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Cylinder Orientation Mechanism in Block Copolymer Thin Films Upon Solvent Evaporation

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ABSTRACT: Ultrafiltration membranes based on cylinder-forming block copolymers are made by orienting the cylinders perpendicular to the membrane surface followed by selective etching of the minority component. Such membranes promise fast fluxes and superior molecular weight cut-offs. The perpendicular orientation of the cylindrical domains results from the solvent concentration profile that develops when drying the polymer casting solution. As solvent evaporates, it first causes nucleation of the ordered morphology at the vapor−solution interface. This is followed by cylinder growth. The rate of cylinder growth is the product of two terms—a polymer relaxation rate and a thermodynamic driving force. In regions of high solvent concentration the polymer relaxation rate is high and the driving force is small; in regions of low solvent concentration, the opposite is true. This concentration dependence results in the solvent concentration profile established by evaporation dictating how the growth rate varies as a function of position. For a concentration profile that causes the relaxation rate to increase less rapidly with position than the driving force decreases, the growth rate decreases moving into the film, so cylinders grow parallel to membrane surface. Conversely, when the concentration profile results in the relaxation rate increasing more rapidly with position than the driving force decreases, the growth rate increases further into the film, causing perpendicularly oriented cylinders to form. Analysis based on this picture agrees with a variety of experimental results.

Introduction

Block copolymers can spontaneously self-assemble into a variety of nanostructured morphologies. The cylindrical nanostructure is especially interesting: when the cylinders are formed from an etchable block and the surrounding continuum is a second inert block, nanoporous polymers can be prepared.[1,2] For example, in the poly(styrene)-*b*-poly(lactide) (PS−PLA) system, PLA is the etchable block and PS forms the continuous matrix.[3−8] After etching, thin films based on this polymer can be used as ultrafiltration membranes with monodisperse, close-packed pores that are nanometers in diameter. Such pores give an exceptionally sharp molecular cutoff and promise ultrafiltration fluxes orders of magnitude higher than those currently feasible[5,9−13]

However, achieving such ultrafiltration membranes requires that the cylinders are oriented perpendicular to the surface of the membrane. The thermodynamically preferred orientation is often with the cylinders oriented parallel to the membrane surface, within the plane of the film itself, due to preferentially wetting of one block at the free and/or confined surface.[1,2,7] The parallel cylindrical orientation is not useful for the generation of nanoporous filtration membranes. Perpendicularly oriented cylinders in block polymer thin films have been achieved through solvent annealing approaches and by controlling solvent evaporation rates during the thin film deposition.[3,5,8−10,12,14−18] These studies have shown that the rapid evaporation of solvent from polymer thin films kinetically traps cylinders in a perpendicular orientation whereas the equilibrium structure consists of a parallel orientation. No unifying explanation for the production of the perpendicular cylinders as the result of solvent evaporation exists. Such a theory to guide experiments would be beneficial.

In this paper, we develop a theory for preparing such perpendicularly oriented cylinders. In this development, we seek to explain four observations with PS−PLA diblock copolymers, taken as our model system.[5] First, the solvent from which the film is cast is important, as shown in Table 1. The solvents explored here favor polystyrene, but to varying degrees. Solvents forming perpendicular cylinders usually have large differences between the Flory−Huggins interaction parameters $\chi_{PS-solvent}$ and $\chi_{PLA-solvent}$. On the other hand, solvents not forming perpendicular cylinders usually have smaller differences between $\chi_{PS-solvent}$ and $\chi_{PLA-solvent}$. Second, the copolymer composition affects orientation: one polymer containing 26% (v/v) PLA gives perpendicular cylinders, while a second, containing 28% (v/v) PLA (at comparable molar mass), does not. Third, a copolymer solvent combination that gives perpendicular cylinders under fast evaporation conditions, may result in parallel cylinders under slow evaporation (Figure 1). Finally, if the film is too thick, perpendicular cylinders will not span the membrane thickness, as illustrated in Figure 2.

Examining the physical processes occurring during the drying of the film aids understanding the mathematical framework developed later. The steps in the formation of ordered cylindrical structures are presented in Figure 3. In the casting solution, the dissolved copolymer is disordered because the solvent mediates the unfavorable enthalpic interactions between the constituent polymers (Figure 3.1). Once the polymer solution is cast, evaporation causes the solvent concentration to change as a function of time and position. The concentration at the surface rapidly decreases causing the solvent concentration to fall below the order−disorder solvent concentration $\phi_{1,OD}$. This concentration is the point where the solvent is no longer able to mediate the unfavorable enthalpic interactions between the two polymer blocks resulting in microphase separation.[19−22] As ϕ_1 passes through $\phi_{1,OD}$, the ordered copolymer phase can nucleate at the interface between the polymer solution and the vapor phase (Figure 3.2). After the ordered phase has nucleated at the surface, it will begin to grow at the expense of the metastable

