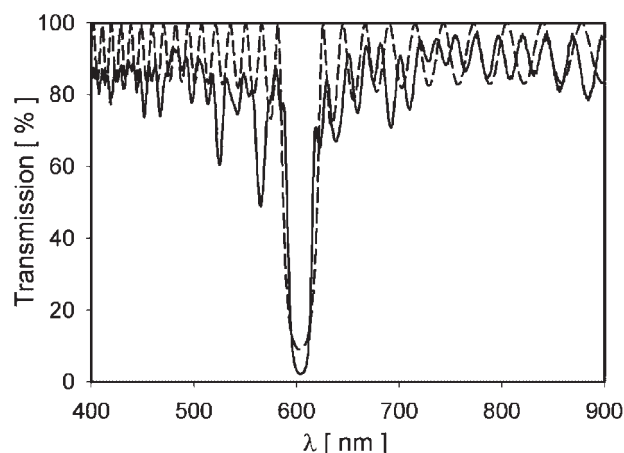


# Polymeric One-Dimensional Photonic Crystals by Continuous Coextrusion

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It is shown that narrowband one-dimensional photonic crystals can be fabricated from polymeric materials using laboratory scale layer-multiplying coextrusion technology. The tuning of the photonic bandgap is demonstrated with films that selectively filter different regions of the visible electromagnetic spectrum. The layer uniformity of the photonic crystals is evaluated by comparing the measured UV-vis transmission spectra with model simulations, and is independently confirmed with atomic force microscopy. Assemblies of alternating polystyrene and poly(methyl methacrylate) layers exhibit a narrow reflection band with close to 100% reflection in good agreement with the prediction for uniform layers. The flexibility of the process is demonstrated by the fabrication of elastomeric one-dimensional photonic crystals. It is anticipated that this technology will enable the rapid and facile realization of new polymeric optical devices.



## Introduction

Photonic crystals are dielectric materials in which there is periodic variation in the dielectric constant and hence in the refractive index.<sup>[1]</sup> Electromagnetic waves can not propagate in these materials at certain frequencies.<sup>[2]</sup> There exists a photonic bandgap analogous with the conduction bandgap in semi-conductor crystals. Photonic crystals with periodicity in the refractive index along one, two, or three axes are defined as one-, two-, or three-dimensional (1D, 2D, 3D) photonic crystals.<sup>[3]</sup> The possibility to mold the flow of light in a manner analogous to the controlled flow of electrons has stimulated interest in any number of applications. Some of these, such as

waveguides, resonators and filters, polarizers, LEDs, optical fibers, and lasers, are being actively explored and in some cases are close to commercialization.<sup>[4]</sup> Other advanced applications such as all-photonic integrated circuits are still being explored theoretically through simulations.<sup>[5]</sup>

Because of the ease of fabrication and light weight, polymers are already being used in optical applications such as Fresnel lenses, gradient index lenses,<sup>[6]</sup> polarizers, and optical filters. Recent attempts to fabricate polymeric 1D photonic crystals include self-assembling structures such as block copolymers,<sup>[7]</sup> block copolymer-homopolymer blends,<sup>[8]</sup> polymer-water colloidal crystal arrays,<sup>[9]</sup> and forced assembly by layer-by-layer spin-coating.<sup>[10]</sup>

Forced assembly by layer-multiplying coextrusion is a method for fabricating layered assemblies with hundreds or thousands of alternating layers of two polymers. The flexibility of the process lies in the almost unlimited range in layer thickness, from the micrometer scale (10 μm) to the nanometer scale (10 nm), and the wide variety of

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polymers that can be coextruded.<sup>[11]</sup> The first coextruded films with the characteristics of 1D photonic crystals were some iridescent microlayer films of polystyrene (PS) and poly(methyl methacrylate) (PMMA).<sup>[12]</sup> The appearance of these films was metallic, and transmission spectra indicated a broadband reflectivity as a result of variations in the layer periodicity. Subsequent process improvements such as a coextrusion feedblock with 16 or more layers,<sup>[13]</sup> and coextrusion with protective surface layers,<sup>[14]</sup> substantially improved the control over layer thickness. Assemblies with a designed gradient in the layer thickness give very high reflectivity over the visible range.<sup>[15]</sup>

The possibility for coextruding virtually any melt processable polymer as microlayers opens up exciting opportunities. Although most efforts to develop polymeric optical systems utilize glassy polymers, layered assemblies of two transparent elastomers could undergo large and reversible changes in the bandgap upon deformation. Potential applications of such elastomeric 1D photonic crystals would be as strain sensors, as tunable filters, or as mirrors.

