst. An increase in catalyst concentration allows more PB sites to be reached simultaneously, leading to increased pore density. However, reaction time should not be ignored, as an increase of reaction time to one hour resulted in overall film degradation. This was observed most significantly with high reaction time and high catalyst concentration (Samples 1, 8)

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