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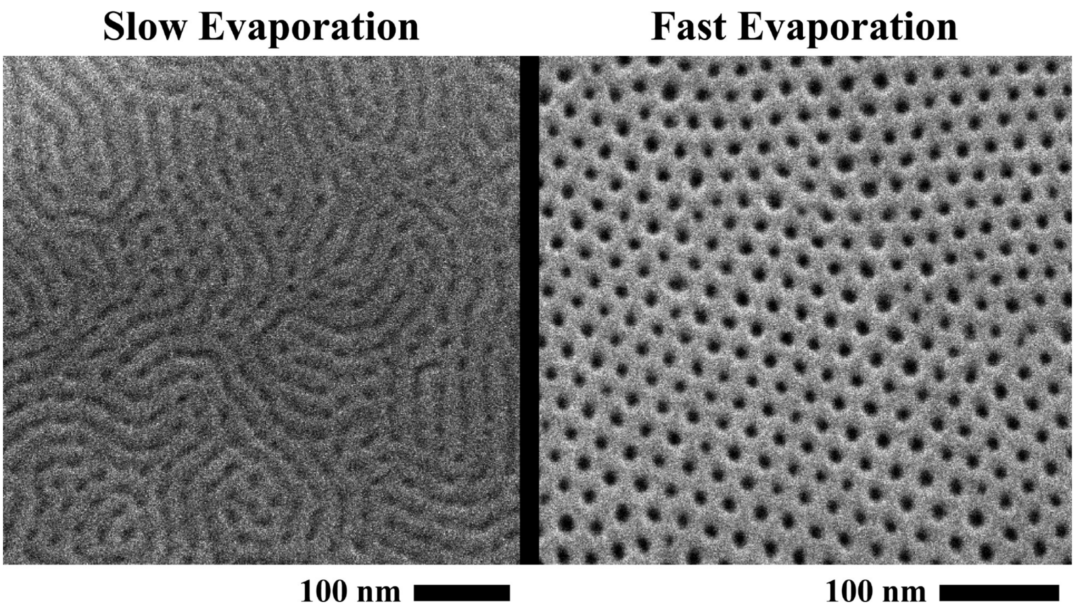

Figure 1. Fast evaporation is needed for perpendicularly oriented cylinders. SEM micrographs of the top surface of PS−PLA thin films show that evaporating toluene slowly produces a parallel orientation, while rapid evaporation aligns the cylinders in a perpendicular orientation. As described previously, the membranes were cast from an 8 wt % solution of poly(styrene)-*b*-poly(lactide).[5] The casting solution was drawn across a microporous support membrane and allowed to dry. For fast evaporation conditions, the cast film was left exposed to the open atmosphere. For slow evaporation conditions, a Petri dish was placed over the drying membrane. Drying times for the fast and slow evaporation conditions were 5 min and 2 h, respectively. Membranes were soaked in a 0.5 M NaOH in 60/40 (w/w) methanol/water solution to selectively etch the polylactide block. The final thickness of the copolymer layer was 4 μm.

Table 1. Estimates of the χ Parameter Used to Determine Solvent Selectivity

solvent	$\chi_{PS-solvent}$	$\chi_{PLA-solvent}$
Perpendicular Cylinders		
benzene	0.28	2.03
carbon tetrachloride	0.72	3.18
chlorobenzene	0.33	2.37
toluene	0.35	2.45
1,1,2-tricholoroethane	0.38	2.38
Mixed-Orientation Cylinders		
chloroform	0.04	0.58
dichloromethane	0.03	0.37
ethylene dichloride	0.03	1.02
xylene	0.22	2.19

disordered phase, advancing into the thin film as a front. The solvent concentration profile when this growth begins (Figure 3.3) is critical to determining the resulting cylinder orientation.

The rate of cylinder growth (i.e., the velocity of the advancing front of ordered copolymer) is the product of two terms—a polymer relaxation rate and a thermodynamic driving force. In regions of high solvent concentration, the polymer relaxation rate is high because the solvent allows higher mobility of the polymer chains, and the driving force is small because the solvent concentration is close to $\phi_{1,\mathrm{OD}}$. In regions of low solvent concentration, the opposite is true. For solvent evaporating from a thin polymer film, the solvent concentration is lowest at the vapor−solution interface. There, the driving force is highest and the relaxation rate is lowest. Moving into the film, the variation in concentration causes the driving force to decrease and the relaxation rate to increase, which makes the growth rate a function of position. Depending on how the relaxation rate and driving force vary, the growth rate can either increase or decrease with position. If the growth rate increases with position into the film (i.e., if the polymer relaxation rate increases with position faster than the driving force decreases), the growth of an ordered structure is able to "accelerate" into the film, forming perpendicular cylinders.

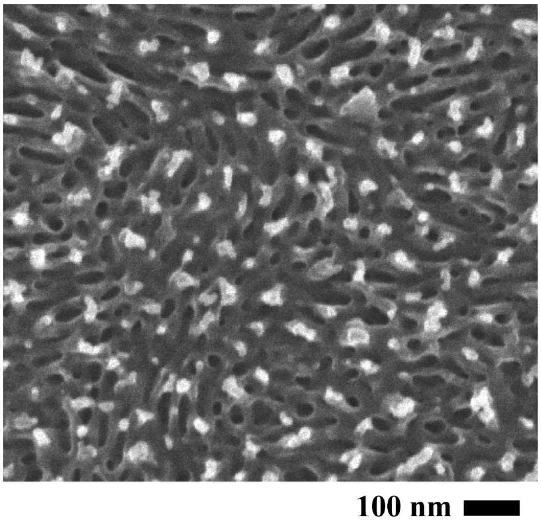

Figure 2. Perpendicular cylinders do not span thick membranes. Using O_2 reactive ion etching (O_2 flow of 80 sccm, at 30 mTorr, with a plasma power of 60 W) to expose the interior of the membrane shows that the cylinders switch from a perpendicular to a mixed orientation 100 nm into the film.