In this communication, the successful fabrication of polymeric, narrowband 1D photonic crystals by layer-multiplying coextrusion using a small-scale facility in an academic institution is described. The exceptional flexibility of the process to a wide range of possibilities is demonstrated by the coextrusion of an elastomeric, tunable 1D photonic crystal.

## Experimental Part

Polystyrene (PS) was provided by The Dow Chemical Company (Styron 615 APR) and poly(methyl methacrylate) (PMMA) was provided by Arkema Inc. (Plexiglas VM-100). This pair possessed the desirable combination of a thin interphase and a relatively large refractive index mismatch. The measured refractive indices of PS and PMMA were 1.585 and 1.491, respectively, at  $\lambda = 633$  nm using a Metricon 2010 prism coupler. The interphase thickness for the PS/PMMA pair was found experimentally to be 6 nm.<sup>[16]</sup>

Films with many alternating PS and PMMA layers were fabricated using the layer-multiplying coextrusion process described previously.<sup>[11]</sup> After the polymer melts were combined in the feedblock, the melt stream flowed through a series of layer-multiplying die elements. Modifications to the die design to minimize the pathlength difference and improve layer uniformity have previously been described.<sup>[17]</sup> Each element split the melt vertically, spread it horizontally, and finally recombined it to double the number of layers. An assembly of  $n$  die elements produced  $2^{n+1}$  layers. Films with 32 and 128 layers were created with assemblies of 4 and 6 multiplying elements, respectively. Low density polyethylene provided by The Dow Chemical Company (LDPE 620I) was applied as a sacrificial surface layer on the top and bottom of the microlayer stack before the layered melt was spread. A feedblock combined the microlayer melt with the surface layers. The surface layer feedblock was fed through a transfer tube

from the surface layer extruder. The sacrificial surface layers improved the layer uniformity and surface quality of the layered films.<sup>[11]</sup> The melt from the surface layer feedblock was spread through a 14-inch film die that had adjustable lips and a rectangular spreading geometry. A laboratory-scale chill roll from Randcastle Extrusion Systems (Cedar Grove, NJ) was used to control the film thickness and consequently, the layer thickness. The chill roll temperature was controlled using a Sterlco temperature controller from Sterling, Inc. (Milwaukee, WI).

The temperatures at each component of the coextrusion system were maintained as follows: extruder (A) feeding PS was set at 225 °C, extruder (B) feeding PMMA was set at 235 °C, the multiplying elements and surface layer feedblock were maintained at 230 °C, and the exit die was maintained at 220 °C. The extruder temperatures were chosen such that the melt viscosities of PS and PMMA would be approximately the same when the two polymer melts entered the feedblock. For this study, PS and PMMA were extruded with equal volumetric flow rates. The volumetric flow rates of both PS and PMMA were maintained at  $3.0 \text{ cm}^3 \cdot \text{min}^{-1}$  and the volumetric flow rate of the surface layer extruder was maintained at  $54 \text{ cm}^3 \cdot \text{min}^{-1}$ . The target composition of the film by vol.-% was 5/5/90, PS/PMMA/LDPE. The temperature of the chill roll was maintained at 57.2 °C for all the films. The final overall film thicknesses were set by the speed of the chill roll. The total film thickness with surface layers of the 32 layer assembly was 28  $\mu\text{m}$  using a micrometer and the corresponding PS/PMMA core was 2.75  $\mu\text{m}$  determined by atomic force microscopy (AFM). The nominal thickness of individual layers in the PS/PMMA stack was estimated from the composition, the number of layers, and the film thickness. The individual layer thickness of the 32-layer films was approximately 100 nm. Additional PS/PMMA 32-layer films with thicker layers were used for stacking. These films had a total film thickness of 65  $\mu\text{m}$  and a PS/PMMA core thickness of 6.5  $\mu\text{m}$  measured using a micrometer. The individual layer thickness was estimated to be 200 nm. The total film thickness with the surface layers of the 128-layer assembly was 110  $\mu\text{m}$  measured using a micrometer, and the corresponding PS/PMMA multilayer core was 10.1  $\mu\text{m}$  measured by AFM. The thickness of the individual layers was approximately 100 nm.

