

Theoretical Prediction of the Optical Waveguiding Properties of Self-Assembled Block Copolymer Films

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ABSTRACT: Block copolymers represent a potentially new class of materials for integrated optics. Before these materials can be used as optical waveguide materials, however, their optical waveguiding properties need to be well understood. In this paper, lamellar-forming block copolymer waveguides are treated and modeled as ideal multilayer structures in which the lamellae are oriented parallel to the substrate and superstrate interfaces. A computer program based on an N -layer waveguide formalism is used to calculate the propagation constants and plot the optical field intensity distributions of some sample diblock and triblock copolymer thin-film waveguides. In a block copolymer thin film, individual block copolymer domains can have anisotropic optical properties due to chain stretching, in the case of coil-coil block copolymers, or due to the presence of a liquid crystalline block, in the case of rod-coil block copolymers. As a result, optical anisotropy of the layers is also treated in the waveguide formalism. Theoretical waveguide calculations show that block copolymer films with a domain size smaller than about $\lambda/5$ behave optically like homogeneous uniaxial films. Consequently, block copolymers represent a convenient way of making waveguides with a controlled birefringence. In contrast, block copolymer films with a domain size larger than about $\lambda/3$ but less than the wavelength of light are found to preferentially segregate the light into the high refractive index domains. When the low-index layer is at the air interface, only the high-order modes are supported and a greater segregation of the light can be achieved. ABC triblock copolymer films, in which the refractive index of the B and C blocks is larger than that of the A block, are found to exhibit even better confinement of the light into the high-index regions. The optical waveguiding properties predicted for large domain size block copolymers are not seen in single slab homopolymer waveguides and may have potential device applications.

Introduction

Homopolymers have played a major role in the optics industry since they were first shown to be suitable as optical waveguide materials^{1,2} (a dielectric film which is able to propagate light in a confined geometry). In particular, homopolymers are excellent waveguide materials because they can be processed easily using existing microelectronics techniques into durable thin films which exhibit low transmission loss and have a low specific gravity. As a result, a large number of integrated optical devices ranging from lenses and gratings to lasers, light couplers, and demultiplexers^{3,4} have been fabricated using homopolymer thin films. In addition to their relative ease of fabrication, homopolymer waveguides have also been extensively studied theoretically^{4–7} and are well understood.

In contrast, block copolymers have not been previously considered as optical waveguide materials, and relatively little work has been done to characterize their optical waveguiding properties. Block copolymers, however, possess unique properties which make them potentially useful as waveguide materials. In particular, block copolymers self-assemble into spatially periodic ordered structures^{8–13} on the length scale of hundreds of angstroms due to the mutual repulsion of the dissimilar blocks and the constraints imposed by the connectivity of the blocks. In the strong segregation

limit, these morphologies are characterized by narrow interfaces and well-defined domain sizes. Although several morphologies have been observed as a function of composition, the lamellar morphology, which is formed by symmetric AB diblock and ABA triblock copolymers, has the simplest structure and is most applicable to integrated optics. Russell and co-workers have shown that spin-coated thin films of a symmetric P(*S*-*b*-MMA) diblock copolymer form lamellae which are oriented parallel to the substrate and air interfaces when annealed.^{14–19} Thin block copolymer films in which the lamellae are oriented parallel to the substrate and superstrate will behave as periodic multilayer films and are expected to have optical properties different from those of homopolymer films. In terms of optical waveguiding, multilayer films have already been shown to be useful for studying nonlinear optical phenomena. In particular, multilayer Langmuir–Blodgett (LB) waveguide structures have been used to study the second harmonic generation (SHG) of certain NLO molecules. In particular, four- and five-layer structures were found to increase the efficiencies of SHG through better phase matching of the fundamental and harmonic wave and optimization of the overlap integral.^{20,21} Besides uses in nonlinear optics, Normandin et al.²² showed that efficient coupling from an optical fiber was possible using a multilayer waveguide structure composed of 34 alternating Al_{0.65}Ga_{0.35}As and Al_{0.90}Ga_{0.10}As layers while still maintaining high nonlinear har-

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monic emission efficiencies. Although the LB and AlGaAs structures mentioned above were both composed of multiple layers, the discrete nature of the structures was not purposely fabricated to achieve preferential segregation of the light.

Block copolymers, in addition to forming ordered structures, are also highly tailorable and offer additional degrees of freedom not achievable in homopolymer slab waveguides. By changing the total molecular weight of the block copolymer, the domain size of the lamellae and also the individual block layer thicknesses can be varied from tens of angstroms to thousands of angstroms, having a profound effect on the resulting optical waveguiding properties. By choosing the chemical composition of each block, the refractive index of each layer can be precisely controlled. In addition, the architecture of the block copolymer (i.e., diblock or triblock) can also be used to influence the resulting microphase-separated morphology. Together, these properties can be used to precisely control the refractive index profile in a block copolymer waveguide, greatly increasing flexibility in the design of novel waveguide structures.

