Polymeric Thin Films by Chemical Vapor Deposition for the Microelectronics Industry

by
Justin F. Gaynor

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APPROVED:

SB Desu.
Seshu B. Desu, Chair

David F. Cox

David F. Cox

Brian J. Love

James Wightman

James P. Wightman

G L Wilkes

Garth L. Wilkes

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(ABSTRACT)

A new approach to the fabrication of polymeric thin films is presented. This approach, chemical vapor copolymerization (CVcP), has all the advantages of chemical vapor polymerization (CVP), including exceptional purity, highly conformal coatings, continuous films even when very thin, low stress, and low environmental impact. The range of film properties available by CVcP is much greater than by CVP.

A specially modified deposition system was constructed to study deposition kinetics. A model was developed which allowed quantification of the order of initiation of paraxylylene (PX), which is the initiation system for all the work reported here. This model suggests a trimer diradical is the smallest stable diradical species formed by PX at room temperature, confirming thermodynamic predictions.

This system also allows the calculation of reactivity ratios of PX with vinylic comonomers. A model is developed in which reactivity ratios can be determined if the following quantities are known: a) thickness vs. position of the final film; b) partial pressures of each reactive species entering the deposition chamber and c) composition vs. position in the final film. This model was tested yielded reasonable values for reactivity ratios.

A polymeric film extremely low in refractive index (1.38-1.39 in the visible region) is presented. This film is formed by copolymerizing poly(para-chloroxylylene), or PX-C, with perfluorooctyl methacrylate (PFOMA). The refractive index of the homopolymers, by contrast, are in the 1.60-1.68 range. Film growth rates are very low for this new material.

Finally, a new deposition procedure is introduced in which a comonomer with a low vapor pressure is codeposited with PX. The reactor temperature is above the ceiling temperature of PX deposition, but at a temperature where the comonomer can condense. This makes the deposition environment extremely rich in comonomer, yielding films whose final properties are nearly identical to films composed entirely of the comonomer. The procedure is demonstrated using n-phenyl maleimide (NPMI) as a comonomer; films produced had thermal stabilities nearly matching those of poly(NPMI). This procedure has great promise for broadening the use of polymeric thin films in the microelectronics industry, as well as other fields.

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I dedicate this dissertation to Anne Gaynor, wife and scientist, without whom I could not have finished this work.

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Chapter 1

INTRODUCTION

1.1 MOTIVATION

The microelectronics revolution was enabled by the emergence of thin film technology. Various methods have been developed for the deposition of patternable films of metals and ceramics, and are still the subjects of widespread research. These techniques are used to fabricate the conducting, insulating and semiconducting layers required in integrated circuits. The trend in chip manufacture is towards ever increasing numbers of components on a chip. This requires both smaller components and smaller distances between components. It has become clear that SiO_2, the most common insulating material, will not meet design requirements in future chips due to its dielectric constant, which, at about 4.0, is too high[1-4].

Polymers generally have lower dielectric constants than ceramics or metals. Their incorporation into integrated circuits has been limited above all by low thermal stability and inability to form high quality thin films. One approach to this problem is to develop a method by which high temperature stable polymers could be deposited in thin film form. Attempts to grow acceptable polyimide films by *in-situ* imidization of condensation monomers, for example, has attracted a great deal of attention both in academia and industry[5,6]. The research presented here takes the opposite approach:

Starting with a reliable deposition method, a novel refinement is developed to grow a polymeric film with higher thermal stability.

The method undertaken here is chemical vapor polymerization, or CVP. CVP, in turn, is a type of chemical vapor deposition, or CVD. The most important difference between CVP and other polymer processing methods is the size of the molecules: In CVP, the surface is coated with small monomers which convert *in-situ* into macromolecules; other processes begin with solutions or melts of large molecules, which suffer from poor surface mobility. CVP dispenses with solvents, eliminating another limiting factor in conventional processing methods. An additional benefit of solventless processing is reduced environmental impact.

