Commercial Applications of Block Copolymer Photonic Gels

by

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ABSTRACT

Block copolymer photonic gels are a simple and easily processed material which responds rapidly to environmental stimuli through a color change. The diblock copolymer that forms the gel self-assembles into a lamellar structure that has the potential to reflect light over a broad range of wavelengths, from the IR to the UV. Application of a stimulus causes a change in the periodicity and/or index of refraction of layers that result in a shift of the stop band. The types of stimuli include temperature, pressure, pH, electric field, salt concentration, and humidity. Due to the high level of tunability of the polymers, it is possible to tailor the response of the gel to achieve a desired effect.

This thesis is an assessment of the commercial applications of the photonic gel technology. First a cost model was developed for the polymerization of the block copolymer, polystyrene-*b*-poly(2-vinyl pyridine). The results indicate that it is cost effective to invest in a small scale production facility at large production volumes. Next, an evaluation of three potential markets was conducted. The anti-counterfeit market is most promising because of large profit margins and the opportunity for future company growth through R&D of new anti-counterfeit measures. The other two markets in color cosmetics and food preservation present potential opportunities for licensing.

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Title: Head of DMSE, Morris Cohen Professor of Materials Science and Engineering

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I. Introduction

The self-assembly of block copolymers is a phenomenon that has potential for use in a variety of commercial applications, ranging from state of the art lithography techniques[1] to thermoplastic elastomers used in footwear, medical devices, and adhesives[2]. Taking advantage of the self assembly process in block copolymers, the Thomas Lab developed a novel colorimetric sensor that responds to environmental stimuli. The purpose of this thesis is to investigate the commercial applications of this technology. First, a survey of block copolymers and photonics will be provided. Next a description of the technology and its main features will be described. An analysis of the manufacturing process for block copolymers will subsequently be used to develop a cost model for the polymerization process. Finally, three commercial markets where the technology can potentially be applied will be explored.

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II. Principles of Block Copolymers

II.A Self Assembly of Block Copolymers

Block copolymers (BCPs) are used in a wide range of commercial applications. These applications include foams, adhesives, surfactants, and elastomers. Collectively, BCPs belong to as a class of materials known as soft materials. Soft materials have molecular constituents that self-assemble on an intermediate length scale, or mesoscale. This characteristic length scale is important because it ultimately dictates the macroscopic properties of the material. The mesoscopic structure of BCPs can be tailored by using different chemistries, molecular weights, and chain lengths to achieve specific properties. For instance, it may be desired to engineer mechanical toughness, to modify surface properties, or to develop a particular material with high temperature resilience and low temperature flexibility. By controlling the chemical identity and the number of blocks, a variety of unique features can be achieved.

Chemically, BCPs are materials made from two or more distinct polymer blocks that are joined by a covalent bond. They are classified by the number of chemically distinct blocks and the type of connection: linear or branched. The simplest BCP is a linear diblock copolymer, AB, composed of a chain of type A monomers covalently bonded to a chain of type B monomers. More complex blocks such as ABA triblocks and $(AB)_n$ multiblocks can be made by covalently attaching additional blocks. Use of three different monomers can be used to make ABC triblock terpolymers. Differences in the sequence, such as ABC compared to ACB, can result in large differences in properties. Linear attachment results in segmented linear chains whereas side chain attachment can lead to star and branched geometries (Figure II.1).

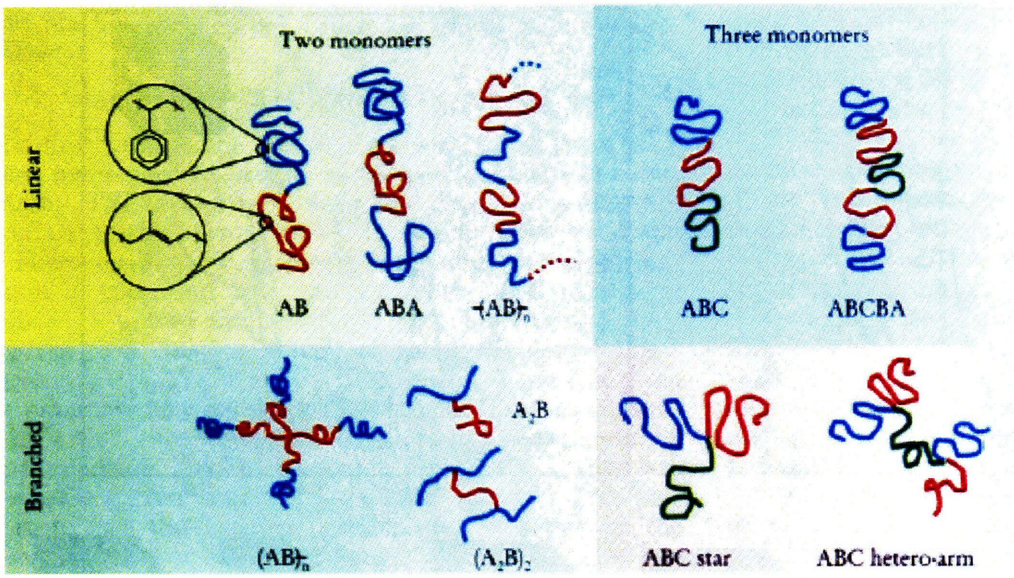

Figure II.1 Geometry of different types of polymers: linear and branched polymers, diblock and triblock[1].

The focus of this thesis is on diblock copolymers, the most studied type of BCPs. Their behavior is governed by the thermodynamic incompatibility of the two blocks, which gives rise to complex structures in a drive to lower the free energy of the polymeric system[3]. Though the blocks would like to completely phase separate, the length scale of the separation is limited by the covalent bond between the two blocks. The structures that are formed minimize the interaction between the immiscible blocks. There are three main factors that determine the spatial features of the resulting structure[4]:

1. N – degree of polymerization, which is proportional to molecular weight.
2. Composition, f_A – the volume fraction of the A block, which also determines the

volume fraction of the B block, f_B.

3. Flory-Huggins interaction parameter, χ – a non-ideal enthalpic interaction term between the A and B blocks. The parameter has the temperature dependence $\chi \approx \frac{\alpha}{T} + \beta$, where α and β are constants for a given value of f_A and T is the absolute temperature.

The phase diagram and resulting structures as a result of increasing f_A are shown below[3].

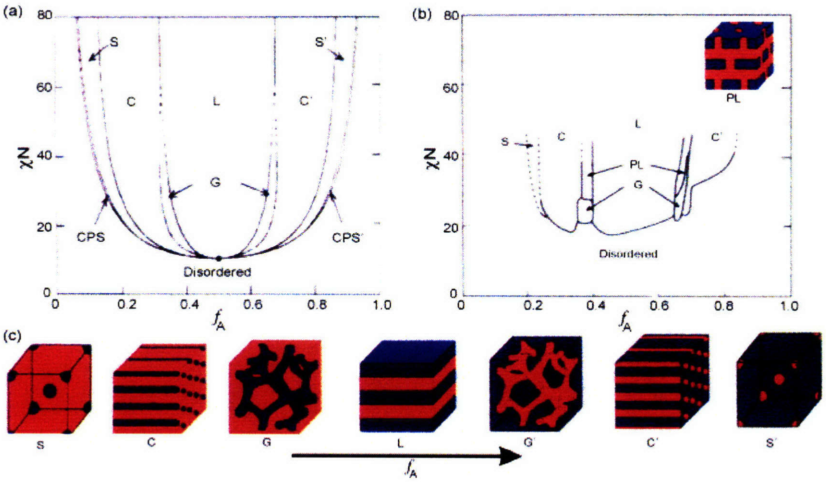

Figure II.2 Phase diagram of a diblock BCP as a function of the volume fraction of A[3].

The structures range from close packed spheres (f_A:f_B ~ 80:20), to cylindrical rods (~70:30) and lamellae (50:50). At sufficiently high f_A, they form the inverse structure. Though other more complex features i.e. double gyroid can be formed, the most interesting for lithography applications are the regular ordered structures previously mentioned.

It is possible to control the microstructure and hence macroscopic properties of the BCP by changing the molecular properties of the polymer. The entropic component of phase behavior is determined by N and f_A, while the enthalpic component is determined by χ.

When N is large, there is an energy advantage to losing configurational entropy by local ordering to reduce the contact between the A and B blocks and phase separation occurs[4]. Similarly when χ is large, there is a large incompatibility between the two blocks and phase separation is favored. Lowering the temperature has the same effect as increasing χ.

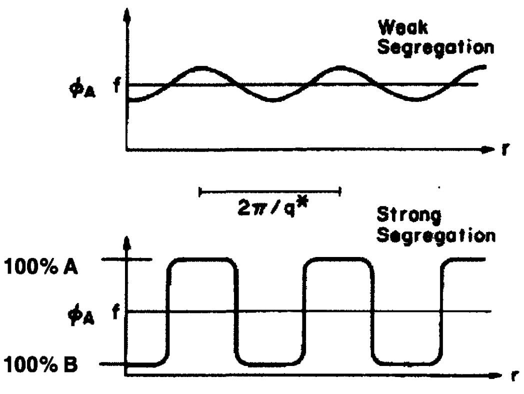

Figure II.3 Comparison of the 1D compositional profiles for the weak (WSL) and strong (SSL) segregation limits[4].

The conditions for ordering are described by an order-to-disorder transition (ODT) that is dependent on N, χ, and temperature and can be quantified by the term χN. For example, for $f_A = 0.5$, the melt is disordered and homogeneous when $\chi N << 1$, and the spatial distribution of the polymer chain follows a Gaussian random walk distribution because of weak A-B interactions[4]. As χN increases to 10.5, the polymer blocks become weakly separated and form a sinusoidal composition profile, a regime referred to as the weak segregation limit (WSL)[4]. In the WSL, the composition profile varies sinusoidally about an average composition, with the feature size given by $D \propto N^{1/2}$. In contrast, upon further increase of χ^N >> 10.5, another state of ordering known as the strong segregation limit (SSL) is reached. The composition profile in the SSL is distinct from the WSL. A sharp interface with an interface of width $w \propto \chi^{-1/2}$ separates the A and B block components of the copolymer. Figure II.3 shows the difference in the composition profile for the weak and strong segregation limit as a function of distance. The feature size in the SSL is given by $D \propto \chi^{1/6} N^{2/3}$. The focus of this thesis will be on properties of block copolymers in the strong segregation limit, where rich well-ordered phase behavior is exhibited.