In the sections below, we develop a theory based on the picture above that is capable of explaining the experimental observations. The theory centers on the assumption that these cylinders are oriented as a result of the solvent concentration profile formed during drying. To explore this assumption, we develop approximate equations for this profile. We then estimate the rate at which an ordered copolymer region advances into a region of metastable disordered copolymer, extending the arguments of Goveas and Milner[23] to systems with nonuniform concentration. Finally, we use these results to suggest conditions when perpendicular cylinders can be expected.

Theory

We begin by imagining a homogeneous block copolymer solution cast onto a support. Figure 4 shows such a solution.

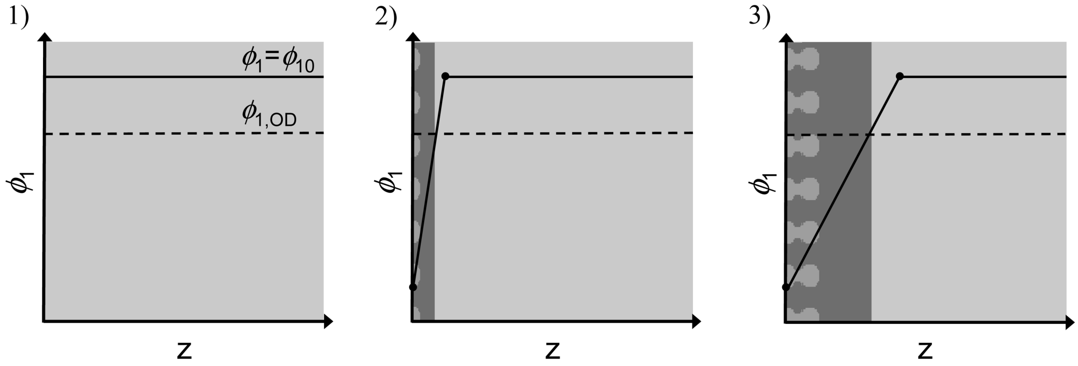

Figure 3. Ordered copolymer structure forms as a result of nucleation and growth. (1) Initially the solvent concentration ϕ_{10} is uniform throughout the film and the copolymer is disordered. (2) Solvent evaporation at the free surface causes ϕ_1 to fall below $\phi_{1,\mathrm{OD}}$ driving the nucleation of an ordered copolymer structure. (3) Solvent diffusion through a thin film of thickness ℓ controls the evaporation rate. Once nucleation is complete, the thickness of the ordered phase ℓ_{OD} grows.

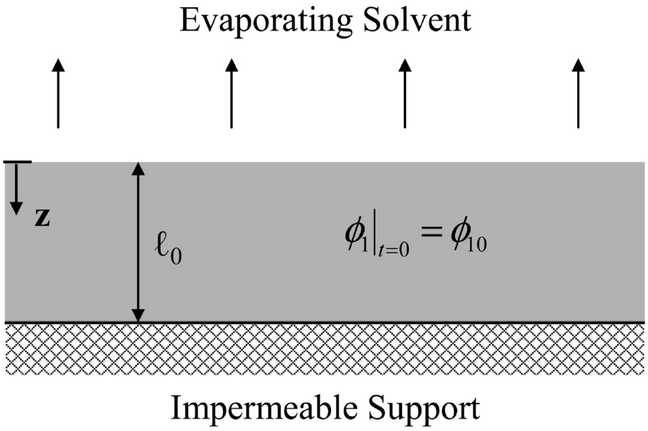

Figure 4. Solvent evaporating from a thin polymer film. The solvent concentration in an initially uniform film changes as a function of time and position as the solvent evaporates from the free surface.

One surface of this film, exposed to the support, has no solvent flux. The other surface, exposed to the open atmosphere, allows for solvent evaporation. While the solvent concentration in the bulk gas may be zero, the concentration of solvent in the vapor immediately adjacent to the polymer film may be nonzero and in equilibrium with the polymer solution at the interface.

The concentration profile that results is described by a solvent mass balance on a differential volume:

$$\frac{\partial\phi_1}{\partial t} = D\frac{\partial^2\phi_1}{\partial z^2} - \frac{\partial}{\partial z}(v\phi_1) \tag{1}$$

where ϕ_1, is the solvent volume fraction in the film, D is the diffusion coefficient of solvent in the film, and v is the convective velocity. Because the coordinate system z begins at the interface between the vapor and the film, this mass balance is subject to the initial and boundary conditions

$$t = 0 \qquad \text{all}z \qquad \phi_1 = \phi_{10} \tag{2}$$

$$t > 0 \qquad z = 0 \qquad -D\frac{\partial\phi_1}{\partial z} = \frac{k}{H}(\phi_1 - \phi_1^*) \tag{3}$$

$$t > 0 \qquad z = \ell_0 \qquad -D\frac{\partial\phi_1}{\partial z} = 0 \tag{4}$$

where k is the mass transfer coefficient in the gas at the interface; ℓ_0 is the initial film thickness; ϕ_1^* is the solvent concentration that would be in the polymer solution if it were in equilibrium with the bulk vapor; and H is the partition coefficient, i.e., the solvent concentration in the film divided by that at equilibrium in the vapor.[24] Equation 3 is thus a mass balance at the vapor–film interface, and eq 4 reflects the impermeable interface at the far side of the film.