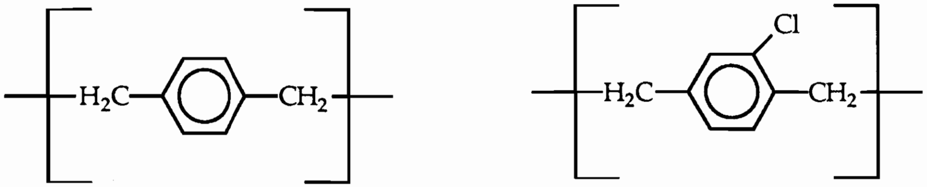
This dissertation is concerned primarily with development of methods suited to the fabrication of polymeric interlayer dielectrics for the microelectronics industry. However, polymers are ubiquitous in modern technology, and polymeric thin films are becoming increasingly important in diverse areas ranging from engine gaskets to biomedical implants. The procedures developed here are general and may ultimately be used for different applications than can be predicted at present. Accordingly, there is little reference here to specific applications; the emphasis is on general processing methods, the details of which can be altered to suit a specific purpose.

1.2 LITERATURE REVIEW

The vacuum polymerization of paraxylylene, or PX, was first reported by Swarc in 1947[7]. The process was made commercially attractive by Gorham in 1966, who found dicyclo-*p*-xylylene could be cleaved efficiently at temperatures as low as 600°C; the higher temperatures used in earlier efforts produced extraneous reactive species, leading to undesired side reactions, crosslinking, and oligomerization[8]. A great deal of effort has been devoted to describing the properties of polyparaxylylene (PPX) films and their substituted analogues, most notably polyparachloroxylylene (PPX-C), polyparadichloroxylyene (PPX-D) and poly(aliphatic tetrafluoroparaxylyene) (PPX-F). The structures of these polymers are shown in figure 1. The synthesis route developed by Gorham is shown in figure 2.

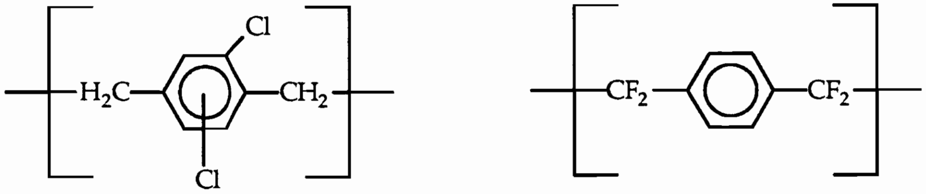
The details of the polymerization chemistry, most notably the initiation pathway, were worked out over several decades[9-19]. Errede and Swarc established a qualitatively correct picture in 1958[20]. More recently, the role played by deposition conditions has been quantified[21-31]. In these papers, the effects of deposition temperature, sublimation rate and partial pressure of inert gases on deposition rate and film morphology were established.

A quantitative model was published by Beach in 1978[32]; to date, no other models have appeared. The approach was to find steady-state solutions to equations in which the amount of monomer entering a volume element equals the amount of reevaporated monomer plus monomer consumed by reaction or removed by convection. It is a one-dimensional model in which