Two of the thicker 32-layer films were combined as a stack. One surface layer was removed from each 32-layered film. The sides without a surface layer were gently pressed together to form a 64-layer stack. The photonic bandgap of the PS/PMMA stack was tuned by biaxially stretching the microlayer film in a Karo IV multiaxial stretcher from Brückner Inc. The stretching rate was 5% per second and the stretching oven temperature was 130 °C. A stretching ratio, defined as the final length divided by the initial length, of  $1.4 \times 1.4$  was employed, which achieved a PS/PMMA multilayer core thickness of 6.6  $\mu\text{m}$  and an estimated individual layer thickness of 100 nm.

Polyurethane (PU) provided by The Dow Chemical Company (Pellethane 2355-95AE) and Pebax provided by Arkema Inc. (Pebax 2533) were used to fabricate a film with 128 alternating layers of PU and Pebax. The sacrificial surface layers were LDPE. The refractive indices of PU and Pebax were measured as 1.55 and 1.48, respectively, at  $\lambda = 633$  nm using a Metricon 2010 prism coupler. The  $\Delta n$  of 0.07 was slightly smaller than the  $\Delta n$  of 0.09 for PS/PMMA.

The extruder temperatures were set at 205 and 210 °C for PU and Pebax, respectively. The temperature of the multipliers, the surface layer feedblock and the exit die was 205 °C. The volumetric flow rate for both PU and Pebax were maintained at  $12 \text{ cm}^3 \cdot \text{min}^{-1}$  and the volumetric flow rate of the surface layer extruder was maintained at  $24 \text{ cm}^3 \cdot \text{min}^{-1}$ . The target composition of the film by vol.-% was 25/25/50, PU/Pebax/LDPE. The temperature of the chill roll was maintained at 57.2 °C. The final overall film thickness was set by the speed of the chill roll. The total film thickness with the surface layers was 42  $\mu\text{m}$  and the microlayer PU/Pebax stack had a thickness of 21  $\mu\text{m}$  measured using a micrometer. The nominal thickness of individual layers in the PU/Pebax assembly was estimated to be 164 nm.

For AFM, films were embedded in epoxy and sectioned perpendicular to the plane of the film and perpendicular to the extrusion direction as described previously.<sup>[18]</sup> Phase and height images of the cross-section were recorded simultaneously using the tapping mode of the Nanoscope IIIa MultiMode scanning probe.

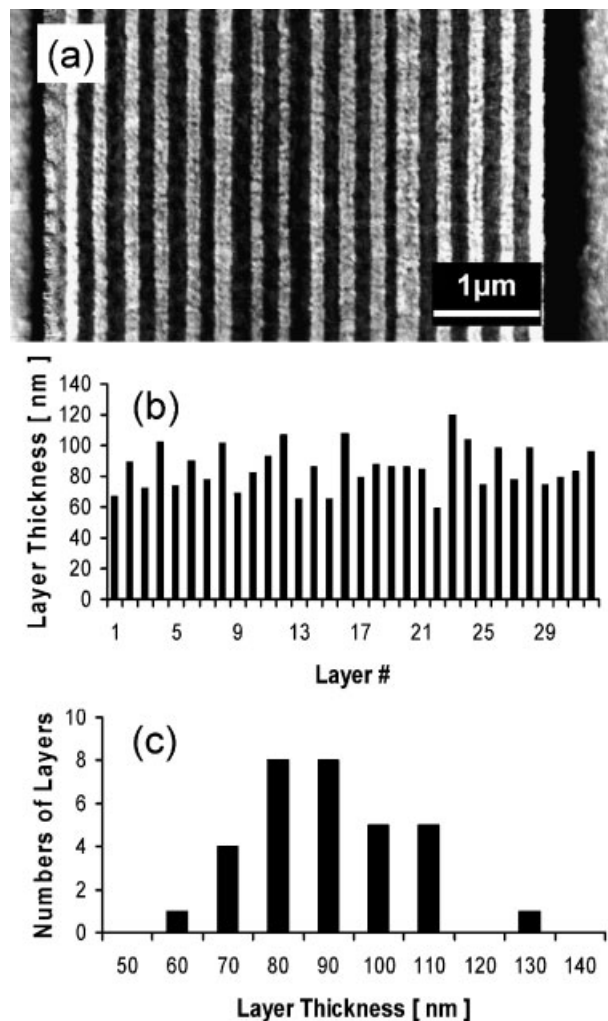
Transmission spectra of microlayered films were collected using an SD2000 Fiber Optics Spectrometer from OceanOptics Inc. All measurements were carried out with unpolarized light at 0° incident angle and at ambient temperature. The polyethylene surface layers were peeled off prior to the measurement. To obtain transmission spectra of the PU/Pebax assembly as it was stretched, a rectangular specimen with gauge length of 5 cm and width of 1 cm was mounted in a stretcher device.