Before block copolymers can be practically used as waveguide materials, however, their optical waveguiding properties need to be understood. Homopolymer slab waveguides are accurately modeled as a simple three-layer structure consisting of a homogeneous, isotropic, dielectric film located between a semi-infinite substrate (e.g., quartz) and superstrate (e.g., air) both of smaller refractive index. In contrast, an ideal lamellar-forming block copolymer film must be modeled as a multilayer waveguide structure. Shakir and Turner developed a method for calculating the waveguide modes of a multilayer structure from the poles of the reflectance in the substrate or superstrate.²³ In a related approach, Chilwell and Hodgkinson²⁴ employed a 2×2 field-transfer matrix method which could be used to calculate the waveguide modes of multilayer structures and trace the electric field profiles across the structure.

In this paper, the optical field intensity distributions for the modes of a given block copolymer film are of particular interest because they show directly how the light is concentrated in the various domains. As a result, a theoretical formalism based on the work of both Polky and Mitchell²⁵ and Marcuse⁷ is used which treats the electric and magnetic fields in each layer explicitly and in a compact way. This formalism can easily be coded into an algorithm and forms the basis of a Mathematica program which can calculate the waveguide modes of an N -layer waveguide structure and plot the corresponding optical field distributions for each mode across the film. The program is then used to calculate the optical waveguiding properties of representative examples of block copolymer films as well as block copolymer structures which exhibit unique optical properties.

Theory and Formalism for Block Copolymer Waveguides

The problem of predicting the optical waveguiding behavior of an ideal block copolymer film is equivalent to solving for the waveguide modes of a multilayer structure. Figure 1 shows a schematic diagram depicting the structure of a multilayer waveguide which consists of N film layers, each characterized by a refractive index n_i , sandwiched between a substrate and

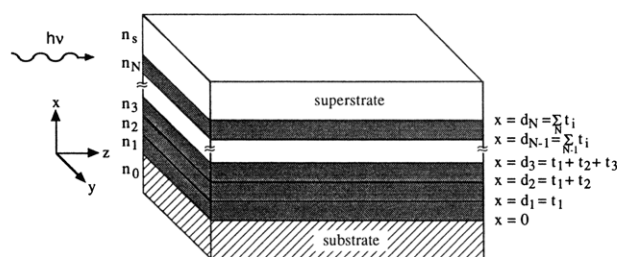


Figure 1. Schematic diagram of a multilayer waveguide structure.

superstrate (air) of refractive indices n_0 and n_s . Typically, the refractive indices of the guiding layers must be greater than the substrate and superstrate indices to ensure waveguiding. In addition, each layer is assumed to be infinite along the y and z directions. For light traveling in the z direction, the waveguide modes are solutions to Maxwell's equations in which the light propagates in the z direction at the same velocity in all the layers and is confined solely in the N film layers. In this case, the electric and magnetic fields in all the layers will have a common time and z dependence which can be expressed by the exponential factor $e^{i(\omega t - \beta z)}$, where ω is the angular frequency and β is the z component of the wavevector. In addition, because the direction of propagation is only in the xz plane, the electric and magnetic fields will not vary in the y direction. Dividing β by the free space wavevector $k_0 = 2\pi/\lambda_0$ yields the propagation constant, n_{eff} , which characterizes each waveguide mode. The waveguide modes, however, can be classified into two groups, the transverse electric (TE) and transverse magnetic (TM) modes. TE modes are characterized by an electric field vector normal to the plane of incidence and have the field components $\mathbf{E} = (0, E_y, 0)$ and $\mathbf{B} = (B_x, 0, B_z)$. TM modes, on the other hand, are characterized by a magnetic field vector normal to the plane of incidence and have the field components $\mathbf{E} = (E_x, 0, E_z)$ and $\mathbf{B} = (0, B_y, 0)$. E_y and B_y , therefore, play analogous roles for the TE and TM modes, respectively. For simplicity, only the solution for the TE modes will be presented. The following results, however, are easily generalized to include TM modes. The full expression for the electric field in each layer will therefore have the form

$$\mathbf{E}(r, t) = E_y(x) e^{i(\omega t - \beta z)} \hat{y} \quad (1)$$

By using eq 1, the original problem of solving Maxwell's equations in each layer can be reduced to solving the one-dimensional Helmholtz wave equation in each layer for $E_y(x)$,

$$\frac{\partial^2 E_y^i}{\partial x^2} + k_0^2 (n_i^2 - n_{\text{eff}}^2) E_y^i = 0 \quad (2)$$

where $i = (0, 1, \dots, N, s)$ labels each layer starting from the substrate, 0, and ending at the superstrate, s . In addition to being a solution of eq 2 in each layer, E_y must also obey the boundary conditions at each interface. In particular, E_y and its derivative must be continuous across all interfaces. Because the waveguide modes are bound modes, E_y is constrained to vanish at $x = \pm\infty$. Solutions of eq 2 which satisfy all the boundary conditions can be written in the following form:

$$\begin{aligned}
E_y^s &= A_0 \left(\prod_1^N B_i \right) \exp[-k_s(x - \sum_1^N t_i)], \quad x \geq d_N \\
E_y^N &= A_0 \left(\prod_1^{N-1} B_i \right) \{ \cos[k_N(x - \sum_1^{N-1} t_i)] + \\
&\quad T_{N-1} \sin[k_N(x - \sum_1^{N-1} t_i)] \}, \quad d_{N-1} \leq x \leq d_N \\
&\quad \cdot \\
&\quad \cdot \\
&\quad \cdot \\
E_y^3 &= A_0 B_1 B_2 \{ \cos[k_3(x - (t_1 + t_2))] + \\
&\quad T_2 \sin[k_3(x - (t_1 + t_2))] \}, \quad d_2 \leq x \leq d_3 \\
E_y^2 &= A_0 B_1 \{ \cos[k_2(x - t_1)] + \\
&\quad T_1 \sin[k_2(x - t_1)] \}, \quad d_1 \leq x \leq d_2 \\
E_y^1 &= A_0 [\cos(k_1 x) + T_0 \sin(k_1 x)], \quad 0 \leq x \leq d_1 \\
E_y^0 &= A_0 \exp[k_0 x], \quad x \leq 0
\end{aligned} \quad (3)$$

where $B_i = \cos(k_i t_i) + T_{i-1} \sin(k_i t_i)$, $S_i = T_{i-1} \cos(k_i t_i) - \sin(k_i t_i)$, $T_i = (S_i/B_i)(k_i/k_{i+1})$ and $T_0 = k_0/k_1$. The electric field amplitude coefficient, A_0 , is a normalization constant defined such that the total power contained in each mode is equal to 1 W/ μm . The electric field expressions in eq 3 were generalized from the three-layer waveguide solutions obtained by Marcuse.⁷ The k_i 's in eq 3 are the x component of the wavevector in each layer and determine the electric field profile across the structure. In addition, the k_i 's are a function of n_{eff} and can be written as

$$\begin{aligned}
k_s &= k_0(n_{\text{eff}}^2 - n_s^2)^{1/2} \\
k_N &= k_0(n_{\text{eff}}^2 - n_N^2)^{1/2} \\
&\quad \cdot \\
&\quad \cdot \\
&\quad \cdot \\
k_1 &= k_0(n_1^2 - n_{\text{eff}}^2)^{1/2} \\
k_0 &= k_0(n_{\text{eff}}^2 - n_0^2)^{1/2}
\end{aligned} \quad (4)$$

where the definitions of k_s and k_0 ensure that the electric field decays in the substrate and superstrate.

Once the electric fields are obtained, the allowed n_{eff} 's must still be calculated. In the three-layer waveguide, solution of eq 2 yields four unknown amplitude coefficients. Imposing the boundary conditions on the electric fields results in a homogeneous system of four equations whose determinant must vanish. The determinant yields the eigenvalue equation whose solutions are the discrete allowed n_{eff} 's. For the multilayer waveguide, a similar derivation yields a $2N + 2$ by $2N + 2$ determinant, which must vanish. Alternatively, a generalized eigenvalue equation for the multilayer waveguide can be obtained based on the work of Polky and Mitchell,²⁵ thus avoiding the determinant entirely.

The generalized eigenvalue equation can be written in the form

$$k_N t_N - \tan^{-1} \left(\frac{k_{(N-1)p}}{k_N} \right) - \tan^{-1} \left(\frac{k_s}{k_N} \right) = m\pi \quad (5)$$

where $m = 0, 1, 2, \dots$, and

$$\begin{aligned}
k_{(N-1)p} &= k_{(N-1)} \left[\frac{\frac{k_{(N-2)p}}{k_{(N-1)}} - \tan(k_{(N-1)} t_{(N-1)})}{1 + \frac{k_{(N-2)p}}{k_{(N-1)}} \tan(k_{(N-1)} t_{(N-1)})} \right] \\
&\quad \cdot \\
&\quad \cdot \\
&\quad \cdot \\
k_{2p} &= k_2 \left[\frac{\frac{k_{1p}}{k_2} - \tan(k_2 t_2)}{1 + \frac{k_{1p}}{k_2} \tan(k_2 t_2)} \right] \\
&\quad \cdot \\
k_{1p} &= k_1 \left[\frac{\frac{k_0}{k_1} - \tan(k_1 t_1)}{1 + \frac{k_0}{k_1} \tan(k_1 t_1)} \right]
\end{aligned} \quad (6)$$

For a given multilayer waveguide structure, eq 5 must be numerically solved to obtain the allowed propagation constants. For a given structure, the allowed n_{eff} 's will have values that range between n_0 and the largest n_i . In addition, the larger the n_{eff} , the lower the order of the waveguide mode and the fewer nodes its corresponding electric field profile will have. For TM modes, the field expressions for B_y in each layer are analogous to eq 3. In addition, the form of the generalized eigenvalue equation is identical to that of eq 5 with one distinction. The k_i appearing in eqs 5 and 6 must be substituted with k_i/n_i^2 .