Poly(paraxylylene), PPX

Polypara(chloroxylylene), PPX-C



Poly(paradichloroxylylene), PPX-D

Poly(aliphatic tetrafluoroparaxylylene), PPX-F

Figure 1

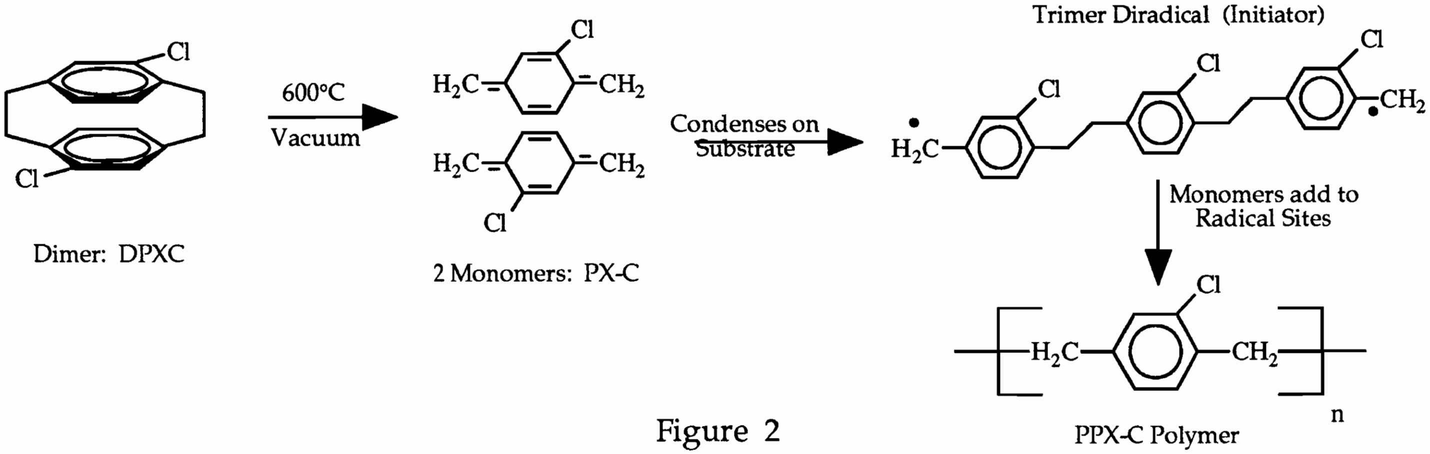


Figure 2

the only spatial dimension is the direction of film growth, perpendicular to the film plane. This model assumes:

i) The concentration of monomer molecules on the surface is related to the partial pressure of the monomer gas by Henry's Law; this, in turn, assumes equilibrium between the gas and surface concentration.

ii) The rate of propagation is high compared to the rate of initiation.

iii) The rate of convection is negligible.

iv) Rates of reaction, diffusion and vaporization follow Arrhenius behavior.

Solving the equations thus obtained leads to the following temperature-independent relations for growth rate and molecular weight:

$$\gamma = \left(\frac{2}{\lambda\rho^3}\right)^{1/4} \left(k_i k_p D^2\right)^{1/4} \left(\frac{\rho}{K_H p_0}\right)^{\left((\lambda+3)/4\right)} p^{\left((\lambda+3)/4\right)}$$

$$\langle M_n \rangle = w(2\rho\lambda)^{1/2} \left(k_p/k_i\right)^{1/2} \left(\frac{K_H p_0}{\rho}\right)^{\left((\lambda-1)/2\right)} p^{-\left((\lambda-1)/2\right)}$$

where γ is the growth rate, λ is the number of molecules required to create the diradical initiator, ρ is the film density, k_i and k_p are the initiation and propagation rate constants, D is the diffusion rate constant of monomer in the film, K_H is the Henry constant, p_0 is the vapor pressure of the monomer, p is the partial pressure of the monomer and w is the monomer molecular weight.

This model is consistent with the limited amount of available data. There has, however, been some discrepancy between growth rates predicted by the model and experimental data[32,33]. Part of Chapter 2 in this dissertation addresses this discrepancy and lends support for the model as originally written.

A great deal of characterization has been performed, most notably to determine crystal structures[34-49], patternability[28,31,50], and electrical[6,33,51-56], thermal[57-60], mechanical[6,53,61,62] and barrier[63-68] properties. The films are highly crystalline as deposited. When deposited at room temperature, crystallization follows polymerization, yielding monoclinic α crystals. When deposited below about -70°C, the monomer first crystallizes into the trigonal β form then polymerizes. The films are easily etched in an oxygen plasma. The high breakdown voltages (200-300 MV/m), low dielectric constants ($\approx$2.65) and low dielectric loss make them attractive capacitor materials. Their thermal stability and mechanical properties are not outstanding. The films are extremely hydrophobic, as is expected of pure hydrocarbons. Optical properties have been studied only sketchily[16,69-71]. A more thorough treatment is provided here.

CVP has been employed or studied commercially in the fabrication of high quality capacitors[6,18,33,55,59,73-76], circuit board coatings[6,18,53,56,75], micromotor electrical insulation[53,76], artifact conservation[53], passivation layers for biomedical implants[28,31,77-81], X-ray transparent windows[82], hermetic packaging for water-sensitive equipment[75], coatings for gaskets in harsh chemical environments[83], ion sensitive field effect transistors[84], in fiberglass composites as "internal casts" for bone fractures[81], UV barrier for X-ray CCDs[82], dry lubricant[76] and particle encapsulation, including schemes for controlling the size of particles codeposited with the polyparaxylylene[76,85,86]. The greatest limitation to further commercial use is the narrow range of properties afforded by polyparaxylylene and its derivatives. The bulk of this dissertation is concerned with expanding the range of properties available by CVP.

There have been relatively few attempts to modify the properties of films grown by CVP. Early workers used a variety of different substituents on both the aromatic and aliphatic carbon atoms[72,87-90]. There have been attempts to change the mechanical and barrier properties by post-deposition thermal annealing, increasing crystallinity[67,89]. Ion implantation has been studied as a method to change the dielectric properties[91]. Finally, alternate synthetic routes to that shown in figure 2 for the formation of PPX have been developed[92-94].