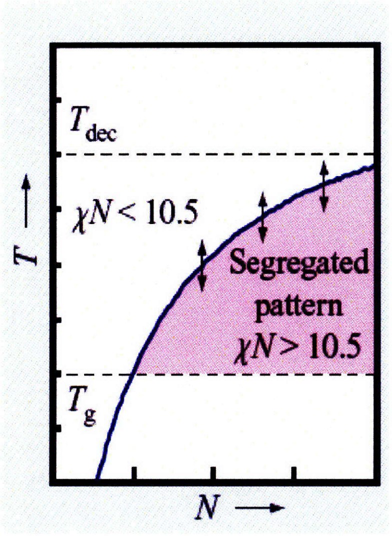

Figure II.4 Phase diagram for forming a segregated pattern in BCP films[7].

In order for ordering to occur, χN must be greater than 10.5. Figure II.4 graphically describes the conditions for ordering based on temperature and molecular weight. The temperature must be above the glass transition temperature (T_g) of the BCP to allow sufficient mobility for reorganization. However, above the decomposition temperature (T_{dec}), the polymer will degrade. Therefore, the stability of the segregated pattern decreases with increasing temperature and a minimum N must be met for self assembly to occur.

As the arrows, indicate, the boundary between order and disorder is not a hard limit, but a general indicator of when the BCP is weakly segregating or strongly segregating. For instance, it is possible for ordering to occur above the bulk order-disorder temperature (T_{ODT}) by modifying the surface energy of the substrate to cause preferential adsorption of one block and subsequent patterning of the thin film BCPs[7].

II.B Thin Film BCP Morphology

Morphologies of bulk BCPs are dictated by free energy reduction associated with phase separation. In bulk, BCPs form regions of ordered domains that are randomly oriented, much like a grain structure. In thin films, there are additional constraints imposed by the surface energy of the interfaces of the film and the relationship between the period of the blocks L_0 and the film thickness t.

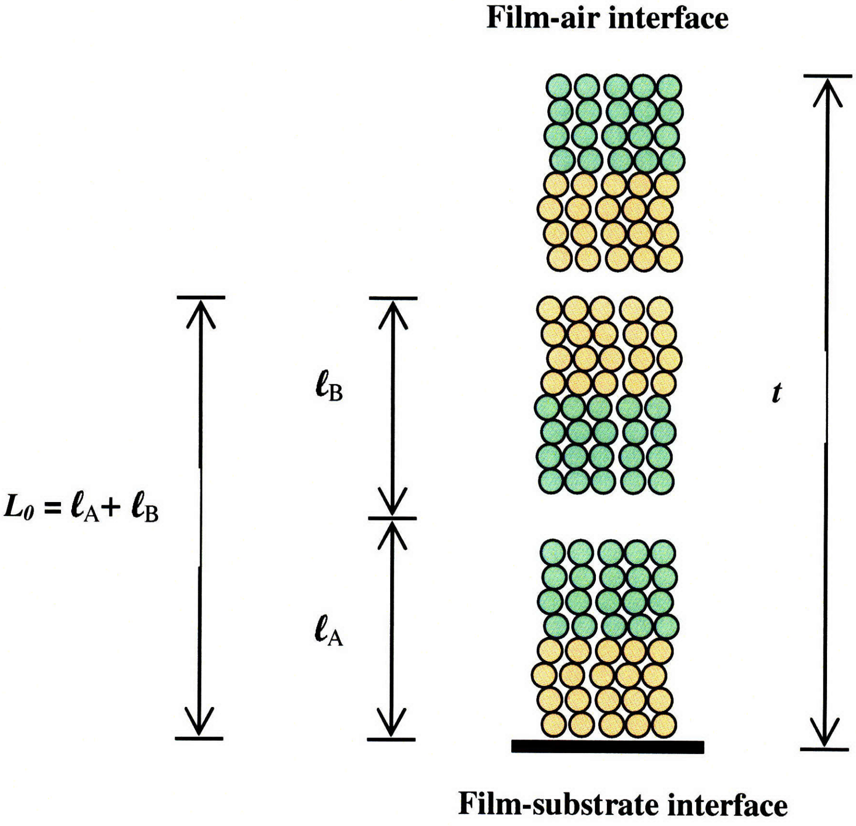

Figure II.5 Schematic representation of a diblock copolymer film, where ℓ_A is the thickness of the A block, ℓ_B is the thickness of the B block, and L_0 is $\ell_A + \ell_B$. The thickness of the entire film is t.

Surface energy minimization affects the orientation of the lamellar structure and the polymer block present at the surfaces that bound the film. Lamellar BCPs can be oriented in one of two ways: parallel to the substrate or perpendicular to the substrate. When $t > L_0$ the film typically adopts a parallel orientation. Symmetric wetting occurs when the same polymer block is present at both bounding interfaces and anti-symmetric wetting occurs when two different blocks are present at the bounding interfaces. The block at the surfaces exhibits a preferential wetting for that particular surface. Symmetric wetting indicates that surface wetting conditions are the same at both boundaries, for instance in a free standing film or a film between the same two substrates. At equilibrium, the relationship between film thickness and period is given by $t = nL_0$ for symmetric wetting and $t = (n + 1/2)\ L_0$ for antisymmetric wetting, where $n = 1, 2, 3, 4$[9].

The perpendicular orientation is observed when the energetics of forming parallel lamellae are too costly. It occurs when film thickness and lamellar period are incommensurate ($t \neq nL_0$) or as film thickness decreases $t < L_0$ [8]. Moreover, if both bounding surfaces are energetically neutral, the perpendicular orientation is also stable at equilibrium. Thus, it is possible to control the surface properties and orientation of the BCP film by changing film thickness and wetting conditions.

II.C Preparation Method of BCP Films

Typical preparation of a block copolymer film involves three major steps. First some surface preparation, such as coating with a random A-B copolymer to render the surface energetically neutral, may be used to orient the resulting film structure.

Next, the polymer film is deposited on a substrate. Uniformly thick films over large areas with low surface roughness are often desired. The most common method for film deposition is spin-coating. The block copolymer is dissolved in a solvent that is a mutually solvent for both blocks to form a low weight percent polymer solution. Then the solution is deposited on a spinning substrate via spin coating. Factors that control the film thickness and uniformity are: 1) spin speed, 2) concentration of the block copolymer solution, and 3) solvent volatility. Studies of spin cast block copolymers indicate that faster spin speeds reduce film roughness while increased solvent volatility results in increased roughness[10]. The observed relationship is due to competition between film leveling and solvent evaporation. A fast evaporation rate results in flow instabilities that are frozen in before film leveling can occur[10].

Finally, annealing at elevated temperatures causes spontaneous ordering of the structures. Typical temperatures for vacuum annealing in the polystyrene-*b*-poly (methyl methacrylate) (PS-*b*-PMMA) system are between 140-200°C[8], above the glass transition temperature ($T_g \approx 105°C$) for both polymers. Solvent annealing may be used to lower the T_g of both blocks to enable enhanced chain movement so that annealing can occur at lower temperatures.

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III. Polymer Photonics

III.A The Photonic Band Gap

Photonic crystals are dielectric materials with periodic structures on the length scale of light which affects the propagation of photons. Much like the periodic potential in a crystal lattice, the dielectric periodicity affects light propagation and can result in the formation of a photonic band gap or a specific range of frequencies where light cannot propagate. The first photonic crystal was proposed by Yablonovich[1] in 1987. Since then, research into photonics has lead to the use of photonics to control light in three dimensions and in spectral regions ranging from ultraviolet to microwave wavelengths[2]. Photonic crystals have been used to block the propagation of light, to localize photons, and to serve as a lossless waveguide along a specific path. In particular it has been shown that photonic crystals can guide light through 90° turns over a distance comparable to the wavelength of the light, thus greatly miniaturizing optical components[3].

Photonic band gaps can be one-, two-, or three dimensional in nature. Figure III.1 shows conceptualized examples of photonic structures that have periodicity in one, two, and three dimensions[4].

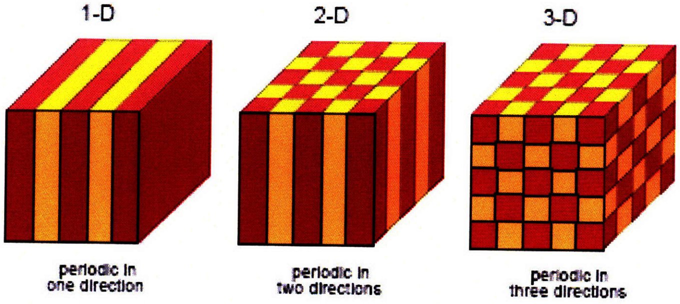


Figure III.1 Schematic representation of photonic structures which exhibit one, two, and three dimensional periodicity[4].

One- and two-dimensional band gaps are relatively easy to fabricate. For example, one-dimensional photonic band gaps are made by sequentially depositing different dielectric materials to form a structure of alternating dielectric materials. Two-dimensional band gaps materials are made through common techniques in microfabrication such lithography and etching. These 1 and 2D materials have been used for many optical devices such as filters, mirrors, and gratings[3]. 3D structures are more challenging, though they have been produced by a layer-by-layer sequential stacking approach of 1D rods[5]. Recent research has shown that they can be fabricated on the large scale using colloidal crystal templating[6] and through 3D interference lithography[7].

A complete photonic band gap is one in which light of all polarizations is prevented from propagation in any direction. It is difficult to achieve due to restrictions on index of refraction contrast and crystal geometry[8]. The factors that affect the completeness of the band gap include lattice structure, lattice symmetry, and the minimum of the refractive index contrast[3]. An incomplete band gap, or stop band, is more often observed photonic crystals. Unlike a complete band gap, a stop band only prevents light propagation of a particular wavelength in certain directions. The wavelength of the band gap depends on index of refraction contrast and periodicity of the crystal.

