

Development of Porous Thin Film Polymers using Metathetic Etching on Block Copolymers

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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.

Keywords: metathesis, block copolymers, degradation

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.

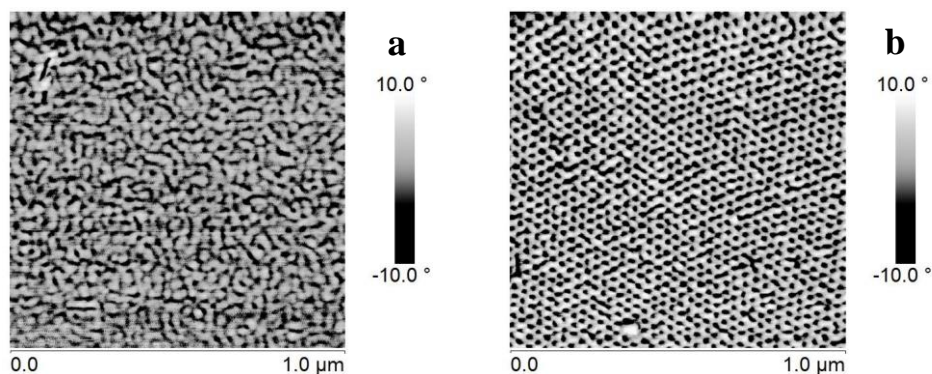
Metathesis is the reaction of a transition metal centered catalyst acting on a C=C where an exchange of groups via a metallocyclic ring intermediate occurs. Traditionally, metathesis catalysis has been used for polymerization. More recently the reverse process, polymer degradation, has received attention [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) (Figure 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 ($d = 24.3 \text{ nm}$).

Figure 1



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 (2³) 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.

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

^aThese samples could not be analyzed.

2.3 Characterization

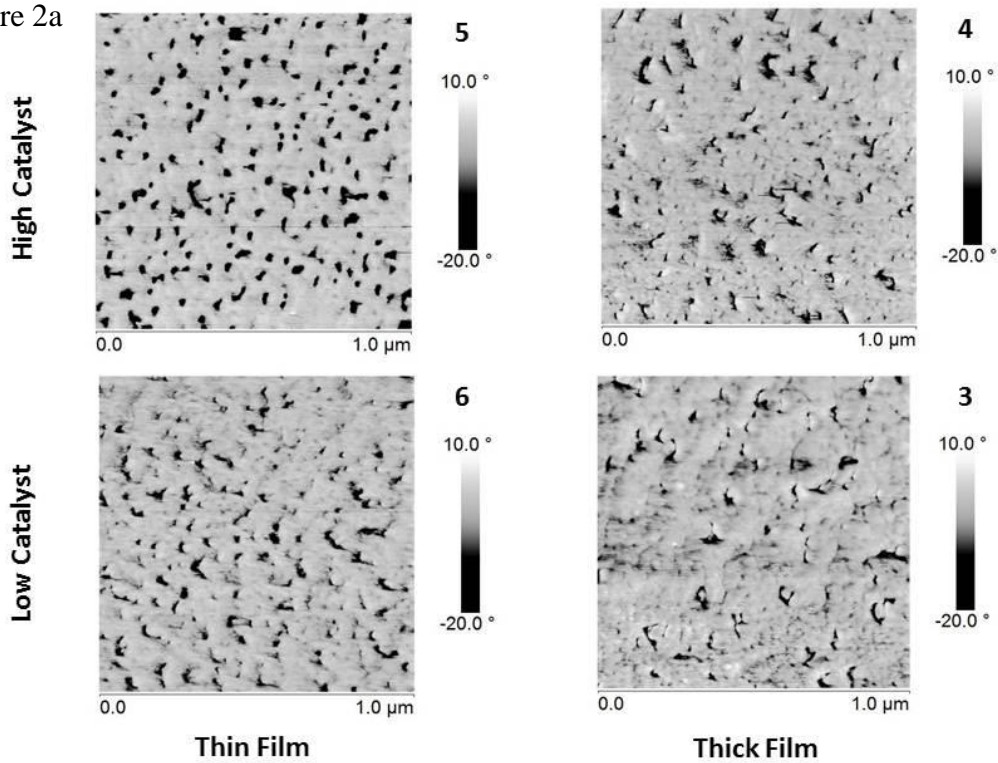
AFM (Veeco Dimension 3100 Scanning Probe Microscope) with μmasch tips (8 nm diameter, 325 kHz frequency, 46 N/m spring constant) and image (tapping mode) scan sizes of 1 μm at a scan speed of 2 Hz with 512 points/line were used.