Solvent Concentration Profiles. While a complete solution of eqs 1–4 is available, we can gain considerably more insight by considering a series of special cases. First, we consider how the solvent concentration at the surface of the film varies at small times, which is given by[25]

$$\frac{\phi_1 - \phi_1^*}{\phi_{10} - \phi_1^*} = \exp\left(\frac{k^2 t}{DH^2}\right)\operatorname{erfc}\left(\frac{k}{H}\sqrt{\frac{t}{D}}\right) \tag{5}$$

Strictly speaking, this result is for films that are very thick (i.e., the boundary condition at the support side of the membrane can be treated as if it were an infinite distance from the vapor–film interface); but it will be accurate as long as the Fourier number ($\ell_0^2/4Dt$) is large.[24,26] For a typical system described here with ℓ_0 equal to 100 μm and a constant D equal to 10^{-7} cm^2/s, the Fourier number remains greater than 5 for 50 s. For us, eq 5 is valuable because it gives a characteristic time (DH^2/k^2) for reducing the solvent concentration at the surface to a value in equilibrium with the bulk vapor. This time determines the concentration profile within the film and is important in starting the nucleation of an ordered copolymer phase. Nucleation is possible as soon as the concentration at the order–disorder transition $\phi_{1,OD}$ is reached.

What structure forms depends on how quickly the solvent evaporates compared to how quickly nucleation occurs. To make this more definite, we postulate that there is a characteristic nucleation time, τ_N. This is the time needed to nucleate an ordered phase after ϕ_1 passes through $\phi_{1,OD}$. The time when growth can begin (i.e., τ_N after $\phi_1 = \phi_{1,OD}$) controls the orientation of any ordered structures.

We want to know whether the film's drying is influenced more by diffusion or by interfacial mass transfer. Understanding which mechanism is more important will help to develop an approximate concentration profile. Such consideration depends on the Biot number, Bi, defined by

$$Bi = \frac{k\ell_0}{DH} \tag{6}$$

When the mass transfer coefficient k is small, Bi is small; the solvent concentration profile is nearly flat; and the drying time for the film t_{D} is controlled by gas phase mass transfer:[24,26]

$$t_D = \frac{\ell_0 H}{k} \tag{7}$$

Alternatively, when diffusion in the film is slow, the Biot number is large, and the solvent concentration varies abruptly with position. In this case, the drying time can be estimated from:[24,26]

$$t_D = \frac{\ell_0^2}{4D} \tag{8}$$

Note that both these limits depend on the initial film thickness ℓ_0.

To illustrate these ideas more completely, imagine that we have a system in which the diffusion coefficient of the solvent in solution is 10^{-7} cm^2/s and the partition coefficient is about 800. If we cast a 100 μm film and dry rapidly so k is 1 cm/s, we find *Bi* is over 100 and the drying time found from eq 8 is around 4 min. This is close to our previously observed experimental results.[5] Thus, under most conditions, we expect drying is controlled by diffusion of the solvent within the polymer solution.

We now calculate a useful approximate concentration profile for the solvent in the drying membrane. To do so, we return to eq 1 and identify z as the coordinate originating at the film's surface, and thus moving toward any support layer. For the films studied here the convective velocity v is small and $\partial(v\phi_1)/\partial z$ near zero.[27] We also assume the concentration profile near the surface is established quickly, so the region near the surface is near a pseudosteady state. Now, $\partial\phi_1/\partial t = 0$, and eq 1 reduces to

$$0 = D\frac{\partial^2\phi_1}{\partial z^2} \tag{9}$$

This mass balance is subject to the boundary conditions:

$$z = 0 \qquad \phi_1 = \phi_1^* \tag{10}$$

$$z = \ell \qquad \phi_1 = \phi_{10} \tag{11}$$

where ℓ is the position where the concentration reaches the original value. Notice that the boundary condition at the interface has been modified to reflect the large Biot number. These equations are easily solved:

$$\frac{\phi_1 - \phi_1^*}{\phi_{10} - \phi_1^*} = \frac{z}{\ell} \tag{12}$$

However, ℓ does vary slowly with time

$$\phi_{10}\frac{d\ell}{dt} = \frac{D}{\ell}(\phi_{10} - \phi_1^*) \tag{13}$$

This is subject to the initial condition

$$t = 0 \quad \ell = 0 \tag{14}$$

Thus,

$$\ell = \sqrt{2Dt\left(1 - \frac{\phi_1^*}{\phi_{10}}\right)} \tag{15}$$

and

$$\frac{\phi_1 - \phi_1^*}{\phi_{10} - \phi_1^*} = \frac{z}{\sqrt{2Dt\left(1 - \frac{\phi_1^*}{\phi_{10}}\right)}} \tag{16}$$

This approximate concentration profile differs from the exact solution of eq 1 in two ways: it does not show an inflection near $z = 0$ at small times; and it does not curve in the region where $z = (2Dt)^{1/2}$. These are not severe constraints on the following analysis.

Cylinder Nucleation and Growth. The concentration profiles developed above determine the location of the nucleation events that lead to the growth of the cylindrical phase. In the copolymer melts, where no solvent is present, preferential wetting of one block at the free surface can drive the formation of a microstructure prior to the system crossing the order–disorder transition. In the system examined here, the solvent mediates the interactions between the free surface and the two blocks preventing the formation of structure at the free surface prior to the order–disorder transition. The arguments show that the lowest solvent concentration is at the vapor–solution interface, where $z = 0$ and $\phi_1 = \phi_1^*$. This concentration is achieved quickly, at times about equal to (DH^2/k^2). Using the estimates above, this means that the concentration reaches ϕ_1^* after $[(10^{-7}\ \mathrm{cm^2/s})\ 800^2/(1\ \mathrm{cm/s})^2]$, or 64 ms. As ϕ_1 passes through $\phi_{1,OD}$, the ordered copolymer phase begins to nucleate at $z = 0$. The nucleation of the ordered phase at the interface takes a finite amount of time τ_N. After this period of time, the ordered copolymer structure will begin to grow, advancing into the thin film.[28,29]