As recently as 1976, Swarc reported that attempts at chemical vapor copolymerization (CVcP) were unlikely to be successful due to the high reactivity of PX[72]. Despite this, Sochilin et. al. demonstrated four copolymers grown at low temperature by CVcP in 1991[95]. This dissertation demonstrates significant changes in composition, and thus ultimate properties, of polymeric films can be achieved by CVcP.

1.3 OBJECTIVES

A great deal of fundamental information about the relationships between process parameters and film growth in CVP is poorly understood. This can be attributed to the difficulty in measuring properties of the growth interface. Any measurement probe introduced into the reaction chamber will be rapidly coated with polymer, either ruining the device or rendering its measurements unacceptable. Before beginning systematic evaluation of deposition procedures, reliable methods for linking process parameters with growth rates and compositions of copolymer films had to be established.

Growth rates and compositions of films taken *ex-situ* are more easily obtained than within the reaction chamber. The approach taken in Chapter 2 and Chapter 5 was to deposit films in a long tube, remove them from the reactor and measure changes in properties, rather than absolute properties, as a function of position in the tube. In addition to reducing the importance of absolute value measurements, this procedure allowed accumulation of a great many data points for each run, eliminating error due to run-to-run irreproducibility. Reasonable models were proposed linking reactive gas pressure and composition to position; comparison of these changes with changes in the final film allowed a great deal of information to be inferred. Though not a specific objective of this dissertation, the experimental design developed here has proven fruitful, and it is hoped other workers will both refine the models presented here and pursue new avenues of investigation using similar methods.

The first specific objective undertaken in this work was to resolve the discrepancy between Beach's thermodynamic prediction and experimental data. Beach predicted the initiated species in PX polymerization was a trimer diradical, as shown in figure 1, and predicted growth rates vs. PX partial pressure based on this prediction. The only experimental data, taken several years before his model was published, did not agree with his predictions. In Chapter 2, his model is extended to two dimensions, allowing a more precise method of measuring growth rate vs. monomer partial pressure. The results presented here agree with thermodynamic predictions.

The second objective was to develop a model for chemical vapor copolymerization which allows the calculation of reactivity ratios. Reactivity ratios are of fundamental practical interest in free radical copolymerization, as they allow copolymer compositions to be accurately predicted. In solution, they can be determined for a given monomer pair by measuring the initial reaction mixture, allowing a small fraction of the monomer to convert to polymer, and measuring the composition of the polymer or remaining reactant mixture. In chemical vapor polymerization, the initial reactant mixture cannot easily be measured, necessitating a different experiment. This work is also described in Chapter 2.

The third objective was to find a comonomer for forming low refractive index copolymers during CVcP. Such polymers might also have low dielectric constants at high frequencies, making them attractive as interlayer dielectrics in the semiconductor industry. This work is described in Chapter 4.

The final objective was to develop a process for growing high temperature stable copolymers. Because of the inherent instability of PPX to hot oxygen, any such compolymer would require an extremely small amount of PX in the copolymer. This presents a challenge, as PX is extremely reactive towards itself, and, by definition, propagation proceeds much faster than initiation. At the same time, any process successful in creating PX-poor copolymers would have potential uses far beyond microelectronics, as the range of available properties would be limited only by the properties of the comonomer chosen. In Chapter 5, a novel approach is presented in which the physical, rather than chemical, nature of the comonomer controls final film composition. This is an important chapter which demonstrates a wide variety of polymers can be grown by chemical vapor polymerization.

1.4 PRESENTATION OF THIS WORK

Like many technical works, this dissertation is presented in the form of journal publications. There is one common idea uniting these chapters, however, which is the process of chemical vapor copolymerization to expand the range of properties available in polymer films deposited by CVD. The ultimate goal of the dissertation is realized in Chapter 5, which demonstrates a method by which a great number of polymers may be grown by chemical vapor deposition. Chapters 2 through 5 are presented as freestanding articles, containing their own abstracts, introductions, procedures, results, discussions, summaries and references. Chapter 2 extends Beach's model to two dimensions and two monomers, allowing determination of the order of initiation and reactivity ratios during copolymerization. Chapter 3 presents a few experimental results from early work in copolymerization. Chapter 4 describes the optical properties of the three commercially available homopolymers and presents a copolymer with much lower refractive index. Chapter 5 introduces a new method of copolymerization with which the concentration of paraxylylene in the film is negligible; this allows films with significantly different properties than polyparaxylylenes to be deposited. Chapter 6 summarizes the dissertation in its entirety. Finally, Chapter 7 discusses useful directions in which this research might proceed in the future.