III. B 1-D Periodic Structures

The simplest photonic band gap structure is a 1-D periodically varying structure or Bragg reflector. Commercially, Bragg reflectors are used in optics for a variety of purposes including in imaging spectroscopy, for wavelength selection, narrow-band filters, and as mirrors[10]. A Bragg reflector is constructed of two or more materials with different refractive indices and a spatial periodicity that causes a difference in the optical path length between layers (Figure III.2). At each boundary of the periodic stack, part of the wave is reflected. When the layers have an optical thickness of one-quarter of the principal wavelength λ, the constructive interference of reflecting waves will result in the maximum reflectivity. This special condition is referred to as a quarter-wave stack where light of λ/4 is completely reflected.

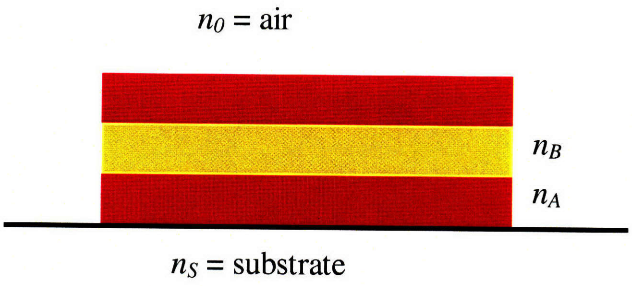


Figure III.2 Representation of a one-dimensional Bragg reflector, where n_A and n_B are the indices of refraction of material A and B, n_S is the index of refraction of the substrate and is n_O the index of refraction of the medium, which in this case is air.

The region where all optical waves are reflected and prevented from propagation inside the material for a 1-D material is referred to as the stop band. For that range of wavelengths, the material exhibits high reflectivity or equivalently, low transmission. The region of high reflectivity can be tuned by either changing the index of refraction or periodicity of the layers. The reflectivity R can be calculated by the following equation[9]:

$$R = \left[\frac{n_0(n_B)^{2L} - n_s(n_A)^{2L}}{n_0(n_B)^{2L} + n_s(n_A)^{2L}}\right]^2$$

The bandwidth Δv_O of the stopband is given by:

$$\Delta \upsilon_0 = \frac{4\Delta \upsilon_0}{\pi} \arcsin(\frac{n_B - n_A}{n_B - n_A}),$$

where n_o and n_s are the refractive indices of the medium and the substrate and n_A and n_B are the refractive indices of the layers. L is the number of layers. To increase the reflectivity, the number of layers or the index of refraction contrast, Δn, can be increased. The bandwidth also increases when the index of refraction increases. Figure III.3 below shows the effect of increasing the number of layers[10]. The center of the stop band remains at 600 nm while the % reflectance increases from 20% to 60%.

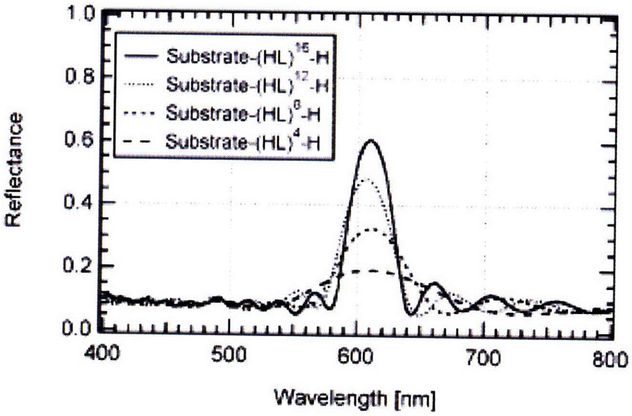
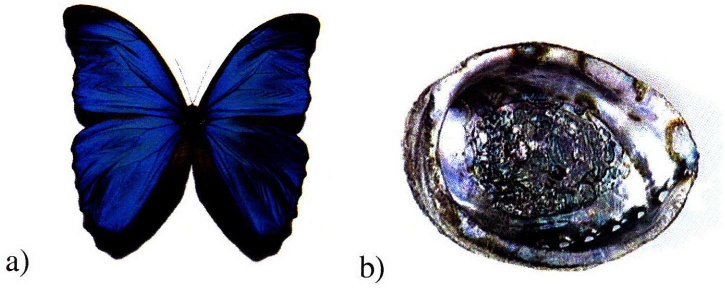


Figure III.3 The increase in reflectance as the number of substrate periods increases from 4, 6, 12, and 16[10].

For 1-D Bragg reflectors, the reflected wavelength also depends on the angle of incidence; that is, the reflected wavelength changes based on the angle of viewing. The band gap shifts due to changes in periodicity experienced by light when at varying angles relative to the normal. In nature, this phenomenon can be observed in butterflies, abalone shells, and soap bubbles.

Figure III.4 Natural iridescence of a) the Morpho butterfly and b) an abalone shell, where surface color changes depending on angle of viewing.


a)
b)

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IV. Block Copolymer Photonic Gels

IV.A Technology Overview

The polymer photonic gel invented by the Thomas Lab is a smart gel technology that allows dynamic control of optical properties. A block copolymer consisting of a hydrophilic block and hydrophobic block self-assembles into an alternating lamellar structure that forms a 1-D photonic crystal with a tunable stop band. By changing the periodicity of the layers or the index of refraction contrast, it is possible to shift the stop band position and therefore the reflected color of the gel. Rather than dyes, the color response is mediated by the structure of the gel, which consists of alternating hydrophobic and hydrophilic layers. The hydrophilic layer is a polyelectrolyte that forms the active layer of the stimulus response, which swells or deswells when exposed to solvents of varying types. The glassy hydrophobic region confines the swelling of the active layer to one dimension so that the active layer is capable of swelling to 1,200% of its original size. Due to the possibility for a large change in thickness of the active layer, the stop band can be shifted over the UV to IR region (λ = 350-1600 nm), which includes the entire visible spectrum (400-700 nm).

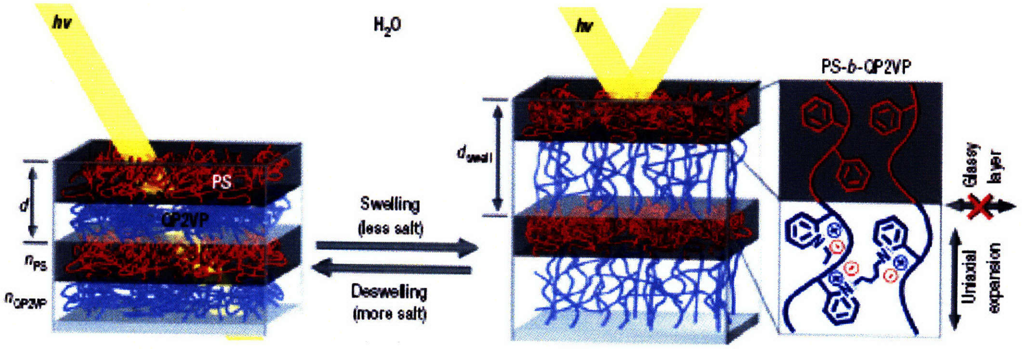

Figure IV.1 Swelling and deswelling of PS-P2VP that responds to changes in environmental stimuli via a color change[5].

The block copolymer used in this research was polystyrene-*b*-poly(2-vinyl pyridine) (PS-P2VP), with PS forming the glassy layer and P2VP forming the active polyelectrolyte layer. Molecular weights of the two blocks are both equal to 190 kg mol^{-1}. Further control of the optical properties is achieved by varying the cross-linking density and quaternization of the P2VP layer. These variables control the maximum amount of swelling that can occur. The gels are made by spin casting the block copolymer solution onto a substrate and annealing at elevated temperature. Thickness of the dry film is between 1-3 μm and can increase up to 18.6 μm when fully swollen. Imaging of the samples reveals the presence of defects, which are advantageous because they enhance solvent penetration into the gel and allow fast response times.

One unique aspect of this technology is its tunability over the entire range of wavelengths in the visible region. The optical properties can be easily controlled by changing the properties of the gel. These include molecular weights of the polymers, degree of cross-linking and quaternization, choice of polymers, and concentration of the spin casting solution. Work that shows its tunability is the example of multicolor patterning of the gels outlined in the Thomas paper[5]. In the experiment, a second layer of the film that has a different degree of quaternization from the first layer is deposited through a mask. Since the maximum level of swelling is controlled by the degree of quaternization, the swelling behavior of the two layers is different when a solvent is added. As a result, a dual colored patterned gel is formed.

The ideal application for this technology in its current state takes advantage of the ease of determining a response to a chemical stimulus. It is suited for applications where a simple qualitative observation rather than a precise quantitative measurement is desired. The gel acts as a simple signal transducer, converting a chemical stimulus into a visible color change. Outputs of the stimulus are easy to observe and require no expensive equipment or a power supply to read. Moreover, the achievable color contrast between two states is high because the entire visible range of colors is accessible. In addition, the gel has a very rapid response to applied stimuli because the solvent can readily diffuse through film defects.

Although there are many advantages to this technology, there are also limitations. The film must be used in a solvent and currently has only been deposited on glass and silicon substrates. Further testing may show compatibility with flexible substrates such as polyethylene terephthalate (PET). It also has relatively weak mechanical properties, especially when fully swollen. In addition, although the material cost is low, the ultimate cost will depend on the ability to find a cost effective manufacturing process for the desired application. Ultimately, the photonic gel will require further optimization for the chosen sensing application.

IV.B Homopolymer Blends

As previously mentioned, the BCP gel is tunable based on external conditions. However, the features may be further tunable by manipulating the types of polymer used, or incorporating other materials in the gel. One particular effect of interest is blending homopolystyrene (hPS) into the gel. The ultimate goal is to modulate the color by changing the spacing of the layers.

Due to polymer thermodynamics, when the hPS is introduced into the system, it will preferentially migrate to the PS block of the diblock copolymer. Previous work on blends has shown that the PS layer thickness increase as hPS concentration increases, but the thickness of the other block layer decreases[1,2,3]. The reason is that when hPs is added, it swells the PS layer both laterally and axially. Since the P2VP is covalently attached, lateral expansion of the PS layer also causes lateral expansion of the P2VP layer. This allows the P2VP brush to adopt a more relaxed Gaussian state that causes axial shrinkage of the P2VP layer.