3. Results and Discussion

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

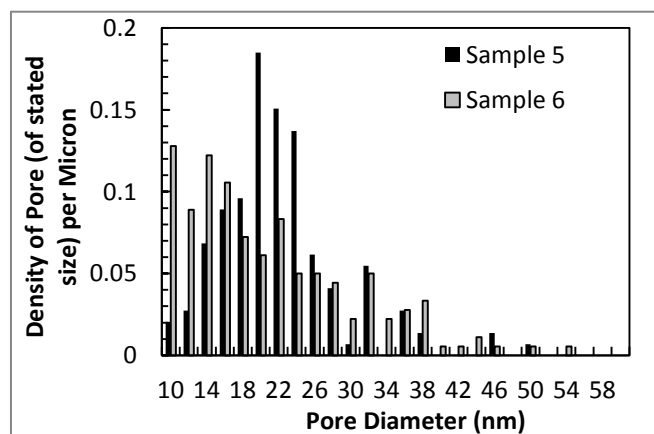
In the presence of voids, tapping mode shows the light-colored PS matrix with dark regions, which have a different phase angle than that for PB. The identification of these dark regions as voids has been corroborated by filtration of polyethylene oxide, silver, and silica nanoparticle solutions (this 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.

Figure 2a



1

Figure 2b

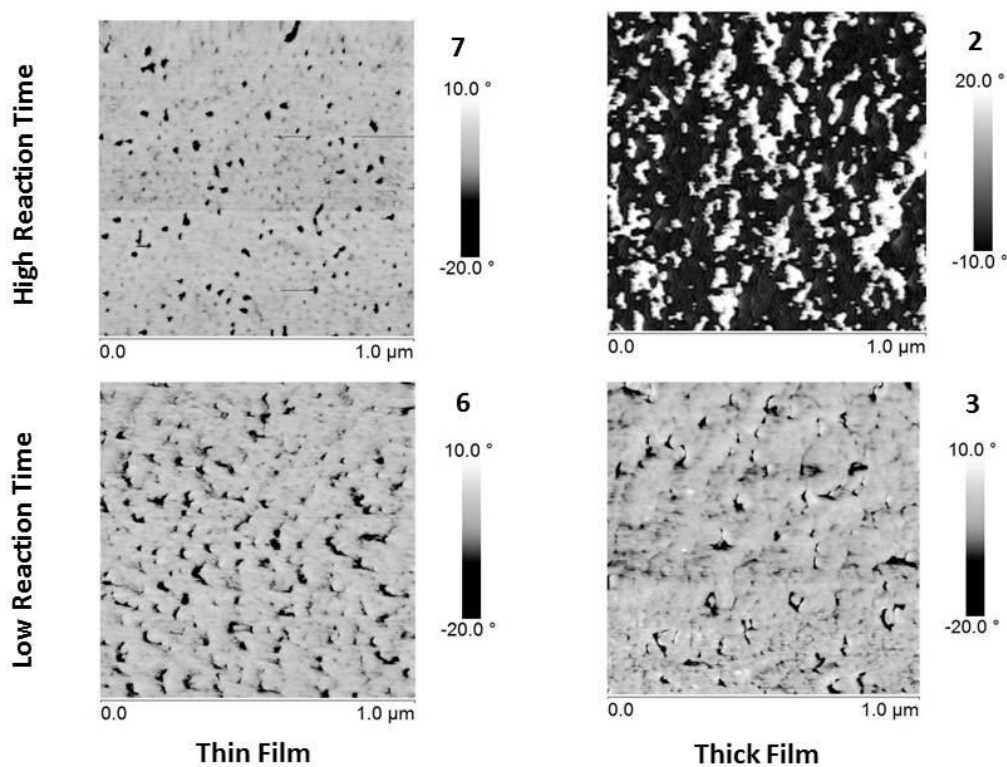


The influence of catalyst concentration on the degradation of the block copolymer thin films was considered. Two thicker films at low reaction time in hexane are compared: Sample **3** (Table 1) at low catalyst concentration to Sample **4**'s high one. Sample **3** (Figure 2a) exhibits voids slightly 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 ($148 \text{ pores } \mu\text{m}^{-2}$ 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) (Figure 2b). Increased pore density is observed in Sample **5** ($176 \text{ pores } \mu\text{m}^{-2}$) 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**) which were not fit for observation at the conclusion of the experiments.