The chapters presented here are not identical to the papers which have appeared or will appear in the literature. Small corrections, modifications and clarifications have been made as needed. No attempt has been made to remove repetitious material from the various chapters' introductions. There is also one large discrepency between Chapter 2 and Chapter 3. In Chapter 3, Figure 4, a linear composition gradient for films grown in a long tube is claimed. The range of data was only a few centimeters, leading to this erroneous conclusion. In Chapter 2, the composition gradient is clearly not linear. An example of correct composition gradients across a wide range is seen in Figure 8 of Chapter 2.

Greater experimental detail of the reactor and wavelength dispersive analysis are presented in a pair of appendices at the end of the dissertation.

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CHAPTER 2

A Model for Chemical Vapor Copolymerization of Paraxylylenes with Vinylic Comonomers: Order of Initiation and Reactivity Ratios

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Justin F. Gaynor, Seshu B. Desu and J. J. Senkevich

ABSTRACT

A model for chemical vapor homo- and copolymerization is presented in two dimensions, allowing determination of order of initiation in homopolymers and reactivity ratios in copolymers. The model assumes a linear pressure gradient along the flow direction and allows calculation of the order of initiation if thickness vs. position are known, and r_1 and r_2 if the gas flow rates, final film thickness and film composition vs. distance are known. Experiments indicate the number, λ, of paraxylylene molecules required to initiate polymerization: For polyparaxylylene and polyparachloroxylylene, $\lambda = 3$; for polyparadichloroxylylene, $\lambda = 4$. Tentative values for the reactivity ratios of polyparachloroxylylene with perfluorooctyl methacrylate have been determined at different temperatures. At 20°C, $r_1 = 13.04$ and $r_2 \approx 0$; r1 increases with increasing temperature, while r_2 remains vanishingly small.

A Model for Chemical Vapor Copolymerization of Paraxylylenes with Vinylic Comonomers: Order of Initiation and Reactivity Ratios

INTRODUCTION

The chemical vapor polymerization (CVP) of polyparaxylylene (PPX), first reported in 1947[1], was first modeled by Beach[2] and has been thoroughly reviewed[3-6]. Di-cyclo-paraxylylene sublimates under vacuum and passes through a hot pipe where it decomposes into two paraxylylene (PX) molecules. The monomer then flows into a cooler deposition chamber; though still at a pressure below its vapor pressure, it has a finite residence time on the chamber walls. A small fraction are consumed by either initiation or propagation; the remainder reenter the gas. Spontaneous initiation occurs when a small number (λ) of PX molecules convert into a single diradical, as shown in figure 1. Because λ is greater than 1, polymerization in the gas phase is unlikely; the monomer is present in sufficient concentrations for initiation only after adsorption on the chamber walls. After a stable diradical has formed, both PX and vinylic comonomers can add by free radical addition.

Recently, several vinylic monomers, including maleic anhydride, 4-vinyl-biphenyl, 9-vinylanthracene and perfluorooctylmethacrylate, have been found to form copolymers when deposited at room temperature, significantly altering the final properties of the film[7,8]. Copolymers of polyparachloroxylylene (PPX-C) and perfluorooctylmethacrylate (PFOMA), for