However, the distribution of hPS within the diblock depends on several factors including the molecular weight and percent added of the homopolymer as well as the solvent used[4,5,6]. As Figure IV.2 indicates, the homopolymer may segregate to the middle of the brush or be completely solubilized within the diblock[4]. As molecular weight of hPS increases, there is more of an entropic penalty to mixing of the polymer chains; therefore it is expected that the hPS will not be completely solubilized throughout the diblock. Further increase in molecular weight may cause complete phase separation of the homopolymer phase and the diblock phase.

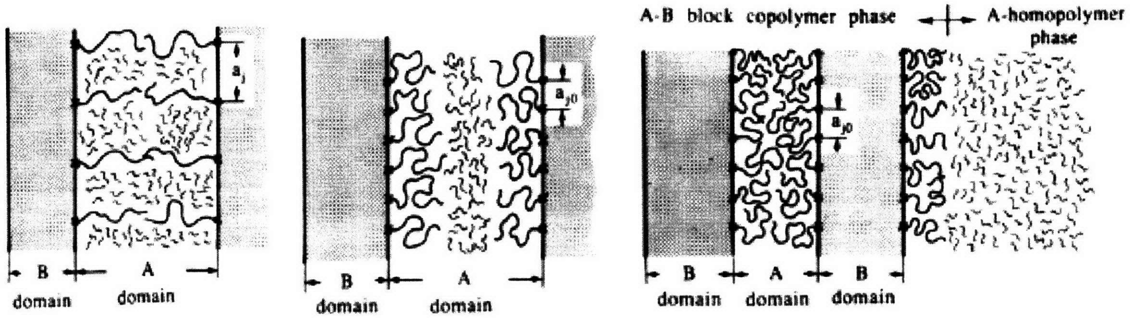

Figure IV.2 Distribution of homopolymer in a diblock copolymer. The homopolymer may be aggregated at the center of one domain or be completely solubilized within the domain[4].

The weight percent of the hPS added also is relevant because it can cause the morphology changes. For small amounts of a particular molecular weight of hPS, the structure will remain lamellar. As the amount of hPS increases, the thermodynamically favorable equilibrium structure will change and the morphology will go from lamellar to cylindrical.

Homopolymer swelling of polymers for photonic structures has been shown in high molecular weight poly(styrene-*b*-isoprene) by Urbas, et al[7]. Although these films are not tunable, the blocks were swelled to change the periodicity of the layers and cause a change in the peak wavelength of reflectivity. Homopolymer of both types were added to cause swelling of both blocks, so that lamellar structure was maintained for high weight percent of the homopolymer. The results show that as the weight percent of homopolymer is increased, the wavelength of peak reflectivity shifts to longer wavelengths.

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V. Commercial Applications

V.A Overview

In order to find a suitable market for the technology, the advantages it offers as well as its limitations must be assessed (Table V.1). The first advantage is the range of colors achievable with a single device. As mentioned in the technology discussion, the gel is tunable from the UV to IR range (λ = 350-1600 nm), a range of 1250nm. Previous technology based on tunable hydrogels are only able to achieve a 200 nm tunable range. Next, the advantage of this system is derived from the fact that it is a polymeric material. The literature on polymeric materials is extensive; hence it is possible to engineer the device to achieve the requirements for the desired applications. These polymers are lightweight, can be conformal on a variety of substrates, and can be fabricated with solution processing. Moreover, the active layers of the films are on the order of a few microns: there are low material requirements and low material costs.

Limitations of the material include the fact that it is limited to a qualitative application. Usefulness of the color change lies in the fact that it is easily observable, rather than providing precise quantitative information. As a result, the technology is suited to consumer level products rather than industrial or scientific measurements where more accurate data is required. In addition, due to the fact that it is a polymeric material, it has limited mechanical and temperature stability. Its use is limited by the order to disorder transition temperature where the self-assembled structure will be disrupted. Given the advantages and limitations of this technology, three applications will be discussed: the cosmetics market, the food preservation market, and the security/anti-counterfeiting market.

Table V.1 Advantages and limitations of tunable BCP gels

Advantages	**Limitations**
High-tunable color change	Qualitative response
Reversible properties	Mechanical stability
Low material costs	Temperature stability
Lightweight	Most types of sensing requires solvent (exception: humidity)
Conformal on substrates	
Solution processing such as casting or spraying	

V.B Manufacturing Cost Model

A critical component of the BCP technology is the type of copolymer used. Therefore a cost model for production of PS-P2VP will be developed. In order to develop an accurate model that reflects the true costs of production, it must be based on the technical processes involved the polymerization method. First a description of the types of polymerizations used will be presented, followed by a process-based cost mode.

V.B.1 Living Polymerizations

A typical polymerization process involves three sequential steps: initiation, propagation, and termination. In living polymerizations, chain termination is prevented: chain growth continues until the monomer is exhausted. A different monomer can be added to the living chain to produce a block copolymer. Use of different coupling schemes results in the creation of star, comb, and other branched architecture copolymers [1]. When the reaction is complete for a linear polymer, termination can be purposefully achieved by treating the polymer with an agent that neutralizes the active end.

There are several conditions that define a living polymerization. The required criteria are[2]:

1. Termination reactions are insignificant compared to the chain growth reaction during the time of the polymerization.
2. It is a step growth reaction where the molecular weight is directly proportional to conversion percent.
3. The number average degree of polymerization DP_n is determined by [M]/[I], the ratio of monomer concentration to initiator concentration.
4. The molecular weight distribution (MWD), as given by the ratio of the weight average degree of polymerization to the number average degree of polymerization X_w/X_n, follows a Poisson distribution: $X_w/X_n = 1+1/X_n$. Therefore at a high degree of polymerization, the polymer becomes monodisperse. This assumes the rate of initiation is fast relative to rate of propagation, so that all chains start growth at the same time.

Since the discovery of living anionic polymerization by Michael Szwarc and collaborators in the 1950s [3], living polymerizations have been used to elucidate understanding of polymer physics and polymer chemistry because it allows precise control of molecular weight, polydispersity, and molecular architecture[4]. In addition to anions, cations and free radicals have been used as active ends of a living chain. Two common methods of synthesizing block copolymers are anionic polymerization and atom transfer radical polymerization (ATRP).

In order to develop a cost model for small-scale production of PS-P2VP, two methods of polymerization were compared using a process based cost model. The goal of the model is to determine which type of polymerization would be most cost effective. Though the monomers for the copolymer are readily available at low cost, the block copolymer is relatively expensive. PolymerSource uses the anionic polymerization method (http://www.polymersource.com/) to synthesize PS-P2VP. It is sold at $300 per gram or $30,000 for 5 kg[5]. Polydispersities of the polymers are between 1.03-1.25. ATRP Solutions (http://www.atrpsolutions.com/) is another company that synthesizes PS-P2VP, but uses ATRP as a polymerization method. It is sold at $6,000 for 250 g or $15,000 for 2 kg and the achievable PDIs are between 1.15-1.3[6]. By determining the per unit cost using a process cost model, the feasibility of investing in a production facility compared to purchasing from an external supplier can be determined.

In order to develop the model, the relevant cost of production must first be identified. Table V.2 identifies the relevant cost elements and separates them into variable and fixed costs. Variable costs are dependent on the volume of production; these costs scale directly with increasing production. For polymer production, these include costs of the monomer, chemicals, and consumable lab supplies. During the polymerization process, raw materials which are not part of the final block copolymer are used as solvents and catalysts. Therefore in order to represent material costs, the percentage of each material required to make 1 kg of final product will used to determine material costs. In addition, labor and energy costs will scale with production.

Table V.2 Variable and Fixed costs in Production

Variable	Fixed
Material & Consumables	Equipment
Labor	Building
Energy	

Fixed costs are capital costs that are required regardless of production volume and are distributed over time. These costs include equipment and building costs. The most important factor in determining the amount of equipment required and contribution to cost is time available for production. For instance the number of production lines required is given by time required to make the target output divided by available time, $\#productionlines = \frac{requiredTimeforDesiredOutput}{availableTimeforDesiredOutput}$. The required time for the target output is directed related to the cycle time of each process while the available time is related to annual hours that are available for production minus anticipated downtime.

The production process for both polymerizations is divided into three steps: purification, polymerization, and precipitation. For each step of the process, fixed and variable cost factors are determined. The final per unit cost depends on the production volume and the production capacity. Production volume is the amount of output actually produced whereas the production capacity indicates the maximum volume capable of being produced. For instance, the greater the production capacity, the more capital equipment is required. Production capacity is usually greater than production volume to allow for future growth, though the closer the two numbers are, the more efficient the production process.

V.B.2. Anionic polymerization

Anionic polymerization is a type of living polymerization most commonly used to produce block copolymers. Commercially, it is used by large polymer manufacturers (Kraton, Dow, Shell) to produce thermoplastic elastomers. Examples include triblock styrenic polymers like styrene-butadiene-styrene or styrene-isoprene-styrene (Kraton). The polymers are used in a wide variety of applications ranging from adhesives to foams, coatings, modifiers, and packaging. Proprietary formulations are engineered to give desired properties in modulus, tensile strength, temperature performance, and visual clarity.

For commercial anionic polymerization of vinyl monomers i.e. polystyrene, initiation occurs with an alkyllithium initiator, such as n-butyl lithium[7]. The reaction occurs in hydrocarbon solutions at room temperature. Common solvents used with n-butyl lithium are hexane, toluene, benzene, and tetrahydrofuran (THF)[8]. Once in solution, the butyl lithium dissociates to form an ion pair. The carbanion on the initator then attacks the electron deficient carbon of the styrene monomer to form a bond, and a new anionic species is formed at the end of the molecule[9].