Figure 3a



2

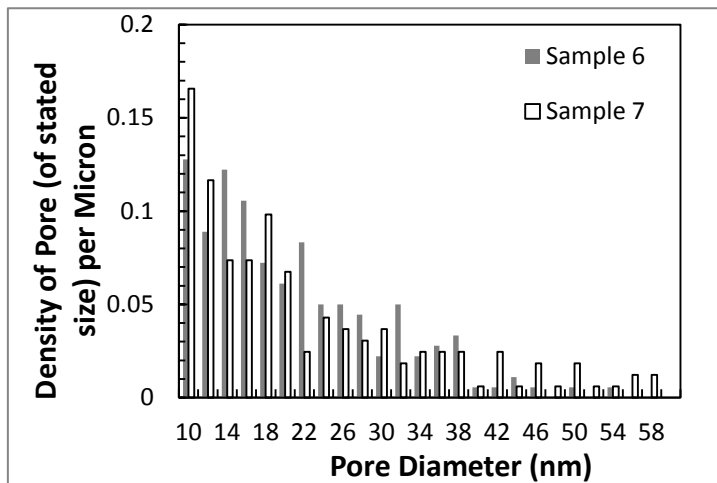


Figure 3b

Experiments with long reaction times at low catalyst loading (Samples 2 and 7) provide useful insights (Figure 3a). Sample 7 (Figure 3a) shows comparable pore size (18.5 ± 7.3 nm) and pore density (136 pores μm^{-2}) to a sample having had shorter reaction time (Sample 6) (Figure 3b). The integrity of this film is attributed to its thinness allowing more stabilization from the substrate. By comparison, Sample 2 shows a loss of structural integrity due to the loss of stability with a thicker film, after undergoing an extended reaction. This behavior, and that observed in Samples 1 and 8 highlight that

increased reaction time permits mass transfer to occur more extensively. These extreme conditions leave only a PS homopolymer behind after all the PB is reacted. This is more vulnerable to an entropically favorable rearrangement, resulting in a lack of structural integrity; also found in other less controlled techniques. However, in less extreme conditions the pore size, all somewhat smaller than the expected, point to a small remaining PB component helping to retain the structure [12]. As a result, reaction time should be controlled to avoid total structural loss, and catalyst concentration considered carefully.

4. Conclusions

This proof-of-concept study has successfully demonstrated that the development of porous thin films can be achieved using catalytic metathetic reaction. For a short period of time, the reaction rate dominates over polymeric rearrangement. To capitalize on this, thinner films allow extensive mass transfer. Thus, short reaction time with thinner films and relatively little catalyst, produce good metathetic etching of polybutadiene in a block copolymer thin film, for the production of a porous film. These behaviors indicate promise in controlling the porosity and structure not achieved by other methods. Now polymers such as polybutadiene can be used for porous polymer applications, thereby bringing alternative materials which may not previously have been possible.

5. Acknowledgements

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Figures:

- 1: AFM tapping mode phase images for a 1 μm film after (a) spin-coating (b) annealing.
- 2: (a) AFM tapping mode phase images of Samples **3** – **6** comparing main effects: thickness and catalyst loading. (b) Image analysis of pore density as a function of diameter (nm) (Samples **5** and **6**). Small number of pores with diameter of $<9\text{nm}$ were excluded due to noise.
- 3: (a) AFM tapping mode phase images of Samples **2-3** and **6-7** comparing main effects: thickness and reaction time. (b) Image analysis of pore density as a function of diameter (nm) (Samples **6** and **7**). Small number of pores with diameter of $<9\text{nm}$ were excluded due to noise.

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).

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