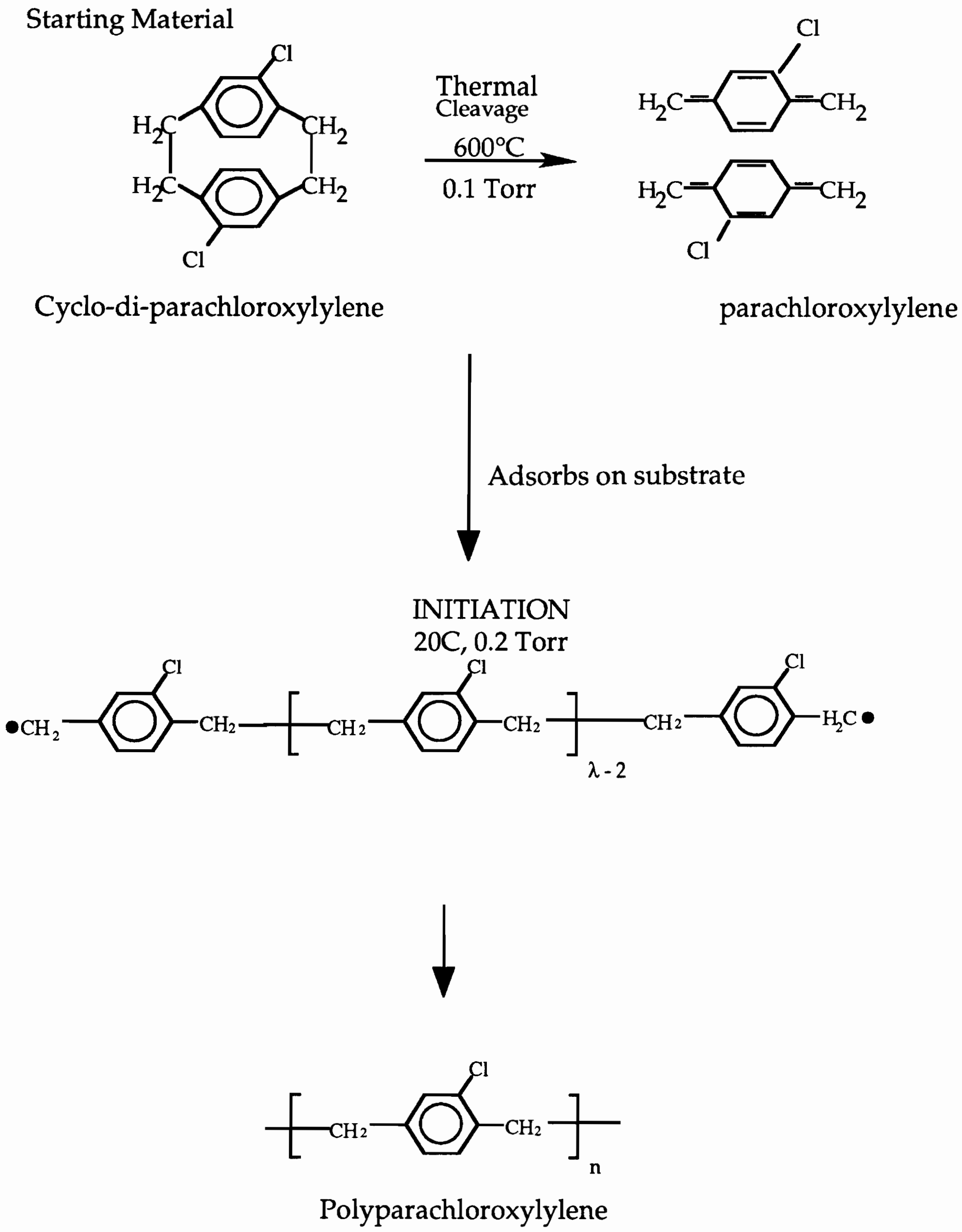

Figure 1. Reaction pathway for initiation and polymerization

example, show lower dielectric constants than PPX-C homopolymers; we have grown copolymers with dielectric constants of 1.92 at optical frequencies, compared to 2.66 for the homopolymer. Other copolymers may show higher thermal stability than PPX-C homopolymers, which degrade above 230°C.

Here, we extend the model proposed by Beach to two dimensions, allowing calculation of reactivity ratios and determination of the order of initiation. Homopolymers of the three commercially available monomers and a copolymer film of PPX-C and PFOMA will be discussed in the experimental section to demonstrate the method.

Order of initiation An unanswered question in the PPX literature is the exact order of the initiation reaction; in other words, the exact number of monomers, λ, required to form a stable aromatic diradical from the aliphatic monomers. Beach derived the following equation[2] relating growth rate to monomer partial pressure:

$$\gamma = \left(\frac{2}{\lambda \rho^3}\right)^{\frac{1}{4}} \left(k_i k_p D^2\right)^{\frac{1}{4}} \left(\frac{\rho}{K_H p_0}\right)^{((\lambda+3)/4)} p^{((\lambda+3)/4)} \qquad (1)$$

where γ is the growth rate, p is the monomer pressure, k_i and k_p are the initiation and propagation rate constants, D is the diffusion rate constant of monomer into the film, p_0 is the monomer vapor pressure, and K_H is the Henry constant. Thermodynamic calculations[3] predict $\lambda = 3$, implying the growth rate increases as $p^{1.5}$. However, a widely cited early paper shows the growth rate increasing as the square of monomer pressure[9]. It is difficult to judge the reliability of these results, though, as neither data points nor error bars were supplied, nor the experimental method described. By considering changes in gas flow direction as well as growth in the radial direction, we are able to suggest a simple method to determine λ. If we define the direction of gas flow as z, then the growth rate will depend on z as follows:

$$Gt = T; \qquad \frac{\partial G}{\partial z} = \frac{\partial G}{\partial P}\frac{\partial P}{\partial z} \qquad (2)$$

where G is the growth rate, T is film thickness, t is time and P is monomer partial pressure. dT/dz is easily measured; we suggest a relation for dP/dz to find the dependence of growth rate on pressure.