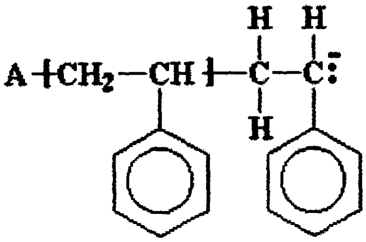
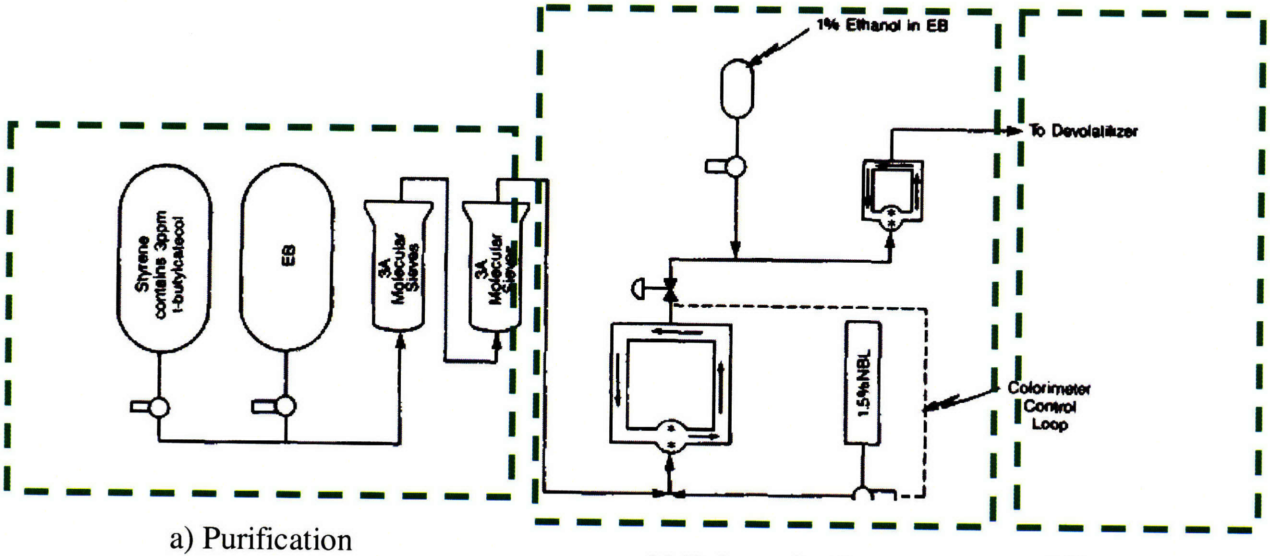


Figure V.1 Anionic chain end of polystyrene.

The propagation step involves sequential addition of monomers to the living end of the chain. There are several factors which influence the kinetics chain growth: type of chain end, polarity of solvent, chain-end concentration, and temperature[9]. An in-depth review is provided by Basakarn and Muller[9]. The living end of a polymer chain can be maintained for extended periods of time, on the order of 10 to 10^6 sec[10], as long as no termination reactions occur. Termination can be deliberately achieved by transferring to water or other solvent, such as methanol, with a proton donating group to neutralize the anion at the living end.

Anionic polymerization offers precise control of the polymerization process so that high molecular weight, low polydispersity, and uniquely structured polymers can be synthesized. However, there are several disadvantages to using anionic polymerization. First, there are limited types of monomers which can be used. Monomers with side groups that react with the initiator or with side groups that react with the anion after initiation will not form a living chain. For example, acrylates have slightly acidic hydrogens that can be transferred to the end of the anion to terminate the chain. Moreover the system will be sensitive to impurities that cause side reactions and thus prevent living polymerization. These impurities include water, oxygen, amine groups, and other types of protic compounds with hydrogen donating groups.

Figure V.2 shows the three step process for anionic polymerization[12]. There are several reactor designs that can be used to conduct the polymerization: batch reactors, continuous stirred tank reactors (CSTR), or plug flow reactors.



a) Purification b) Polymerization c) Precipitation

Figure V.2 Anionic polymerization of PS-P2VP, showing a) purification b) polymerization c) precipitation[12].

Because the polymerization is sensitive to small amounts of impurities, monomer purification is necessary to keep the reaction living. There are several ways to purify the monomers including fractional distillation[11], molecular sieves[12], or reaction with agents to scavenge the impurities. In batch or plug flow reactors, impurities are less significant because they react with the n-butyllithium rather than styrene and hence do not cause termination[10]. The most common and simplest method for monomer purification uses 3Å molecular sieve columns to remove moisture and oxygen[10,13]. Vacuum distillation is further necessary to remove stabilizers for commercially sold styrene[11]. During the polymerization, the living PS block is first synthesized in benzene then transferred to tetryahydrofuran (THF) via vacuum distillation. Copolymerization with P2VP occurs at -78°C. Finally the products are precipitated in heptane.

The steps in the polymerization process indicate the materials and capital equipment required for the polymerization. See Appendix A for full details of data in the cost model. Figure V.3 shows the results of the model on a log-log scale. The cost per kilogram is shown as a function of production volume for three different production capacities. As expected, the unit cost decreases with increasing volume. For anionic polymerization, the product offered from PolymerSource was $6000 per kilogram when in purchased in bulk. In order to make the investment cost effective, the total annual production would have to exceed 15 kg for the 500 kg capacity, 25 kg for the 2,500 kg capacity, and 45 kg for the 5,000 kg capacity.

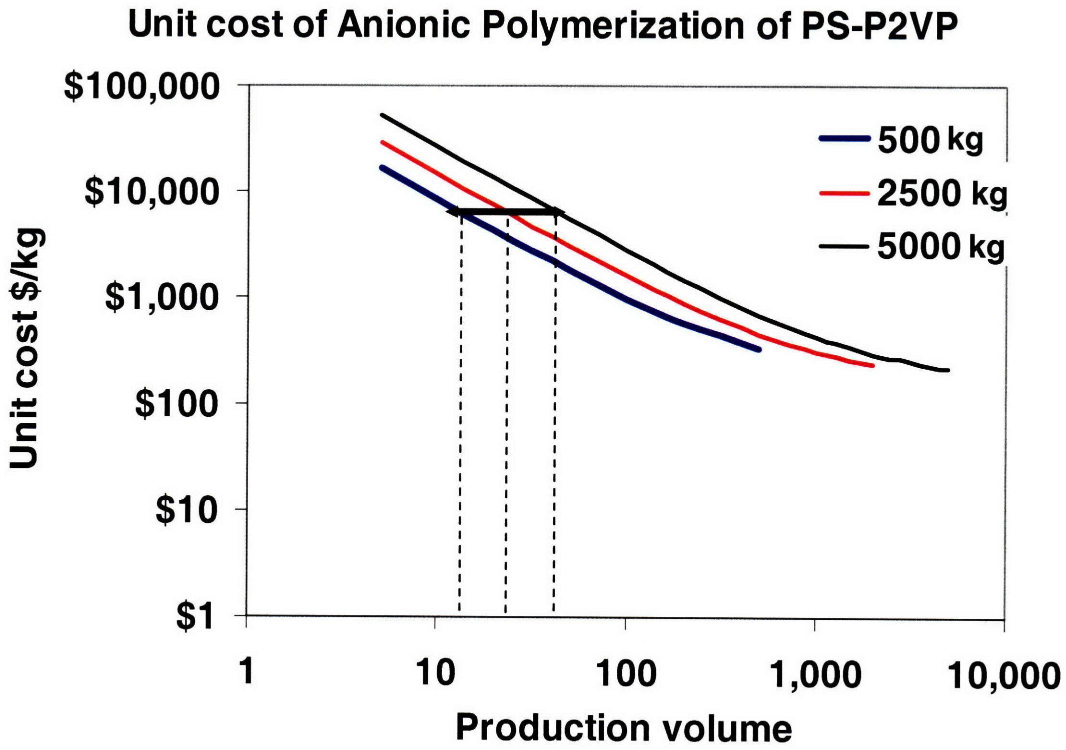


Figure V.3 Unit cost per kg as a function of production volume for three different production capacities using anionic polymerization of PS-P2VP

V.B.3. Atom Transfer Radical Polymerization (ATRP)

Atom transfer radical polymerization is a subset of radical polymerization. Free radical polymerization offers several advantages over anionic and cationic polymerizations:

1. Most types of monomers can be used.
2. Can be produced by a number of polymerization techniques, including emulsion, suspension, and bulk polymerization.
3. It is a more robust polymerization method because it tolerates impurities, and atmospheric conditions better.

However, typical radical polymerization has many limitations because of termination and side reactions that cannot be controlled. It results in polymers with broad molecular weight distribution, ranging from 1.15 to 1.3[6], and it is difficult to produce precise structures. Due to the advantages of free radical polymerization, efforts have been made into developing a living free radical polymerization method. Only in the past two decades has it been successful. ATRP was developed by Matyjaszewski in 1995[14], and uses a reversible reaction to activate and deactivate a dormant chain for polymerization[15]. By decreasing the concentration of active polymer radicals, the possibility of irreversible chain termination is low. Instead there are a large number of living dormant chains. Figure V.4 shows the mechanism for a general ATRP reaction.

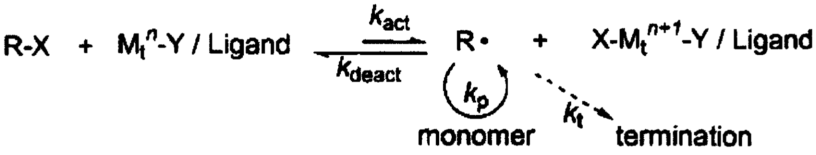


Figure V.4 Reaction mechanism for ATRP

There are several essential components of the reaction:

1. R—X is the alkyl halide initiator (or the dormant species), where R represents the alkyl group and X represents the halide group.
2. M_t^n—Y/Ligand is the transition metal complex which undergoes a redox reaction and abstraction of the halogen atom to activate/deactivate the polymer.
3. There are several reaction rate constants: the activation constant k_{act}, the deactivation constant k_{deact}, the propagation constant k_p, and the termination constant k_t. The equilibrium constant of the reaction is given by $K_{eq} = k_{act}/ k_{deact}$.

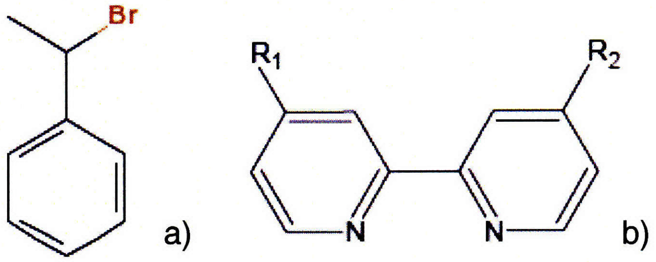


Figure V.5 Typical components used in ATRP of PS-P2VP with a) 1-bromoethylbenze as the initiator and b) 2,2'-Bipyridine as part of the metal ligand catalyst complex

R—X is the initiator/dormant species that contains the growing chain. The transition metal complex catalyzes the activation reaction which produces a radical. The radical will react with the carbon-carbon bond of the monomer to which monomer is added to the chain. There may also be termination reactions due to radical coupling or disproportionation, but these are minimized because X very quickly migrates from the complex to the end of the radical chain. The deactivation reaction is highly favored. This results in a living polymerization system.