The formalism discussed above for the electric fields and the eigenvalue equation of a multilayer waveguide was used as the basis for a program written using the software package Mathematica by Wolfram Research, Inc. Given $n_0, n_1, \dots, n_N, n_s$, and t_1, \dots, t_N for a given $(N + 2)$ -layer waveguide and the wavelength of light, the program first determines the allowed propagation constants using eq 5. Computation time increases significantly with the number of layers in the waveguide. As a result, for systems with more than seven layers, eq 5 is more easily solved graphically. Even so, the propagation constants can still be determined to any specified degree of precision. Once the n_{eff} 's are calculated, the corresponding optical field distributions of each mode can be plotted across the structure using eqs 3 and 4. The integrated intensity or power in each layer normalized to the total power of a given mode can also be calculated easily. In addition, the propagation constants can be used to calculate the predicted prism coupling angles, given the refractive index and angle of the prism. A determination of the accuracy and reliability of the N -layer waveguide formalism and program was made by successfully reproducing the propagation

constants and electric field profiles of three different model structures whose solutions have been previously published.^{5,24,26,27} The results also showed that the multilayer formalism is useful not only for waveguides with step index profiles but also for waveguides which possess slowly varying refractive index profiles.

Optical Waveguiding Properties of Block Copolymer Films

Having developed the computational means to accurately model multilayer waveguides, the optical waveguiding properties of block copolymer films can now be investigated. As a reminder, the following discussion will deal only with ideal lamellar-forming microphase-separated block copolymer films in which the lamellae are oriented parallel to the substrate and superstrate interfaces. Considering the work of Russell and co-workers, however, such an assumption is reasonable for annealed strongly segregated films. Considerable insight into the waveguiding properties of block copolymer films can be obtained by first analyzing their optical properties as a whole. An individual microscopic block copolymer lamellar grain and thus a macroscopically microphase-separated AB block copolymer film are both optically anisotropic materials.²⁸⁻³¹ In particular, a block copolymer film which forms lamellae oriented parallel to the air and substrate interfaces behaves optically as a uniaxial material characterized by a finite birefringence $\Delta n = n_e - n_o$. The ordinary and extraordinary refractive indices, n_o and n_e , are the refractive indices associated with light polarized perpendicular and parallel to the optic axis, respectively. The birefringence present in coil-coil block copolymers which form lamellae arises from two contributions. First, the one-dimensional ordering of the alternating A and B layers gives rise to anisotropic optical properties for light polarized perpendicular and parallel to the plane of the lamellae. Second, the A and B domains both exhibit an intrinsic birefringence due to chain stretching away from the AB intermaterial dividing surface (IMDS).

As a first approximation, a microphase-separated AB block copolymer film can be modeled as an alternating multilayer structure composed of isotropic A and B polymer layers whose refractive indices are n_A and n_B , respectively. When the individual A and B layer thicknesses are much smaller than the wavelength of light, the following expressions derived by Born and Wolf³² are valid for the ordinary and extraordinary refractive indices of the film:

$$n_o = (f_A n_A^2 + f_B n_B^2)^{1/2} \quad (7)$$

$$n_e = \left(\frac{n_A^2 n_B^2}{f_A n_B^2 + f_B n_A^2} \right)^{1/2} \quad (8)$$

In addition, using eqs 7 and 8, a block copolymer film can be shown to be uniaxially negative (i.e., $\Delta n = n_e - n_o < 0$) with its optic axis perpendicular to the film. These results are in agreement with attenuated total reflection studies performed on P(S-*b*-MMA) and P(S-*b*-2VP) block copolymer films using visible light with a wavelength of 6328 Å.³³ In eqs 7 and 8, f_A and f_B are the volume fractions of each block, which equal $1/2$ for a symmetric block copolymer.

In an actual block copolymer film, however, each A and B domain is itself an optically anisotropic layer due

to the chain stretching of the blocks away from the IMDS and can be characterized by an intrinsic birefringence Δn_i . By analyzing the chain stretching experienced by a polymer brush, the following expression was derived by Lodge and Fredrickson³⁴ for the intrinsic birefringence of a given block copolymer domain:

$$\Delta n_i = \frac{\pi^3}{90} (\alpha_{||} - \alpha_{\perp}) \frac{(n^2 + 2)^2}{n} \left(\frac{\rho N_A}{M} \right) \frac{L^2}{\langle h^2 \rangle_0} \quad (9)$$

In eq 9, n , ρ , M , L , and $\langle h^2 \rangle_0$ are the refractive index, density, molecular weight, half the layer thickness, and mean squared end-to-end distance of the block, respectively. The polarizability parallel and perpendicular to the monomer unit and Avogadro's number are $\alpha_{||}$, α_{\perp} , and N_A , respectively. Because each block copolymer domain is uniaxial, the values of the refractive index for a given block used in eqs 7 and 8 will be different. The refractive indices used in eq 7 will be those which result for light polarized perpendicular to the optic axis (perpendicular to the IMDS) of a given domain, $n_{A\perp}$ and $n_{B\perp}$. Similarly, the refractive indices used in eq 8 will be those which result for light polarized parallel to the optic axis, $n_{A||}$ and $n_{B||}$. For a given block, n_{\perp} and $n_{||}$ can be simply related to the isotropic refractive index, n , and the intrinsic birefringence, Δn_i , using the relations

$$n_{\perp} = n - \frac{1}{3} \Delta n_i \quad (10)$$

$$n_{||} = n + \frac{2}{3} \Delta n_i \quad (11)$$

where $\Delta n_i \ll n$ is assumed. Although the importance of intrinsic birefringence depends on the particular block copolymer and varies with molecular weight for coil-coil block copolymers, it cannot be neglected for block copolymer systems which have liquid crystalline or rod blocks. In such materials, the rod domains will possess very different optical properties perpendicular and parallel to the rod axis. For block copolymers exhibiting significant chain stretching or liquid crystalline behavior, anisotropy must be taken into account to accurately predict the resulting optical waveguiding properties.