Reactivity ratios. The only information required for the determination of reactivity ratios in solution is the feed composition, f, and final composition, F, along with the precision with which they are measured[10]. (Throughout this paper, we use the convention that f and F refer to the mole fraction of PX.) In CVP, it is difficult, if not impossible, to measure the gas composition at the growth interface. Any model to determine CVP reactivity ratios must sidestep this problem. To do this, we recognize a feature unique to CVP: The two monomers will generally be consumed at different rates as they flow through the reaction vessel, generating a steady-state monomer concentration profile in both the gas and the film. For a given composition profile in the gas, there will result a unique composition profile in the film. We show it is sufficient to determine the film composition and thickness as a function of position to determine reactivity ratios. We also note that during CVP, in contrast to solution reactions, the reaction continues indefinitely without drift in feed composition at any given point, making the problem time-independent.

All reactivity ratios show a temperature dependence, as they are simply ratios of reaction rate constants. PX polymerization typically occurs near its "ceiling temperature"; this is not the thermodynamic ceiling temperature[11] but rather an arbitrarily assigned temperature at which growth rates are negligible. Under typical deposition conditions, the growth rate will decrease with increasing temperature because the molecules reside for a shorter time on the surface. The reactivity ratios as calculated by the model presented here contain both residence time and reaction rate components, and may be expected to show a larger temperature dependence than is found in solution work.

THE MODEL

Introduction. The model is presented in cylindrical coordinates to describe deposition in a cylindrical deposition chamber held at constant, uniform temperature. PX molecules (and, during copolymerization, a vinylic comonomer) are forced through the chamber by a pressure gradient and react on the walls. Polymerization starts upon adsorption and proceeds inwards in the negative r direction; the monomer concentrations and growth rate change in the flow direction, z, as monomers are consumed. We assume the comonomer does not affect the initiation reaction, there are no penultimate effects or complex formation, and film growth has no θ dependence.

Order of initiation. There are two sources of pressure gradients in a PX reactor. The first arises from the pressure difference between the monomer sources and the pump. The second arises from the monomer depletion region immediately above the growth surface, leading to radial diffusion. However, for every molecule added to the film, 10^3 - 10^4 adsorbed molecules reenter the gas without reacting[3]. The radial pressure gradient is negligible, therefore, and we ignore its contribution to the pressure profile.

Assumption 1: *The pressure gradient is linear within the deposition pipe.* Within the chamber,

$$P_{(z)} = (z_f - z)(P1\text{-}P2) \qquad (3)$$

where P1 is the pressure at the chamber entrance, P2 is the pressure at the downstream end of the pipe and z_f is the position of the downstream end of the pipe. This assumption allows a simple experiment to determine λ by combining equations (2) and (3): By measuring the thickness of a film vs. position in the reactor, the data should fit a curve of $T = kz^{((\lambda+3)/4)} + k'$, where k and k′ are empirical constants. If $\lambda = 3$, G should decrease as $z^{1.5}$. Experiments to determine λ for each of the three commercially available homopolymers are described in the experimental section.

Reactivity ratios We begin with the following differential form of the Lewis-Mayo equation[12]:

$$F = \frac{(r_1 - 1)f^2 + f}{(r_1 + r_2 - 2)f^2 + 2(1 - r_2)f + r_2} \qquad (3)$$

and its integrated form as written by Meyer and Lowry[13]:

$$x = 1 - \left(\frac{f}{f_0}\right)^{\alpha} \left(\frac{1-f}{1-f_0}\right)^{\beta} \left(\frac{f_0 - \delta}{f - \delta}\right)^{\gamma} \tag{4}$$

$$\alpha = \frac{r_2}{1-r_2}; \qquad \beta = \frac{r_1}{1-r_1}; \qquad \delta = \frac{1-r_2}{2-r_1-r_2}; \qquad \gamma = \frac{1-r_1 r_2}{(1-r_1)(1-r_2)}$$