Cylinder Formation and Growth. We now turn to why the fast evaporation condition leads to perpendicular cylinders and slow evaporation conditions lead to parallel cylinders. To do this, we use an analysis developed by Goveas and Milner,[23] which predicts the rate at which one block copolymer phase will advance into an adjoining metastable phase. This analysis, valid for a disordered copolymer phase transitioning into an ordered phase and for one ordered phase transitioning into another ordered phase (e.g., spheres into cylinders),[30−33] presumes that a single nucleation event has already occurred; in our case, this happens near the vapor–film interface. After this event, the transformation from a disordered to an ordered phase occurs at a front, located at a distance ℓ_{OD} less than ℓ (i.e., at a location in the film that is closer to the free surface than the location at which the concentration of solvent is the same as the initial concentration ϕ_{10}). This front grows at a velocity $\partial\ell_{\mathrm{OD}}/\partial t$[23]

$$\frac{\partial\ell_{OD}}{\partial t} = \frac{R_g}{\tau}(\chi N - \chi N_{OD})g(f_{PLA}) \tag{17}$$

where ℓ_{OD} is the thickness of the ordered phase, R_{g} is the radius of gyration of the block polymer, and τ is the longest relaxation time for the polymer chains. The product of χ, the polymer–polymer Flory–Huggins interaction parameter, and N, the overall degree of polymerization, is known as the segregation strength. This product has a value of χN_{OD} at the order–disorder transition. The factor g is a constant of order one and depends on the copolymer composition. This expression is valid as long as the time for drying (ℓ_0^2/D) is large relative to τ_N, the time needed to nucleate an ordered phase.

The experimental work originally done to verify eq 17 was based on a uniform, metastable disordered phase produced by a thermal quench.[30−33] Such a phase has no preferred growth direction. In our case, the metastable disordered phase forms as a result of the solvent evaporation. If $Bi \gg 1$, the sharp concentration gradient that forms creates a preferred direction for growth of the ordered phase.

By considering how each of the terms in eq 17 varies with solvent concentration, we can see how directionality results in perpendicular cylinders. The quantity g has little effect on orientation. The other two groups of terms, R_g/τ and $(\chi N - \chi N_{OD})$, do affect orientation. These terms can be regarded as a rate constant and the degree of supersaturation, respectively. When the solvent concentration is high, R_g/τ is large because τ is small[34] and $(\chi N - \chi N_{OD})$ is small due to the presence of solvent attenuating the magnitude of χ.[19,20,22] When the solvent concentration is low, the opposite is true. How the product of these two factors varies as a function of position within the films dictates the direction in which the cylinders will grow.[35] Mathematically this is expressed as the derivative of eq 17 with respect to position z, $\partial(\partial\ell_{OD}/\partial t)/\partial z$. If $\partial(\partial\ell_{OD}/\partial t)/\partial z$ is positive, growth of the cylinders into the film is faster, and cylinders form perpendicular to the polymer solution interface. If $\partial(\partial\ell_{OD}/\partial t)/\partial z$ is negative, the growth of cylinders is faster in the plane of the ordering front, driving cylinders to form parallel to this interface.

In more physical terms, imagine we are at the position ℓ_{OD}, where ordered cylinders are growing. These cylinders can either grow at ℓ_{OD}, or at a somewhat greater position of $\ell_{OD} + \Delta z$. The location of further growth determines whether cylinders grow parallel or perpendicular to the membrane interface. The growth depends on a rate constant (R_g/τ), and a driving force ($\chi N - \chi N_{OD}$). At ℓ_{OD}, both of these have some reference value. At distances slightly greater than ℓ_{OD}, the rate constant is bigger, but the driving force is smaller, because the amount of solvent is greater. The growth of cylinders depends on the product of these terms. If the product is larger at distances Δz from ℓ_{OD}, the growth of cylinders will be faster further into the film, and perpendicular cylinders will form.

We can be more explicit about the variables that impact the sign of $\partial(\partial\ell_{OD}/\partial t)/\partial z$ by using a change of variables to rewrite eq 17 as

$$\frac{\partial}{\partial z}\left(\frac{\partial\ell_{OD}}{\partial t}\right) = R_g g(f_{PLA})\left(\frac{\partial\phi_1}{\partial z}\right)\left[\frac{\partial}{\partial\phi_1}\left(\frac{1}{\tau}(\chi N - \chi N_{OD})\right)\right] \tag{18}$$

where ϕ_1 is again the solvent volume fraction. Writing eq 18 in this form ignores the weak dependence of R_g on solvent concentration and factors out $\partial\phi_1/\partial z$. From eq 16, we see that $\partial\phi_1/\partial z$ will always be positive and thus will have no effect on the sign of $\partial(\partial\ell_{OD}/\partial t)/\partial z$.