As a result, the equations derived for the N -layer waveguide need to be slightly modified. The anisotropic nature of the layers is manifested in the formalism by different expressions for the x component of the wavevector in each layer. For TE modes, the electric field in each layer is always polarized perpendicular to the optic axis. As a result, the refractive index of a given layer appearing in eq 4 is simply $n_{TE} = n_{\perp}$. For TM modes, however, the electric field in each layer has components both perpendicular and parallel to the optic axis. Consequently, the effective refractive index of a given layer is now dependent on the direction of light propagation and can be shown to be

$$n_{TM} = \left(\frac{n_{\perp}^2 n_{||}^2}{n_{||}^2 \cos^2 \theta + n_{\perp}^2 \sin^2 \theta} \right)^{1/2} \quad (12)$$

where θ is the angle between the wavevector and the optic axis (normal to the layers). The form of the refractive index given in eq 12 results in the following modified expressions³⁵ for the x component of the wave vector in each layer:

$$\begin{aligned}
 k_s &= k_0(n_{\text{eff}}^2 - n_s^2)^{1/2} \\
 k_N &= k_0 \left(\frac{n_{N\perp}}{n_{N\parallel}} \right) (n_{N\parallel}^2 - n_{\text{eff}}^2)^{1/2} \\
 &\cdot \\
 &\cdot \\
 &\cdot \\
 k_1 &= k_0 \left(\frac{n_{1\perp}}{n_{1\parallel}} \right) (n_{1\parallel}^2 - n_{\text{eff}}^2)^{1/2} \\
 k_0 &= k_0(n_{\text{eff}}^2 - n_0^2)^{1/2} \quad (13)
 \end{aligned}$$

where the substrate and superstrate are still taken to be optically isotropic. Aside from the modified expressions in eq 13, the k_i appearing in eq 5 must be substituted with $k_i/n_{i\perp}^2$ for the TM modes.

The optical waveguiding properties of three particular block copolymer waveguide structures will now be investigated. The first block copolymer waveguide consists of a 1.55 μm P(S-*b*-MMA) diblock copolymer film located between air and a quartz substrate. A lamellar domain spacing of 1000 Å is chosen, which corresponds roughly to a total molecular weight of 400 000 as estimated from an experimentally determined relationship between molecular weight and domain spacing.¹⁷ In addition, previous work on this system has showed that PMMA and PS preferentially segregate to the substrate and air interfaces, respectively, in order to reduce interfacial energy. Consequently, the block copolymer film consists of 32 alternating layers of PMMA and PS where the first and last layers are half-layers of 250 Å and all other layers are 500 Å. The isotropic refractive indices³⁶ of PMMA and PS at a wavelength of 4880 Å are 1.4945 and 1.6008, respectively. For the TE modes, the PMMA and PS refractive indices become 1.4945 and 1.6010 after correcting for the intrinsic birefringence. The resulting alternating step index profile of this waveguide is shown in Figure 2A. Using the Mathematica program, the waveguide was found to support three TE modes whose optical field intensity distributions (OFI's) are plotted in Figure 2B. The OFI's closely resemble those resulting from a homogeneous slab waveguide of the same thickness. Unlike the OFI's which result from a slab waveguide, however, the OFI's of the P(S-*b*-MMA) film exhibit a small oscillation commensurate with the periodic refractive index profile. In particular, the intensity of light is slightly augmented in the high-index layers and slightly reduced in the low-index layers.

The similarity in OFI's between the 32-layer P(S-*b*-MMA) waveguide and a homogeneous slab waveguide is not coincidental. In fact, the 32-layer block copolymer waveguide can be closely approximated by an equivalent homogeneous optically uniaxial slab waveguide whose average ordinary and extraordinary refractive indices are given by the n_o and n_e of the block copolymer film discussed previously. The values of n_o and n_e calculated for the 32-layer P(S-*b*-MMA) waveguide using eqs 7 and 8 are 1.54867 and 1.54473, respectively. The resulting propagation constants for the 32-layer waveguide and its equivalent slab waveguide using these values are compared in Table 1. The agreement between the two sets of propagation constants is good and the mean squared error is only about 0.02%. These results show