## Results and Discussion

### 1D Photonic Crystals

Layer-multiplying coextrusion produced microlayer films with 32 and 128 alternating layers of PS and PMMA. The AFM image in Figure 1a shows the cross-section of the 32-layer film. The 32 continuous layers are readily distinguished; the bright layers are PMMA and the dark layers are PS. The layers were not perfectly uniform; rather, measurements from the AFM image resulted in the sequence of layer thicknesses given in Figure 1b. The layer thickness had close to a normal distribution having an average thickness of 86 nm with an error of 17% (Figure 1c).

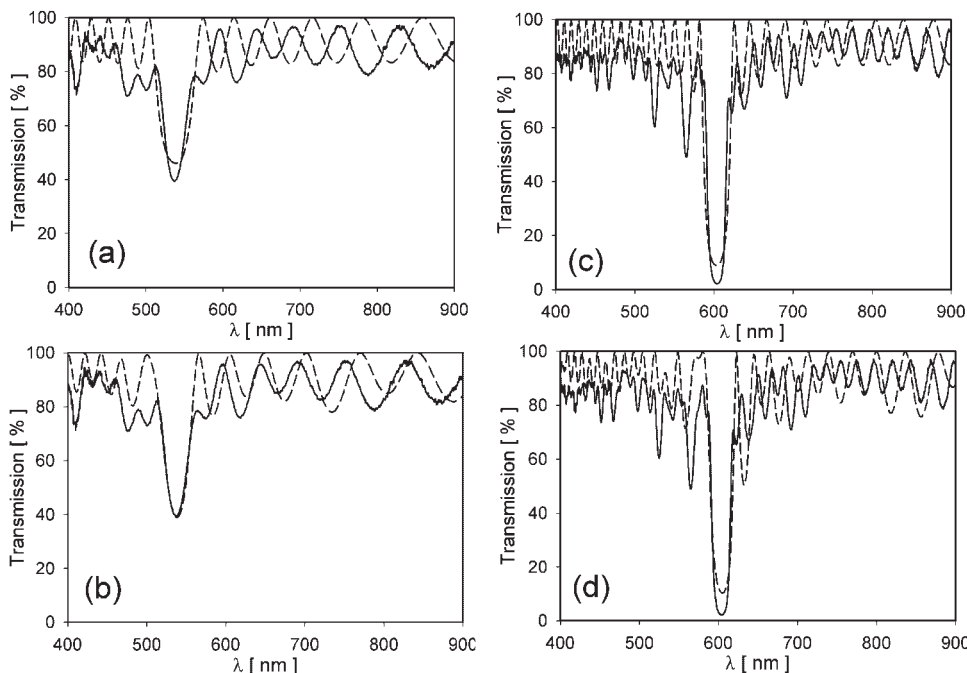
The quality of the 1D photonic crystals was evaluated using the matrix method of Vasicek<sup>[19]</sup> to calculate the transmission spectrum through a non-absorbing multilayer assembly. The result of the simulation is a plot of transmission versus wavelength. The model simulation gives the position, intensity, and shape of the primary reflection band, and the number and position of the side bands. The effect of refractive index mismatch on the shape and intensity of the main reflection band, and the strength of higher order bands, can also be predicted using this model. The model simulations were performed for ideal assemblies of alternating PS and PMMA layers ( $\Delta n = 0.09$ ) of equal thickness and for assemblies having layer thicknesses measured using AFM.



**Figure 1.** Layer thickness distribution in the 32-layer PS/PMMA film: a) An AFM phase image of the film cross-section, b) the layer thicknesses through the cross-section, and c) the layer thickness distribution.