The derivative in the square brackets in eq 18 determines the sign of the whole expression and hence the resulting cylinder orientation. Evaluating this derivative requires estimates of the longest relaxation time and the segregation strength as a function of solvent concentration. Polystyrene self-diffusion data from Wesson et al.[34] and the radius of gyration of a polymer chain[36] are used to estimate the longest relaxation time. Wesson et al. measured the self-diffusion coefficient of polystyrene D_s by using forced Rayleigh scattering to track the diffusion of photochrome-labeled polystyrene molecules in THF solutions of varying PS concentration.[34] These data fit an exponential function:

$$\tau = \frac{{R_g}^2}{D_s} = \tau_o \exp(-a\phi_1) \tag{19}$$

where τ_o is the longest relaxation time of the polymer in the presence of no solvent and a is an empirical constant, specific to a polymer−solvent pair, that quantifies the solvent dependency of the relaxation time. Physically, $1/a$ can be thought of as a solvent concentration where the dependence of the relaxation time on the solvent concentration becomes large.

The dilution approximation[22] is used to estimate the segregation strength as a function of solvent concentration

$$\chi N = \chi_{AB} N(1-\phi_1) \tag{20}$$

where the melt phase segregation strength is scaled with the polymer volume fraction. We recognize that experiments have shown that the dilution approximation accurately predicts order−order transitions in block copolymer systems, but fails to predict the order−disorder transition.[20,22,37,38] Combining eq 18−20, we find

$$\frac{\partial}{\partial z}\left(\frac{\partial\ell_{OD}}{\partial t}\right) = \left(\frac{R_g}{\tau}\right)_o \exp(a\phi_1)\chi_{AB}N\left(\frac{\partial\phi_1}{\partial z}\right)\times \\ [-1 + a(\phi_{1,OD} - \phi_1)] \tag{21}$$

When the term in square brackets is positive, perpendicular cylinders will form.

We now look at the contributions to the term in the square brackets of eq 21. The term (−1), which reflects how the degree of polymer supersaturation varies with concentration, is always negative and so favors parallel cylinders. The second term, $a(\phi_{1,OD} - \phi_1)$, which results from the variation of the relaxation time with solvent concentration, is positive, and so can produce perpendicular cylinders. This makes physical sense: the degree of supersaturation (i.e., the driving force) decreases further into the film, favoring growth in the plane of the ordering front (i.e., parallel cylinders). However, the higher polymer mobility in the regions of higher solvent concentration further in the film may be large enough to offset the influence of the degree of supersaturation, producing perpendicular cylinders.

Identifying the conditions when the expression above is positive suggests why fast evaporation can lead to a perpendicular orientation. Equating eq 21 to zero identifies the concentration at which the transition from perpendicular to parallel cylinders occurs:

$$\phi_{1c} = \phi_{1,OD} - \frac{1}{a} \tag{22}$$

If the solvent concentration is below this critical concentration ϕ_{1c}, perpendicular cylinders will grow. If the solvent concentration is above this value, parallel cylinders will grow in the advancing plane of the ordering transition. The concentration $1/a$ is where τ begins to depend strongly on solvent concentration. Thus, ϕ_{1c} being $1/a$ below the order−disorder concentration indicates that to form perpendicular cylinders the solvent concentration needs to drop to a value where the relaxation rate is a strong function of concentration. This allows the relaxation rate to increase with position more rapidly than the driving force decreases resulting in a positive value of $\partial(\partial\ell_{OD}/\partial t)/\partial z$.

Results

The analysis above gives the basis on which to predict when the cylinders in a block copolymer thin film will form perpendicular to the surface of the film. It presumes that nucleation begins at the vapor−film interface.[17] Once nucleation occurs, the solvent concentration where growth begins determines what type of structure will form. In many cases, the concentration of solvent at the surface will be above the critical concentration defined by eq 22, so the ordered structure that grows will tend to be parallel to the film's surface. In cases where the surface concentration falls below the critical concentration, cylinders will tend to grow perpendicular to the film's surface—into the film.

We demonstrate these two limiting cases in Figure 5. In these plots, the position z is scaled by the total film thickness. The dashed line is the solvent concentration at the order−disorder transition; once the solvent concentration passes through the order−disorder transition, ordered nanostructures begin to form. The dotted line is the critical concentration, defined by eq 22, where the orientation of the forming cylinders changes from perpendicular to parallel. The solid line is a representative solvent concentration profile determined using eq 16. Below the plots of concentration vs position (Figure 5, parts a and b) is another set of plots showing the variation of $\partial\ell_{OD}/\partial t$ as a function of position (Figure 5, parts c and d).