The initiators are usually compounds where X is bromine or chlorine. During styrene polymerization, alkyl bromides are used as initiators with Cu^{I} as a metal catalyst and Cu^{II} as the oxidized form of the catalyst. Cu^{II} also acts as the deactivator. The reaction is typically carried out between 110-130°C. Solvents vary depending on the polymerization technique (bulk, emulsion, solvent) and the type of monomer used. Commonly used solvents are benzene, toluene, acetone, dimethyl formamide (DMF), alcohol, and water. The solvent is used to reduce viscosity at high conversion rates.

Figure V.6 shows the results of the cost model for ATRP of PS-P2VP on a log-log scale. Appendix A includes the detailed information about the costs. Compared to the P2VP provided by ATRP Solutions at $7,500 per kg in bulk quantities, it becomes cost effective to invest in a production facility when production exceeds 9 kg for the 500 kg plant capacity, 28 kg for the 2500 kg plant capacity and 55 kg for the 5000 kg plant capacity.

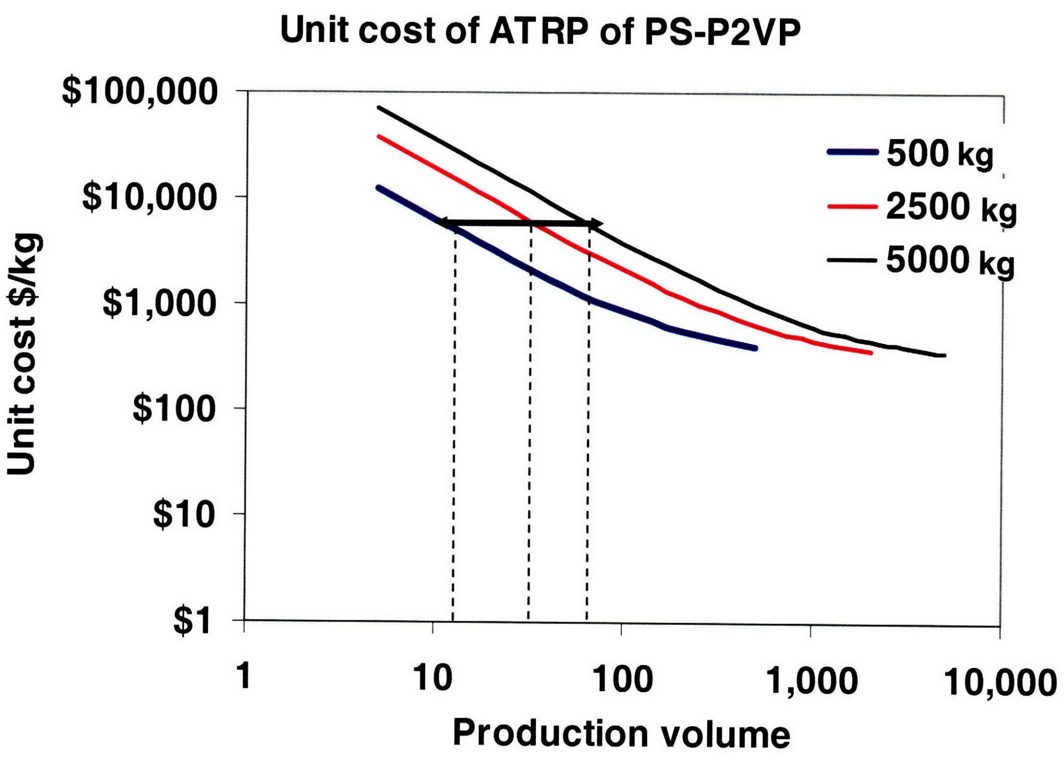


Figure V.6 Unit cost per kg as a function of production volume for three different production capacities using anionic polymerization of PS-P2VP.

V.B.4. Anionic versus ATRP Polymerization

ATRP is an alternative to anionic polymerization that requires less stringent conditions for monomers, and therefore more amenable to manufacturing processes. It tolerates the presence of moisture and oxygen much better. However, anionic polymerization remains the more commonly used living polymerization for commercial polymers. There are several reasons: first, the PDI of polymers produced via anionic polymerization is still lower than that produced through ATRP. Though low PDI ~ 1.15 can be achieved, it becomes more expensive because additional purification steps are necessary in ATRP. Another major obstacle for using ATRP is that the transition metal complex used as a catalyst remains in the product and needs to be removed or recycled. This requires additional extraction and filtration steps, which become costly. However, research is being conducted to find more effective ways to remove the catalyst[15].

Table V.3 compares the two methods of production for PS-P2VP as well as the cost of purchasing from external suppliers, PolymerSource or ATRP Solutions. For very small quantities, on the order of a few grams, purchasing from an external supplier is expensive, but more cost effective than investing in a production facility because of high capital costs. As the quantity increases, the fixed costs are distributed over larger quantities so it becomes more cost effective to invest in a production facility. These results suggest that for small scale production with greater than 10-15 kg annual production of the copolymer, it is efficient to invest in a production facility rather than purchase from an external supplier.

Table V.3 Comparison of various sources of PS-P2VP

BCP Source	1-5 grams ($/kg)	250-500g ($/kg)	1-5 kg ($/kg)	> 5 kg ($/kg)
PolymerSource (anionic)	$200,000-$300,000	N/A	$6,000	N/A
Small scale anionic production	N/A	$165,000	$16,000	$400-$16,000
ATRP Solutions	N/A	$6,000	$6,000	N/A
Small scale ATRP production	N/A	$120,000	$12,000	$400-12,000

V.C Color Cosmetics Market

V.C.1 Technology Requirements

Polymers have been used extensively in cosmetics for a wide variety of applications, including as film formers (i.e. poly(vinyl pyridines)), thickeners (i.e. acrylates), emulsifiers, fixatives, stabilizers, and surfactants. Stimuli responsive polymers, as encapsulated by this technology, might be useful in cosmetics as a blemish concealer. By expanding in volume upon application to the skin, the polymer can fill in defects rather than accentuate them by penetrating into wrinkles. The volume contraction of a polymer may be triggered by evaporation of a volatile solvent or a thermally induced volume transition upon application to the face. This technology is capable of exhibiting both thermal and solvent evaporation color change effects. Another potential use is in new sunscreen technology. Since the films can be tuned to reflect in the UV range, UV filters can be produced using these BCPs.

More generically, the requirements include 1) product durability on the skin, 2) relatively ease of removal with alcohols or surfactants, 3) ability to encapsulate other features such as perfumes, texture, and preservatives, 4) remain stable over the shelf life of the product and 5) have a suitable matrix. The cosmetic needs to remain on the skin for hours at a time under environmental conditions, yet still be removable. Moreover, the skin feel and scent are aesthetics that are also important for consumer use. However, the most challenging technical hurdle for this gel technology is finding a suitable matrix. Due to the structural imparted color of the gel, disruption of the structure will also disrupt the color. In its current state, the most feasible application is as a colorful glitter. By using a non-volatile solvent such as glycerol, the gel can be applied to surfaces for extended periods of time without significant evaporation of the solvent and loss of color. However since the uniformly layered structure is likely to be disrupted, a range of colors rather than a single color will be observed. This is due to the angle dependence of the wavelength of reflected light, a property known as iridescence. For color cosmetics, this may be a desired property that presents a new feature to existing cosmetic technologies.

V.C.2 Regulatory Issues

The cosmetics market is regulated by the Food and Drug Administration (FDA). There are two major regulations that govern the development of new cosmetic products. The first is the 1938 Food, Drugs, and Cosmetics Act (FD&C), and the second is the 1967 Fair Packaging and Labeling Act (FPLA). The regulations indicate that while pre-market approval is not required, manufacturers are responsible for not misbranding or mislabeling their products. Federal prosecution can be pursued for non-compliance to labeling regulations.

V.C.3 Market Dynamics

Supply Chain

The supply chain for the color cosmetics market is described in the figure below[9]. Raw materials such as oils and dyes are purchased by manufacturers who produce cosmetic products. Those products are then shipped to a retail distribution center through a carrier. Finally, the products arrive at a retail store where they are available for consumer purchase.

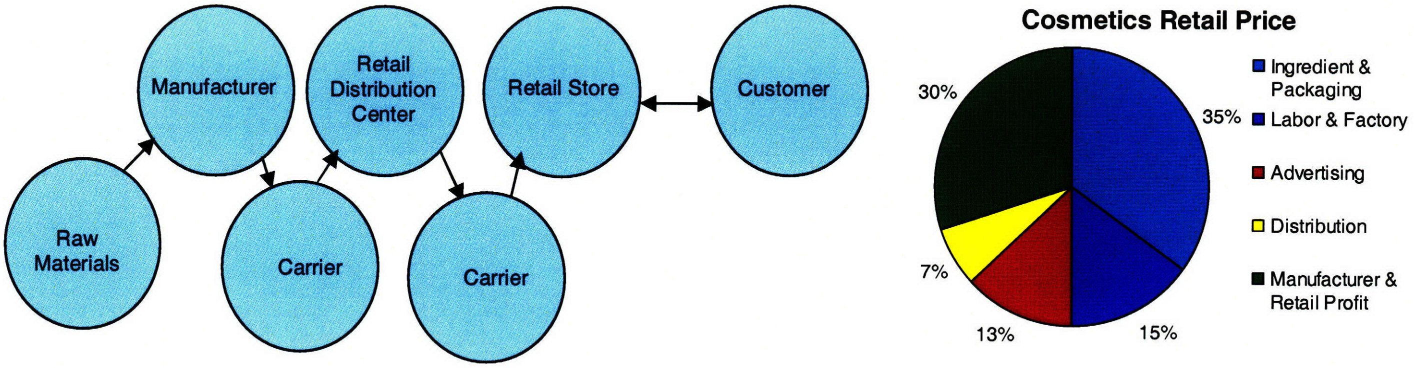


Figure V.7 Supply chain for the color cosmetics market and the factors which are included in the retail price for cosmetic supplies.