The calculated transmission spectrum of the ideal 32-layer assembly is compared with the measured spectrum of the 32-layer coextruded film in Figure 2a. Despite the distribution in layer thicknesses of the 32-layer film, the agreement between the spectra is very good in terms of the band intensity, the band width, and the intensity of the side bands. Introducing the measured layer thicknesses into the calculation gave even better agreement with the band shape and intensity (Figure 2b).

Even for the ideal case, a PS/PMMA assembly of 32 layers produces a peak reflection of only about 60%. A larger number of layers are required to obtain a peak intensity of 100% reflection. Stacking two 32-layer films to produce a 64-layer film reduced the width of the reflection band and increased the peak reflection to almost 100%. Again there was good agreement with the calculated spectrum for the



**Figure 2.** Comparison of measured transmission spectra for extruded multilayered PS/PMMA films (solid curves) with model simulations (dashed curves): a) The measured spectrum for 32-layer film and the simulation for uniform 87.3 nm layers, b) the measured spectrum for 32-layer film and the simulation for layers with a thickness distribution measured by AFM (Figure 1b), c) the measured spectrum for a stack of two 32-layer films and the simulation for uniform 98.5 nm layers, and d) the measured spectrum for a stack of two 32-layer films and the simulation for layers with thickness distribution measured by AFM.

ideal assembly (Figure 2c). The primary band in the measured spectrum was actually slightly narrower and more intense than predicted for the ideal assembly. Introducing the measured layer thicknesses into the calculation again gave even better agreement in the peak shape and intensity (Figure 2d). The primary effect of layer non-uniformity was seen in the intensity of the side bands. Although the spacing of the side bands followed the prediction fairly closely, the intensity of the side bands, especially some of those close to the main reflection band, was significantly enhanced.

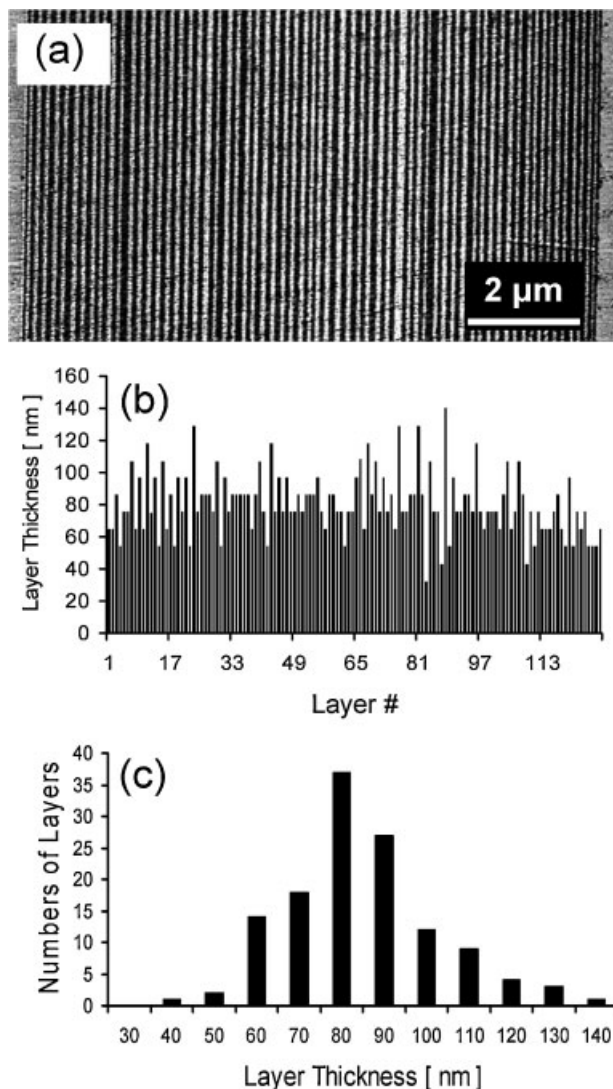
The number of layers in the assembly was increased to 128 by adding additional multipliers to the coextrusion process. The AFM image in Figure 3a shows 128 continuous and relatively uniform layers of PS and PMMA. Measurements from the AFM image resulted in the sequence of layer thicknesses given in Figure 3b. The layer thickness had close to a normal distribution having an average thickness of 86 nm with an error of 24% (Figure 3c).

The ideal spectrum of the 128-layer assembly predicted a peak reflection of 100% (Figure 4a). However, the measured spectrum showed a peak reflection of only 95%. Moreover, the side-band spacing was small enough that the enhanced side bands in the measured spectrum started to overlap with the primary band.