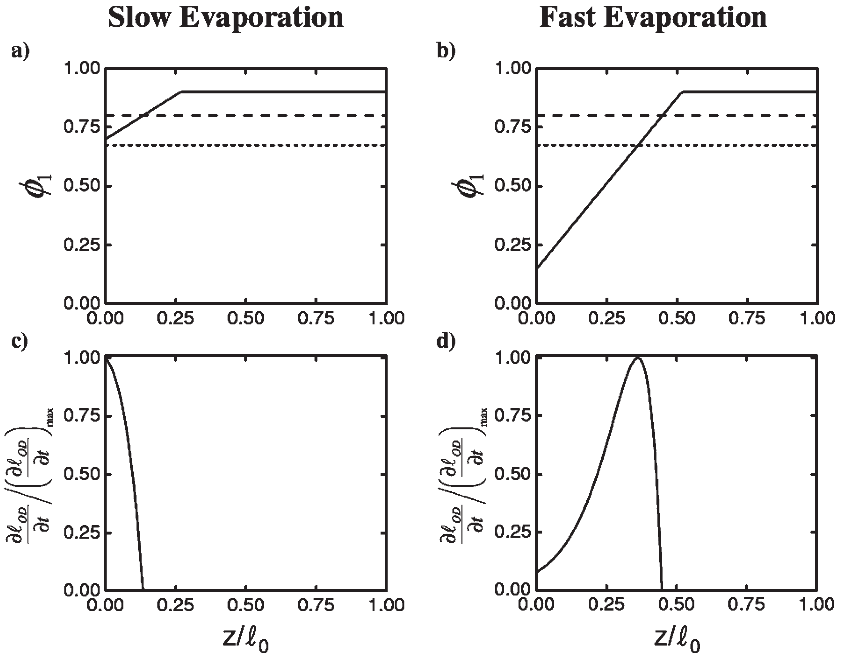

Figure 5. Solvent concentration profiles for slow and fast evaporation conditions. Slow evaporation does not produce a sharp gradient in solvent concentration resulting in the formation of parallel cylinders. On the other hand, fast evaporation conditions do produce a steep gradient that drives the formation of perpendicular cylinders for some finite distance into the film. The solid black lines in sections a and b are the solvent concentration profiles, the dashed lines are the solvent concentration at the order–disorder transition, and the dotted lines are the critical concentration the solvent must fall below in order to form perpendicular cylinders. Sections c and d plot the cylinder growth rate normalized by the maximum growth rate as a function of position.

The case where nucleation occurs above the critical concentration is shown on the left. The solvent concentration profile is plotted in Figure 5a. When the solvent concentration falls below the order–disorder transition, spheres nucleate at the air–solution interface. These spheres then grow into cylinders parallel to the film surface because the solvent concentration has not decreased below ϕ_{1c}, the concentration at which the relaxation time is small enough to allow facile growth of perpendicular cylinders. Another way to see why parallel cylinders are preferred is to examine the plot of the ordering velocity $\partial \ell_{OD}/\partial t$ vs position shown in Figure 5c. The variation shown was calculated using the concentration profile in Figure 5a. The ordering velocity monotonically decreases with position into the film, so the resistance to the transition from nucleated spheres to cylinders is smallest near the interface (i.e., $z = 0$). Thus, cylinders form in the plane of the thin film.

The opposite is true when nucleation occurs below the critical concentration. Now the concentration profile is that on the right. In this case, the rate of solvent mass transfer in the gas phase is much faster than the rate of mass transfer in the polymer solution; this results in a sharp concentration gradient as seen in Figure 5b. Now the solvent concentration at the surface falls below the critical concentration, resulting in the formation of perpendicular cylinders. For a finite distance, the ordering velocity, shown in Figure 5d, increases with position. In this region, the resistance to transitioning from spheres to cylinders decreases with position (i.e., it is easier for cylinders to grow into the film) driving the formation of perpendicular cylinders. However, at a finite distance into the film, the solvent concentration in the film is below $\phi_{1,OD}$ but is above ϕ_{1c}. In this region, the ordering velocity decreases with position similar to the slow evaporation case, and parallel cylinders are formed. This transition from a region where perpendicular cylinders are easier to form to a region where forming parallel cylinders is preferred can explain the mixed orientation observed in Figure 2.

The theory developed here allows us to estimate how far into the selective layer the perpendicular cylinders will grow. Assuming τ_N is small and the ordered copolymer very rapidly consumes the adjacent metastable phase, the concentration profile at time (DH^2/k^2) provides an estimate for the distance into the selective layer that perpendicular cylinders can be sustained. At $t = (DH^2/k^2)$, the distance into the film where $\phi_1 = \phi_{1,c}$ is where the cylinders will begin to transition from perpendicular to parallel. The order–disorder concentration is around a solvent volume fraction of 0.8 and using the Wesson et al. data to estimate a around 10, $\phi_{1,c}$ is estimated as 0.7. Along with the prior estimates for the diffusion coefficient of 10^{-7} cm^2/s, H of 800 and $k = 1$ cm/s, we estimate that the distance perpendicular cylinders will grow into the selective layer is around 800 nm. This is slightly larger than our experimental observation but the correct order of magnitude. The implications of these results are explored next.

Discussion

The arguments above suggest that the key to forming perpendicular cylinders in a drying film of block copolymer is the concentration and concentration gradient at the vapor polymer surface. When the film is rapidly dried in solvent-free vapor, the surface solvent concentration will normally be near zero. In this case, perpendicular cylinders have the greatest chance of forming. They will form if the surface concentration is below the critical value defined by eq 22.

There are thus three cases when perpendicular cylinders will not form, and parallel ones will result. First, if we dry the system slowly such that the surface concentration is greater than ϕ_{1c}, parallel cylinders will form. This will most often happen when the adjacent vapor contains solvent. Second, if the chemical system chosen is such that the critical concentration is negative, parallel cylinders result. For example, if the relaxation times do not vary with solvent concentration, then a in eq 19 is zero and parallel cylinders will always form. In this case, the driving force for forming an ordered phase is largest at the front, ℓ_{0D}, and the rate constant for forming an ordered phase is a constant. In this case, the ordered phase forms at ℓ_{0D}, parallel to the surface of the film. Finally, when the Biot number in eq 6 is small because drying of a very thin film is fast, (i.e., ℓ_0 is small), the solvent concentration in the film changes with time t but not with position z. If the concentration throughout the film drops so rapidly that the polymer chains do not have a chance to rearrange, the ordered microphase is not given the opportunity to nucleate because $t_D < \tau_N$, and a trapped disordered phase is formed.[3,15]

These arguments are consistent with two of the four experimental results quoted at the beginning of this paper. They explain that fast drying is necessary to force the surface concentration below the critical concentration (Figure 1). These arguments also show why few cylinders span thick films (Figure 2), because of the concentration profiles in Figure 5.