In order to determine where in the supply chain to incorporate the technology, the breakdown of the price of a typical cosmetic item is shown in the pie chart[9]. As the figure shows, the margins are highest for the manufacturer. Therefore rather than introducing the photonic gel as a raw material, the technology should be targeted toward cosmetic manufacturers.

Market Drivers

In order to understand the value that the gel technology would bring to the color cosmetics market, the drivers in this market need to be analyzed. First, new cosmetic products typically have short life spans due to changing fashions and the desire for new products by consumers. For cosmetic manufacturers, new products drive sales, and allow them to charge higher margins[9]. As a result, manufacturing companies typically spend 2% of their revenues on R&D in new product development[10]. However, not all product launches are successful. Of the thousands of new product ideas, typically only 15% make it to the market[9]. Consequently, manufacturers are constantly seeking new products. Another aspect of the color cosmetics market is the importance of branding. Manufacturers seek to develop marketing expertise and have high advertising and promotional expenses to achieve brand loyalty.

The benefit that the gel technology offers to manufacturers is that it is a new way to achieve color in cosmetic products. Due to the desire for new product launches, it has potential as a new type of color cosmetic product or novelty makeup item for consumers. Manufacturers would have an interest in developing the technology. However, given the fast turnover of products, it is not a long-term strategy for the technology. Combined with the need for high brand recognition, a new entry company without a familiar name is unlikely to be successful. Therefore another market where a reliable long-term revenue source can be found is desired.

V.D Food Preservation Market

V.D.1 Technology requirements

Sensing the freshness of packaged food can be determined through a temperature responsive volume change that would indicate a certain color when a particular high temperature is reached. Here, an irreversible color change is desired. It is possible to engineer the irreversibility temperature by careful selection of the solvent. For instance, it is possible to engineer the gel so that at a particular temperature, the solvent will phase separate from the gel. This causes the structure to permanently disorder.

Other technological challenges include engineering an activation method. The sensor should not be turned on until the label is on the product. Similar products use UV light to initiate the temperature recording, most likely using the UV light to photopolymerize a thermochromic polymer. In this case, a possible method would be to use a fluid reservoir to encapsulate the lightly sealed solvent next to a dry gel. Physical breaking of the reservoir seal would introduce the solvent into the gel and activate the polymer.

Also the shelf life of the sensor product during use and while in storage need to be established to meet consumer requirements. The gel will be exposed to extreme temperatures, both high and low, and needs to be stable for a given temperature range. It is possible to develop several gels that become irreversible at different temperature regions. Using the temperature ranges would provide a level of quantitation about the temperatures that are reached.

V.D.2 Regulatory Issues

Much like the cosmetics industry, food safety is the responsibility of manufacturers with regulations by the FDA on safety and labeling. The safety and labeling of food products are regulated by the FD&C act and the FPLA. In addition, the FDA works with state regulatory and health agencies and conducts regular safety inspections at food mills and processors [11].

V.D.3. Market Dynamics

Supply Chain

The supply chain for the food industry has several components prior to introduction into the retail supply chain. Raw materials are produced by large scale farmers and ranchers, which are purchased by agriprocessors such as Archer Daniels Midlands and Cargill, Inc. for slaughtering, harvesting, and milling. Both producers and agriprocessors tend to be large, consolidated entities. Packagers include companies such as Kellog, Heinz, and Hershey, which sell finished goods to retailers.

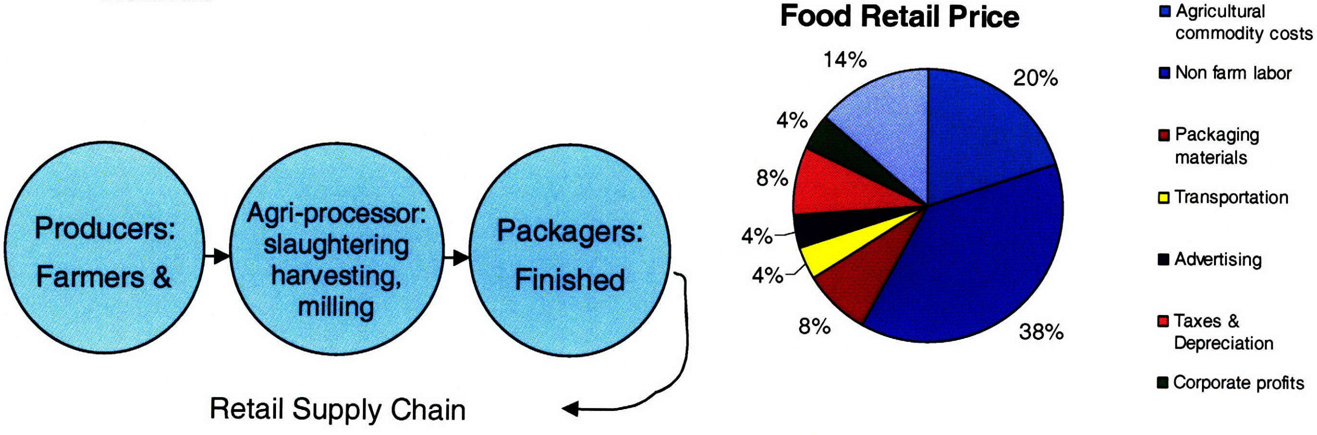


Figure V.8 Supply chain for the food packaging market and the factors which are included in the retail price for a typical food item.

The margins for food packagers at an average of 4% of the retail price are relatively slim[11], with much of the retail price of going toward non-farm labor. During the food supply chain, at each point where goods are transferred, there is an opportunity for monitoring of perishable goods. Given the small margins for packagers, a group which is towards to top of the supply chain, the other players such as the producers and agriprocessors have even smaller margins. Therefore the target customer for this type of gel technology would be the packagers.

Market Drivers

The food and beverage market is a mature market in the U.S. with a well established supply chain. Therefore annual growth is small: retail food sales are expected to grow at approximately 1% per year[11]. As a result, there is limited opportunity for a start-up company to grow. However, food packaging companies are focusing on value-added products such as pre-packaged and pre-cooked foods, where margins are much higher. Moreover, global food safety issues have caused concern for consumers about the safety of the food supply. In recent years, there have been a number of food safety issues, such as contamination of prepackaged spinach in 2006[12].

When a consumer purchases perishable goods on the retail level, there is currently no knowledge of the conditions the food has been exposed to on the supply chain. The gel technology would be introduced on a consumer level as a way of assuring that food has not been exposed to harsh conditions that would make food potentially unsafe. Currently, the only information consumers receive is the sell by date, which is provides no historical information. Although RFID technology would provide the most quantitative history, it is not economically feasible to label food products on an individual package level due to its relatively high costs (Table 5.2). Though a gel sensor would be ideal type of label to provide consumer information, the label must be a consumer demanded product for which they would be willing to pay extra. However, food packagers have a high incentive to keep the food supply safe. The existing supply chain is monitored with digital sensors to alert of spoilage conditions. Given the current lack of demand by consumers, the gel technology is unlikely to be successful in this market.

Table V.2 Comparison of the different types of freshness indicators

	Variable cost	**Type of Information**
Gel Sensor	1-2¢	Historical conditions
Sell by date	Almost 0	Manufacturer's word
RFID	10¢- $1 + significant capital costs	Quantitative historical information

E. Security/Anti-counterfeiting

The security and anti-counterfeiting market encompasses markets where counterfeiters steal intellectual property or trademarks. They produce goods without internalizing the R&D expenses of legitimate companies and hence are able to earn large profit margins from the low cost of replication with goods that are usually inferior in quality. While in some cases, consumers are aware of counterfeits and still purchase them (i.e. luxury goods), in other cases, it is a safety issue (i.e. counterfeit pharmaceuticals). The market of interest for this technology is where knowledge of counterfeit items is valuable for consumers. Therefore, the focus is on counterfeit pharmaceuticals. There is a high incentive for consumers and drug manufacturers to avoid counterfeit transactions.

V.E.1 Technology Requirements

There are two ways to approach the security of pharmaceutical devices. The first approach is to use a proof of authenticity label to ensure that the drugs are from the manufacturer. The second approach is an anti-tampering device that would indicate that the product integrity has not been compromised. The focus of this technology will be on authenticity labels because anti-tampering devices are already commonly used. Anti-tampering devices include blister packs and foil seals.

In order for the authenticity label to be valid, it must be hard to reverse engineer. There are several variables that can be changed to make it difficult for counterfeiters to fabricate. These include color pattern fabrication by varying the cross-link density, changing the index of refraction by changing the solvent, as well as changing the index of refraction contrast by changing the blocks of the diblock copolymer. In addition, the pattern should dynamically change color due to pressure and temperature. For example, by having the consumer press on the label, he or she should see the appropriate color change response.

V.E.2 Market Dynamics

Supply Chain

The supply chain for pharmaceuticals is a complex network of entities before drugs reach the consumer. The figure below shows the major players[12]. The solid arrows indicate where goods are transferred in the supply chain, and the dashed arrows indicate where information is transferred. Counterfeits enter the supply chain through the secondary distribution channel. They consist of small wholesalers and distributors who stock up on excess products from drug manufacturers when manufacturers try to unload inventory. Generally, the secondary distribution channel serves to fill unexpected shortages in supply and can increase the efficiency of the supply chain. However, it is also the channel by which counterfeit drugs can enter the market. By purchasing drugs only with the manufacturer's authentic label, secondary distributors as well as consumers can be assured of authentic products.