For uniform layers, increasing the number of layers enhances the intensity of the reflection band and increases the number of side bands; however, the intensity of the side bands remains unchanged. For the coextruded films, increasing the number of layers by adding more multipliers served to broaden the layer thickness distribution, which resulted in a higher side band intensity and a decrease of the main reflection band relative to the prediction for uniform layers. As the number of side bands and side-band intensity increased, they started to overlap with each other and the primary reflection band, which had the effect of broadening the spectrum. High reflectivity with low side-band intensity was achieved by stacking films with a lower number of layers. This method increased the number of layers while retaining the thickness distribution of the films produced with fewer multipliers. Indeed, a narrow reflection band with close to 100% reflection was achieved by stacking two 32-layer films.

### Elastomeric Photonic Crystals

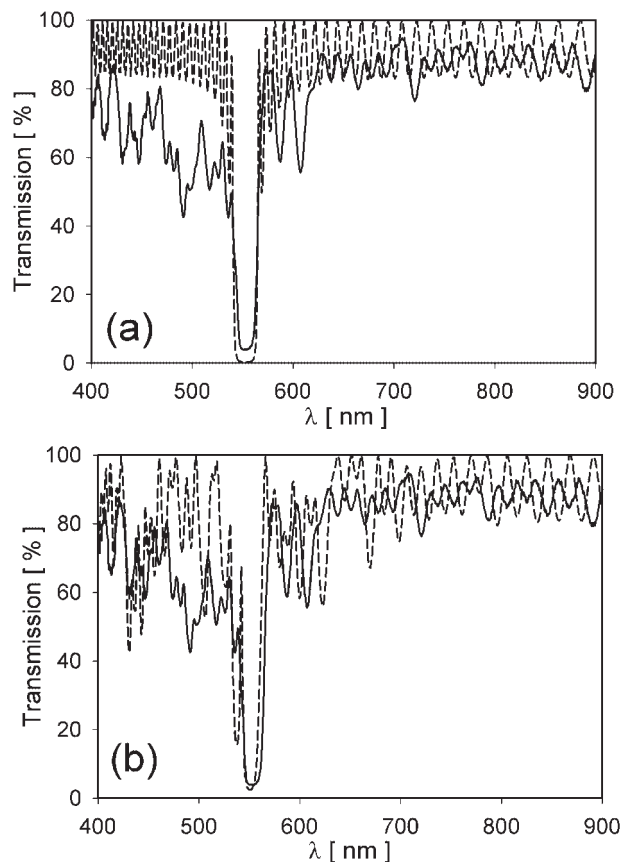
The layers in a film fabricated from two elastomeric polymers will decrease in thickness during stretching, thereby changing the position of the bandgap. The possibility of a



**Figure 3.** Layer thickness distribution in the 128-layer PS/PMMA film: a) An AFM phase image of the film cross-section, b) the layer thicknesses through the cross-section, and c) the layer thickness distribution.

tunable 1D photonic crystal was demonstrated by coextruding alternating layers of PU and Pebax. This pair had the advantages of being coextrudable, possessing good transparency, and having a satisfactory difference in refractive index ( $\Delta n = 0.7$ ).

The transmission spectra of a 128-layer film collected at increasing strains from 0 to 1.25 are collected in Figure 5a. Individual spectra consisted of a main strong band, which appeared to be the superposition of two peaks, and several weak side bands. The complex shape reflected the layer non-uniformity, which resulted from the number of layers and the viscosity mismatch between this particular pair of elastomers. The peak transmission was less than 100% because of the layer non-uniformity and the relatively



**Figure 4.** Comparison of measured transmission spectra for an extruded 128-layer PS/PMMA film (solid curves) with model simulations (dashed curves): a) The measured spectrum and the simulation for uniform 90.3 nm layers, and b) the measured spectrum and the simulation for layers with thickness distribution measured by AFM (Figure 3b).