Less direct arguments can be made to explain how solvent quality is important to cylinder orientation. Introducing solvent to a copolymer system can be understood in terms of trajectories on the $\chi_{\mathrm{eff}}N$ versus f morphology plot. These trajectories will vary depending on solvent selectivity. Neutral solvents follow a vertical trajectory on the morphology plot.[20,21] The solvent swells both blocks equally, keeping f constant, and dilutes the unfavorable interactions between the two blocks, decreasing $\chi_{\mathrm{eff}}N$. Such a trajectory is shown in Figure 6. As the solvent evaporates from the thin film, the copolymer will separate into a cylindrical structure once the order−disorder transition point is reached. When the cylinders form, they do so with a mixed orientation. The solvent concentration gradient is not strong enough to subsequently align the cylinders. Instead, they remain a mix of perpendicular and parallel orientations as seen in our previous work.

The situation is different for a selective solvent. Now the trajectory follows a diagonal path because along with diluting the unfavorable interactions, the solvent selectively swells one of the blocks thereby changing the effective volume fraction.[20−22] Figure 6 shows the trajectory followed when the solvent is selective for the majority block. This moves the copolymer through a larger window of the spherical morphology. As solvent evaporates and the order−disorder transition is reached, spheres form because of the modified volume fraction. These spheres do not have a preferred direction of growth, i.e., they are zero-dimensional. The spheres can then grow epitaxially to form cylinders,[39] with their orientation influenced by the solvent concentration profile which develops due to evaporation.

The dependence of cylinder orientation on the polylactide volume fraction also supports the notion that the cylinders grow through a spherical intermediate. With increases in the polylactide volume fraction, the entropic cost of packing the PLA chain into a sphere can become too large,[40] preventing the formation of a spherical intermediate, and thus causing the disordered phase to transition directly to a cylindrical microphase.

Finally, we want to return to the prediction that perpendicular cylinders will only grow a finite distance into the film before the cylinders switch from a perpendicular orientation to a mixed orientation. This prediction, often supported by experiments, threatens the value of block copolymers as ultrafiltration membranes, and so is a serious challenge. Two ways to avoid this challenge are envisioned. Both have been used successfully to create membranes capable of sieving proteins from a buffer solution[9,10,12] The first method involves casting a very thin copolymer film, between 50 and 500 nm thick, using fast evaporation conditions. This would result in a small Biot, with a nearly flat solvent concentration profile. If the evaporation conditions are selected such that when growth begins, ϕ_1 is less than ϕ_{1c} throughout the film, perpendicular cylinders that span the entire film thickness will be created.[3,9,10,15] However, the film must not be dried too quickly or an ordered copolymer structure will not have sufficient time to nucleate.[3,15] Previous efforts using this method have cast the copolymer thin film onto a nonporous substrate, floated the thin film off the substrate, and picked it up on a porous support before using it as a filtration membrane.[9,10]

Another way to address this difficulty may be to begin with a brief solvent evaporation step prior to plunging the cast film into a nonsolvent.[12] This would result in a dense skin layer forming.[41] If this solvent evaporation step is done under fast evaporation conditions, the top dense layer can form with perpendicular cylinders templated by the copolymer self-assembly, while the underlying porous structure is controlled by the polymer precipitation.[12] This technique will produce a more expensive membrane, because both the selective and support layers are fabricated from the same copolymer, but it should increase the number of perpendicular cylinders spanning the selective layer thickness.

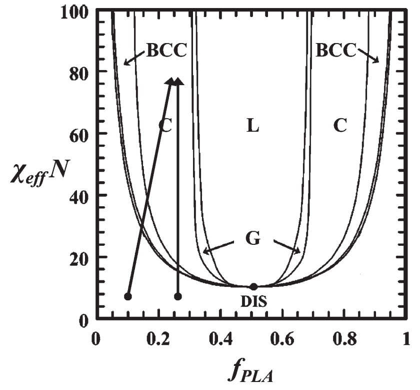

Figure 6. Trajectories for a neutral and a PS selective solvent on the copolymer morphology map. Using a neutral solvent dilutes the unfavorable interactions between the two blocks, resulting in the vertical path shown, while a selective solvent dilutes the interactions and selectively swells one block, as demonstrated by the diagonal trajectory. The diagonal trajectory passes through a larger window of the spherical phase. (Figure 6 is from ref 52).

In conclusion, the analysis proposed above can explain four empirical observations from our efforts to make water filtration membranes with monodisperse pores. These observations rely on examining the membrane structure after the casting process is complete. An interesting area of research would be to following the evolution of the nanostructure throughout the membrane fabrication process. It may be possible to use cryomicroscopy; halting the structure formation at different times to observe discrete structures during the membrane casting process.[42,43] Another alternative could be to use time-resolved GISAXS to continuously monitor the structure as it forms.[2,14] Extension of the above analysis to lamellae forming copolymers would be interesting to explore. All these ideas should aid discovery of new conditions for superior membranes of self-assembled block copolymers.

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(29) Work on these structures has suggested that water vapor is important for nucleation. This seems sensible for block copolymers containing a very hydrophilic block (e.g., polyethylene oxide) which forms cylinders.[14,17,47] For block copolymers that do not include a very hydrophilic component, nucleation probably has a different origin triggered by some other factor. In addition, experimental studies suggest that the nucleation is probably not initially of a cylindrical phase, but probably of a spherical structure which later transitions into cylinders.[18,48−50] These factors do not alter the basic thrust of our arguments.

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