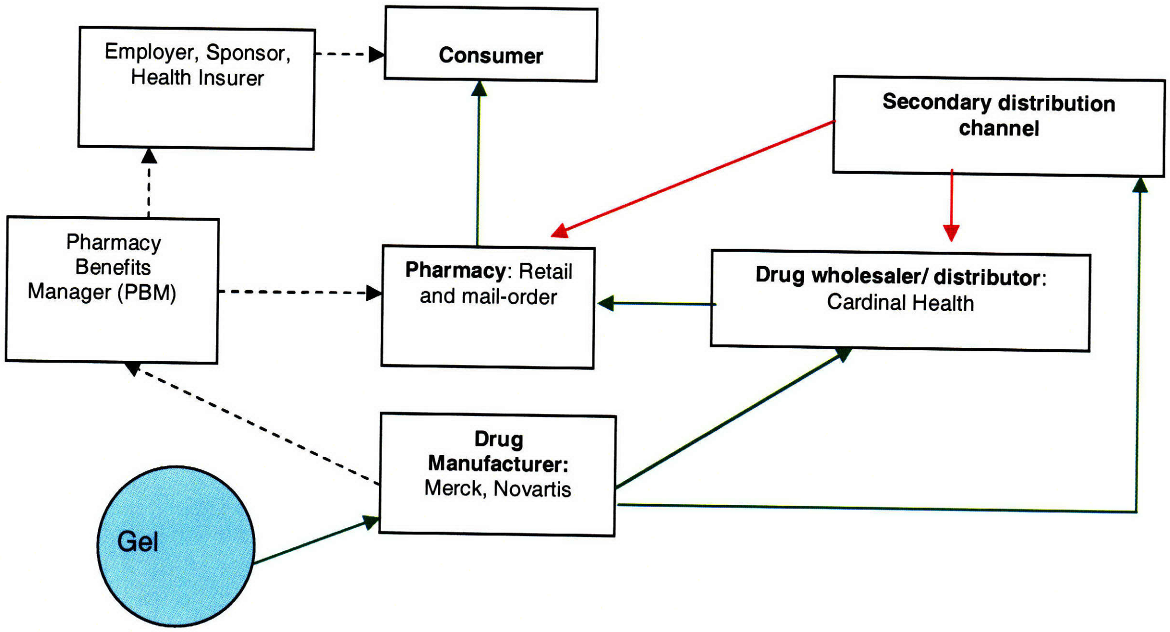


Figure V.8 Supply chain for the pharmaceutical market.

The total US market for pharmaceutical drugs is currently $285B[13]. The industry is highly regulated by the FDA, with pre-market approval required for drugs and medical devices. In developed countries, because of the high degree of regulation, no more than 1% of drugs are counterfeit[13]. However, for online sales, regulation is much more difficult and up to 50% of drugs can be counterfeit. In undeveloped countries, the percentage of counterfeit drugs ranges from 10% to as high as 70%[15]. Even with the small percentage of counterfeit drugs in the U. S., there is still a high incentive to prevent counterfeits and minimize the number of occurrences.

There are 3 categories of competition for the gel technology in the securities market. The first are inks, pigments, and holograms that are used on existing packages to ensure authenticity. Much like the gel technology, there are relatively low fixed costs because fabrication methods like ink-jet printing are inexpensive. Due to the small amount of material required, variable costs are also low. However, given the low costs of production, it is possible to reverse engineer these materials. By keeping manufacturing methods confidential, counterfeiters can be hindered in their efforts. RFID and barcodes are other types of technology used to determine the authenticity of products. However, they are for the benefit of the manufacturer rather than the consumer. Moreover, implementation of RFID requires a significant capital investment and costs more on an individual package level. Barcodes are the least expensive and most easily reverse engineered product.

Table V.3

	Major benefit	**Fixed costs**	**Variable costs**	**Reliability**
Gel label	Covert/easy to observe	Low	Would like it to be ~1¢	Reverse engineering possible
Inks/pigments/ holograms	Easy to observe	Low	Varies, low	Reverse engineering possible
RFID	Quantitative data collection	High ~ 9 M	10-50¢	Reverse engineering possible
Barcode	Used in existing infrastructure	Low – existing infrastructure already exists	< 1¢	Easily reverse engineered

The gel technology represents a new way for consumers to receive information about the authenticity of the product from the manufacturer. Ideally, the gel tag would be available on a per package basis. Though this may not be feasible for all products, it will be especially worthwhile for high value products. The high value products are more costly to produce or are vital medications for consumers. This industry provides an opportunity for a long term business model because counterfeiters will try to replicate the new design. Therefore there must be continuously evolving products to serve pharmaceutical manufacturers.

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VI. Conclusions

The polymer photonic gel developed by the Thomas group is a highly adaptable technology based on self assembly of block copolymers. Its strengths lie in its simplicity and tunability. Although the technology has been highly successful on a proof of concept level in the laboratory, additional product development is needed to bring the idea to market. There are many design features that can be optimized including: the primary wavelength of interest, primary stimulus of interest, temperature of operation, reversibility of reaction, and the speed of reaction. There is a wide body of knowledge that would make it relatively easy to adjust parameters by changing the type of polymers used, the molecular weight of the polymers, and types of additives used to enhance the properties of the gel.

In this thesis, a cost model was developed to compare the cost effectiveness of synthesizing the linear diblock of PS-P2VP. The cost of purchasing from outside vendors compared to developing a small scale production facility showed that the optimal method depends on the volume of PS-P2VP produced. It only becomes more cost effective to launch a production facility for large production volumes because of the high capital costs required to setup the facility. Comparing anionic polymerization versus ATRP revealed that there was not a large difference in unit cost between the two methods. Given that anionic polymerization gives more precise control of molecular weight and structure, it is the preferable method of polymerization.

Finally, three markets where a color photonic gel could have potential applications were examined. Out of the three, the anti-counterfeit market is most promising for a business venture. The main reason is that there are high margins in securing valuable goods. In particular, the pharmaceutical industry where counterfeit products can be lethal is a promising market for this type of technology. Furthermore, the business model allows the company to continue in R&D for future advancements in anti-counterfeiting technology.

The color cosmetics market is another area in which this technology can be applied. However, given the high turnover rate for new products in the market, the photonic gel technology is unlikely to make a lasting business model. In this case, it may be more effective to license the technology to an existing cosmetic manufacturer. Finally, the food preservation market was also examined. It is a low margin industry; therefore high volume sales are necessary to achieve a profit. This would be difficult given the existing low cost and functional alternatives to using a photonic gel technology.

Appendix A

Anionic Polymerization Cost Model Data

PROCESS DATA			
General Data			
Wages, $/hr	$50.00		
Working days per year	250		
Working hours per day	12		
Unplanned downtime	15%		
Time available per year, s	9,180,000		
Electricity price, $/kWh	$0.15		
Price of building space, $/m^2	$2,000		
Price of building space per year, $/m^2*	$200	*Assume amortization of building asset, 10% of building space	
PROCESS STEPS & DETAILS			
Step	**Purification**	**Polymerization**	**Solvent removal**
Machine	Columns, vacuum distiller	Reactor, monitoring	Devolatizer
Number of machines required	1	8	2
Cycle time, s	600	7,200	1,200
Load/unload time, s	300	30	30
Floorspace per machine, m^2	10	60	30
Total floorspace, m^2	10	480	60
Cost, $	$5,000.00	$50,000.00	$5,000.00
Electricity use, kW	15	30	15
Electricity use per piece, kWh	3.75	60.25	5.13
Labor			
# of workers	1	2	1
Dedication, %	50%	50%	50%
Operating time, hr	0.25	2.01	0.34
Material			
PS	5%		

P2VP	5%		
Benzene	30%		
THF	20%		
Heptane	40%		
Material cost, $/kg	$19.93	N.A.	N.A.
Tooling			
Replacement rate, cycles	10	1,000,000	1,000,000
# toolsets needed	2	1	1
Cost, $/toolset	$100.00	$1,000.00	$1,000.00
Reject rate	2%	2%	2%
Effective production volume	53	52	51
COST CALCULATIONS			
Fixed			
Machine cost	$5,000	$400,000	$10,000
Building cost	$2,000	$96,000	$12,000
Tools	$200	$1,000	$1,000
Total, $	$7,200	$497,000	$23,000
Variable			
Electricity	$0.56	$9.04	$0.77
Wages	$12.50	$100.42	$17.08
Material	$19.93	N.A.	N.A.
Total, $/unit	$32.99	$109.45	$17.85
Total, $	$1,750.70	$5,693.81	$910.46
Total	$8,951	$502,694	$23,910

ATRP Cost Model Data

PROCESS DATA			
Process dimensions			
Wages, $/hr	$50.00		
Working days per year	250		
Working hours per day	12		
Unplanned downtime	15%		

Time available per year, s	9,180,000		
Electricity price, $/kWh	$0.15		
Price of building space, $/m^2	$2,000		
Price of building space per year, $/m^2	$200		
PROCESS STEPS & DETAILS			
Step	**Purification**	**Polymerization**	**Solvent removal/precipitation**
Machine	Solution purification	Reactor, monitoring	Devolatizer
Number of machines required	1	4	1
Cycle time, s	600	14,400	1,200
Load/unload time, s	300	30	30
Floorspace per machine, m^2	10	60	30
Total floorspace, m^2	10	240	30
Cost, $	$2,000.00	$30,000.00	$5,000.00
Electricity use, kW	15	30	15
Electricity use per piece, kWh	3.75	120.25	5.13
Labor			
# of workers	1	2	1
Dedication, %	50%	50%	50%
Operating time, hr	0.25	4.01	0.34
Material			
Polystyrene (PS)	10%		
Poly2vinylpyridine (P2VP)	10%		
1 bromoethylbenzene	1%		
2,2'-Bipyridine bipy	1%		
Tetrahydrofuran (THF)	30%		
Cu-Br or Cl, copper bromide	1%		
Acetic Acid	17%		
Benzene	30%		
Material cost, $/kg	$22.92	N.A.	N.A.
Tooling			
Replacement rate, cycles	10	1,000,000	1,000,000

# toolsets needed	2	1	1
Cost, $/toolset	$100.00	$1,000.00	$1,000.00
Reject rate	2%	2%	2%
Effective production volume	5	5	5
COST CALCULATIONS			
Fixed			
Machine cost	$2,000	$120,000	$5,000
Building cost	$2,000	$48,000	$6,000
Tools	$200	$1,000	$1,000
Total, $	$4,200	$169,000	$12,000
Variable			
Electricity	$0.56	$18.04	$0.77
Wages	$12.50	$200.42	$17.08
Material	$22.92	N.A.	N.A.
Total, $/unit	$35.98	$218.45	$17.85
Total, $	$190.92	$1,136.40	$91.05
Total	$4,391	$170,136	$12,091