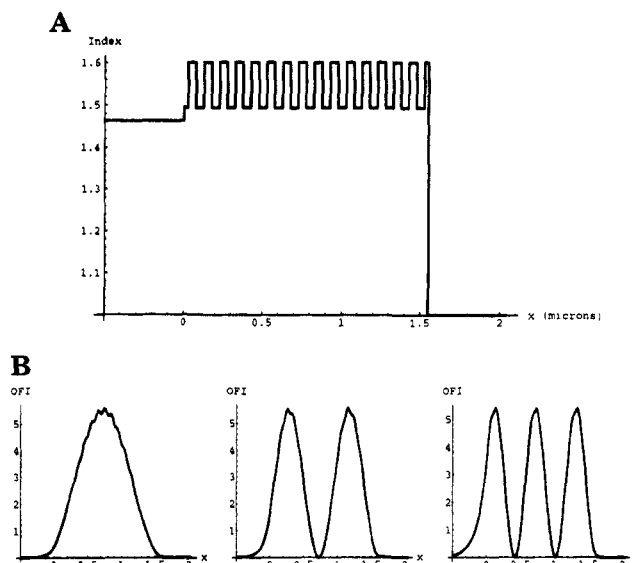


Figure 2. (A) Plot showing the refractive index profile for an ideal 32-layer P(S-*b*-MMA) diblock copolymer waveguide. (B) Optical field intensity distribution plots for the 3 TE modes of the 32-layer P(S-*b*-MMA) waveguide.

Table 1. Propagation Constants for the 32-Layer and Equivalent Slab Waveguide

mode	$n_{\text{eff}}(32 \text{ layer})$	$n_{\text{eff}}(\text{slab})$
TE	1.54284	1.54253
TE	1.52448	1.52415
TE	1.49431	1.49399
TM	1.53854	1.53824
TM	1.51922	1.51890
TM	1.48790	1.48765

that ideal block copolymer films behave essentially like single-film waveguides with a well-defined birefringence if the microphase-separated lamellae have block domain spacings smaller than 500 Å or roughly $\lambda/10$. As a result, block copolymer films may be an excellent material for fabricating thin-film waveguides of controllable birefringence which could possibly be used in SHG studies to achieve improved phase matching of the fundamental and harmonic generated waves. When the individual block domains become larger, however, eqs 7 and 8 are no longer valid and the concept of an equivalent slab waveguide becomes less meaningful.

When the lamellar domain size is less than $\lambda/5$, the periodic refractive index profile only slightly perturbs the optical field intensity distribution of the waveguide modes. The situation changes dramatically, however, if the size of the domains is larger than about $\lambda/3$. In the next example, a 4.05 μm P(S-*b*-MMA) diblock copolymer waveguide consisting of 28 alternating PS and PMMA layers located between quartz and air is considered. All layers are 1500 Å except for the 750 Å half-layers at the substrate and air interfaces. The resulting lamellar domain spacing of 3000 Å corresponds roughly to a total molecular weight of 2 100 000. The refractive indices of PMMA and PS are equal to their isotropic values because corrections for intrinsic birefringence are negligible for such a high molecular weight diblock. The refractive index profile for this structure is shown in Figure 3A. At a wavelength of 4880 Å, the 28-layer structure was found to support nine TE modes whose optical field intensity distributions are shown in Figure 3B. The black and gray portions of each OFI denote the optical field located in the high- and low-index layers, respectively. The OFI's are significantly perturbed from the OFI's which would

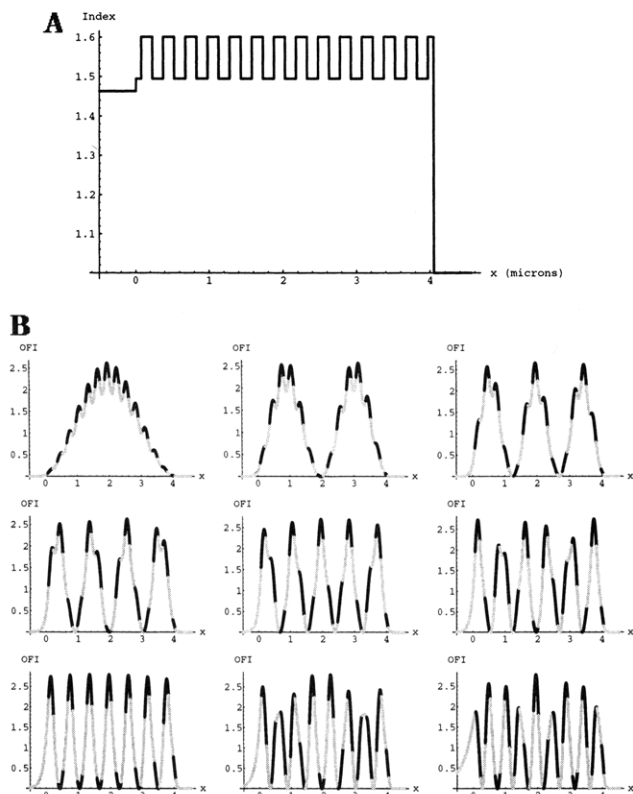


Figure 3. (A) Plot showing the refractive index profile for an ideal 28-layer P(S-*b*-MMA) diblock copolymer waveguide. (B) Optical field intensity distribution plots for the 9 TE modes of the 28-layer P(S-*b*-MMA) waveguide. The black and gray portions of each OFI correspond to the high- and low-index layers, respectively.

result from a homogeneous film waveguide. The OFI of the seventh mode is particularly interesting because the light is preferentially segregated in every other high-index layer. On average, 56% of the optical field intensity found in the guiding layers is segregated into the high-index PS layers. For this structure, preferential segregation of the OFI increases for the higher modes and has a maximum value of approximately 58% for the ninth mode.