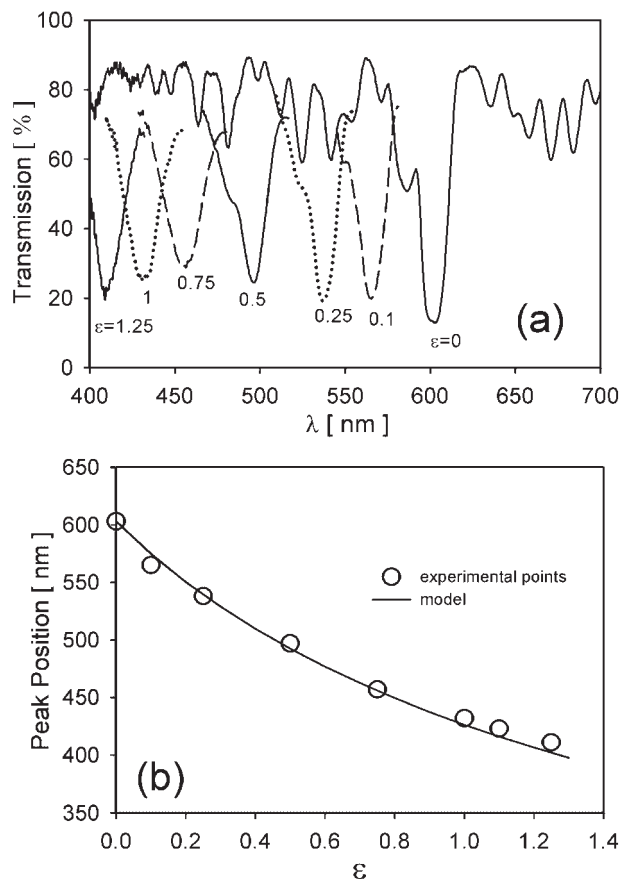
small  $\Delta n$ , which was 0.07 compared to 0.09 for glassy PS/PMMA. However, the key feature was observed as a shift in the peak position from 600 nm to almost 400 nm for  $\epsilon = 1.25$ . Visually, this was seen as a change in the color through the visible range from red to blue. The shape of the main reflection band changed somewhat under strain by gradually evolving from a double peak to a single peak and also by going through a minimum in the peak intensity.

The linear shift in the peak position toward shorter wavelengths with decreasing layer thickness  $d$  is described by

$$\lambda_I = 2(n_A d_A + n_B d_B) \quad (1)$$

where the subscripts A and B refer to the two constituents.

However, a more useful relationship is the one between peak position and strain. It is assumed that the volume



**Figure 5.** Change in the transmission spectrum during stretching of the 128-layer PU/Pebax film: a) A series of transmission spectra collected at different strains, and b) the peak position as a function of strain compared to the calculation from Equation (2).

is conserved during stretching, so that  $dwl = d_0w_0l_0$ , where  $d$ ,  $w$ ,  $l$  and  $d_0$ ,  $w_0$ ,  $l_0$  are thickness, width, and length, respectively, of the deformed and undeformed specimen. The change in dimensions is described as  $x = d/d_0$ ,  $y = w/w_0$ ,  $\varepsilon = (l - l_0)/l_0$  and it is also that  $x = y$ . The relationship between film thickness and strain is then  $x = \frac{1}{\sqrt{1+\varepsilon}}$ . If it is further assumed that changes of the refractive index of the elastomers during stretching can be neglected, Equation (1) leads to:

$$\lambda = \frac{\lambda_0}{\sqrt{1+\varepsilon}} \quad (2)$$

where  $\lambda$  is the peak wavelength at strain  $\varepsilon$ , and  $\lambda_0$  is the peak wavelength at zero strain. Figure 5b compares the prediction from Equation (2) with the experimental points. The agreement is very good. Repeated loading and unloading through ten cycles between 0 and 0.5 strain showed very good reversibility.

## Conclusion

It is demonstrated that one-dimensional photonic crystals with narrow, tunable photonic bandgaps can be fabricated using layer-multiplying coextrusion. A wide variety of materials can be fabricated as photonic crystals by this method, which is demonstrated with stretchable, elastomeric photonic crystals that have potential applications as strain sensors, tunable mirrors, and tunable optical filters. Because the materials are fabricated in quantity as a continuous film, they are also amenable to conventional techniques of film shaping. In particular, biaxial stretching of glassy photonic crystals reduces the layer thickness to produce a film with a designed photonic bandgap. For the coextruded films, increasing the number of layers by adding more multipliers served to broaden the layer thickness distribution. Stacking was shown to be an effective way to increase the number of layers while retaining the thickness distribution of the films produced with fewer multipliers. Indeed, a narrow reflection band with close to 100% reflection was achieved by stacking two 32-layer films.

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