The two diblock copolymer waveguide structures considered above have been characterized by refractive index profiles in which the block adjacent to the air-film interface has had the higher refractive index. When the two structures above are inverted so that the low refractive index layer is at the air-film interface, the optical waveguiding behavior changes dramatically. For the 32-layer structure, the first two modes can no longer be supported given the new boundary conditions and only the third mode survives. For the 28-layer structure, all but the two highest order modes are eliminated. In these two modes, the degree of preferential segregation of the optical field intensity into the high-index layers, however, is found to be the same as that for the original structure. Consequently, block copolymer structures in which the low-index block preferentially segregates to the air interface exhibit advantages in terms of preferential segregation of the light. In particular, only the high-order modes, which generally have a greater degree of optical field intensity segregation in the high-index layers, are supported.

The ability to separate and isolate light into designated layers of a multilayer waveguide is extremely valuable for integrated optics purposes. Diblock copolymer films, as shown above, may be one way to achieve

controlled light confinement in a waveguide structure. The degree of confinement improves for lamellae with larger domain spacings and a higher refractive index difference between the A and B blocks. In practice, the high molecular weights needed for coil-coil diblocks are difficult to obtain synthetically. In addition, well-organized layers may be kinetically hindered by the slow dynamics of high molecular weight materials. As an alternative to using pure AB diblock copolymers, previous studies^{37,38} have shown that the addition of A or B homopolymer can be used to preferentially swell the respective block, resulting in an increase in the block domain spacing. Thus, the addition of both homopolymers can be used to swell the lamellar domains symmetrically and increase the lamellar domain spacing by about a factor of 2. Another possible way of achieving large domain size structures is through the use of rod-coil block copolymers. Because the characteristic length of a rod scales linearly with molecular weight, rather than to the 2/3 power as in coil-coil diblocks, for a given molecular weight, larger domain sizes are possible. Recent work done on a poly(styrene-*b*-hexyl isocyanate) rod-coil diblock copolymer³⁹ showed that the hexyl isocyanate rod domains were nearly 2000 Å in size. Before rod-coil block copolymers can be made into optical waveguides, however, their microphase separation behavior needs to be better understood.

In addition to molecular weight and block composition, the degree of light confinement in a block copolymer waveguide can also be controlled through molecular architecture. Triblock copolymers can also be used as waveguide materials and represent an attractive alternative to diblock copolymers. Figure 4A shows the refractive index profile of a hypothetical 4.05 μm 55-layer ABC triblock copolymer film located between a quartz substrate and air. The molecular weight of this ABC triblock copolymer was chosen to be identical to that of the second AB diblock discussed above. The refractive indices of the A, B, and C blocks at a wavelength of 4880 Å are 1.4945, 1.6008, and 1.6205, respectively, and are representative values found for common homopolymers. For this structure, the A and C blocks are assumed to preferentially segregate to the substrate and air interfaces, forming half-layers of 375 Å. All other layers are 750 Å thick. Inspection of Figure 4A shows that the B block broadens the effective width of the high-index layers, which enables the light to be better confined. The 55-layer triblock copolymer film was found to support 10 TE modes whose optical field intensity distributions are shown in Figure 4B. The black and gray portions of each OFI denote the optical field located in the high-index B and C layers and the low-index A layers, respectively. The OFI's are similar to those of the 28-layer diblock copolymer waveguide and exhibit perturbations resulting from the periodic refractive index profile. In particular, however, each of the high-index C layers together with the adjacent B layers now behaves like an effectively thicker high-index region. As a result, in contrast to the diblock copolymer waveguide, an average of 79% of the optical field intensity located in the guiding layers is now found to be confined within the high-index regions. Thus, a triblock copolymer of equal molecular weight is able to achieve 23% more confinement of the light. As expected, segregation of the light increases for the higher order modes and reaches a maximum of 81% for the tenth waveguide mode. In addition to the high degree of OFI confinement achievable by block copolymer structures,

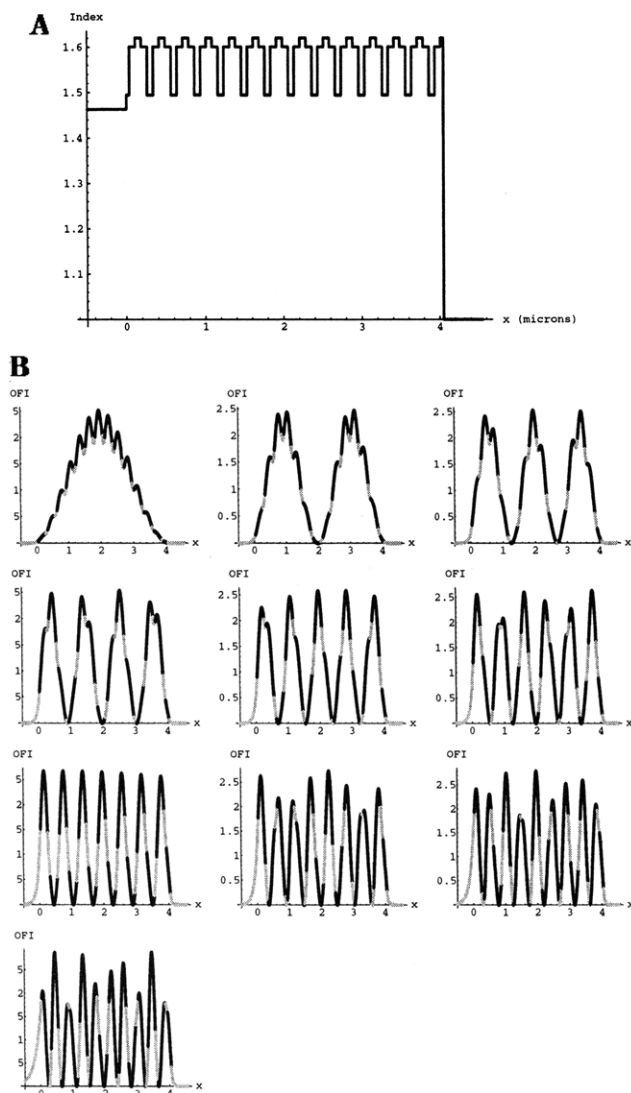


Figure 4. (A) Plot showing the refractive index profile for an ideal 55-layer ABC triblock copolymer waveguide. (B) Optical field intensity distribution plots for the 10 TE modes of the 55-layer ABC triblock waveguide. The black and gray portions of each OFI correspond to the high-index B and C layers and the low-index A layers, respectively.

the intensity of light found in each high-index region is not uniform across the waveguide but varies from mode to mode. Inspection of the first three modes (see Figure 4B) reveals that the light can be concentrated at either the center of the waveguide or the edges. Calculations on triblock structures having layer thicknesses of 1500 Å show preferential confinement of the light approaching 95%. If the block domain thicknesses could be made comparable to or greater than the wavelength of light, however, confinement of the light in the high-index layers is not always possible. In particular, for some theoretical waveguide structures, preferential segregation of the light into the low-index layers is predicted.

Conclusion

The optical waveguiding properties of self-assembled lamellar-forming block copolymer films were studied theoretically. The predicted propagation constants and the corresponding optical field intensity distributions for the waveguide modes of several candidate block copolymer waveguides were calculated and plotted, respectively, using a program based on a theoretical N -layer waveguide formalism. The formalism is a

generalization of the results for a homogeneous slab waveguide and is able to treat both TE and TM modes for waveguide structures with an arbitrary number of layers. For the calculations, block copolymer thin-film waveguides were modeled as ideal multilayer structures in which the lamellae were oriented parallel to the substrate and superstrate interfaces. The waveguide formalism can also be easily modified to take into account optically anisotropic (uniaxial) domains resulting from either chain stretching or the presence of a liquid crystalline block. AB block copolymer films in which the domain spacing is less than about $\lambda/5$ are found to behave essentially like homogeneous films except for slight perturbations in the optical field intensity distributions resulting from the periodic block copolymer morphology. In addition, the ordinary and extraordinary refractive indices of the block copolymer film can be used to characterize an equivalent homogeneous uniaxial film of equal thickness which yields essentially the same propagation constants. These results indicate that low molecular weight block copolymers can be used to make thin films which exhibit the optical waveguiding properties of a uniaxially birefringent material. In addition, the birefringence of the block copolymer waveguide can be controlled precisely by tailoring both molecular weight and composition of the blocks. The effect of the refractive index profile on the OFI's becomes significant when the domain spacing of the lamellae is greater than about $\lambda/3$. For diblock copolymer films with an alternating refractive index profile, the light was found to preferentially segregate into the high-index layers, with the greater segregation found in the high-order modes. On average, a 6% enhancement of the optical field intensity was found in the high-index layers. Inverted block copolymer structures in which the low-index block was at the air interface were found to only support high-order modes. As a result, a slightly greater segregation of the light would be expected in such structures. In addition to AB diblock copolymer films, ABC triblock copolymer films of equal molecular weight were also studied. In particular, an ABC triblock copolymer film in which the refractive indices of the B and C layers was greater than that of the A layers was considered. Significantly better confinement of the light was observed because the B block increased the effective width of the high-index C layer. Up to 79% of the light was confined in the high-index regions. The ability of block copolymers to be processed into self-assembled layered waveguide structures which exhibit confinement of light into designated domains, coupled to their extreme tailorability via chemical composition, molecular weight, and molecular architecture make block copolymers a potentially novel and exciting optical waveguide material over traditional organic and inorganic materials.

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