Solving equation 3 explicitly for f gives a quadratic equation with two real roots. Only the negative root is physically meaningful, however; the positive root yields a negative value of f. The final expression for $X_{(F)}$ is:

$$X_{(F)} = 1 - \left(\frac{\dfrac{(r_1-1)f^2+f}{(r_1+r_2-2)f^2+2(1-r_2)f+r_2}}{f_0} \right)^{\alpha} \bullet$$

$$\bullet \left(\frac{1 - \dfrac{(r_1-1)f^2+f}{(r_1+r_2-2)f^2+2(1-r_2)f+r_2}}{1-f_0} \right)^{\beta} \left(\frac{f_0 - \delta}{\dfrac{(r_1-1)f^2+f}{(r_1+r_2-2)f^2+2(1-r_2)f+r_2} - \delta} \right)^{\gamma} \tag{5}$$

Recognizing that the monomer consumption in CVP is simply the number of monomers incorporated into the film divided by the number of monomers into the chamber, we derive an expression for $X_{(z)}$:

$$X = \frac{\text{monomer in film}}{\text{monomer entering chamber}} = \frac{\frac{VN_A}{V_m}}{(N_{PX} + N_{co})} \qquad (6)$$

where V is the volume of the film, V_m is the molar volume of the film, N_A is Avagadro's number, and N_{PX} and N_{co} represent the number of each monomer entering the chamber in a given period of time.

Assumption 2 *The relative concentration of monomers at the surface is equal to the relative concentration of monomers in the gas.* This approximation was recognized early in theoretical descriptions of low pressure chemical vapor deposition (LPCVD) systems. It is valid if the diffusion rates in the gas phase are very high for each monomer and that the residence time of each monomer on the surface is the same. Gas-phase diffusion in PX chambers are probably higher than other LPCVD systems, as they operate at lower pressures. Differences in residence times are incorporated into the reactivity ratio, as discussed in the introduction.

Assumption 3 *All reactions occur at the surface.* This assumption allows us to ignore the differing rates of diffusion of each species, including monomers and oligomers, into the film. Beach's model suggests reactions occur throughout the top 400nm of the film; however, growth is fastest at the surface and decreases rapidly with distance from the interface.

The volume of the film is given by:

$$V = \pi R^2 \int dz - \pi \int (R - T)^2 dz = 2\pi R \int T dz - \pi \int T^2 dz \qquad (7)$$

We can ignore the final integral; R is typically four or five orders of magnitude higher than T. To let thickness increase with increasing z, we define z = 0 as the downstream end of the chamber, with z increasing upstream to z = L at the chamber entrance. Combining the above two equations and integrating in the direction of gas flow yields:

$$X_{(z)} = \frac{2\pi R N_A}{N_{PX} + N_{co}} \int_z^L \frac{T}{V_m} dz \qquad (8)$$

The success of the model depends on equating $X_{(F)}$ and $X_{(z)}$. The molar volume in the integral above is a function of composition; we cannot solve X explicitly as a function of z. Therefore, we employ an average molar volume, $<V_m>$, which is not a function of position. This restricts the range of the model's validity to monomers with similar molar volumes or to small ranges of composition. Finally, we assume the film thickness varies as $Az^{1.5} + B$ for PPX and PPX-C, and as $Az^{1.75} + B$ for PPX-D; in the experimental section, we demonstrate this is indeed the case for homopolymers. Within the model's range of validity, i.e. where the molar volume of the film can be considered independent of position, this is a reasonable assumption. The final expression from which reactivity ratios are determined is:

$$\left(\frac{\frac{(r_1-1)F^2+F}{(r_1+r_2-2)F^2+2(1-r_2)F+r_2}}{f_0}\right)^{\alpha}\left(\frac{1-\frac{(r_1-1)F^2+F}{(r_1+r_2-2)F^2+2(1-r_2)F+r_2}}{1-f_0}\right)^{\beta}\left(\frac{f_0-\delta}{\frac{(r_1-1)F^2+F}{(r_1+r_2-2)F^2+2(1-r_2)F+r_2}-\delta}\right)^{\gamma}$$

$$=\frac{2\pi RN_A\langle V_m\rangle}{N_{PX}+N_{co}}\left[\left(\frac{AL^{2.5}}{2.5}+BL\right)-\left(\frac{Az^{2.5}}{2.5}+Bz\right)+C\right] \tag{9}$$

The right hand side of this equation will be referred to as $Z_{(z)}$. This equation has interesting consequences. If f = $(1-r_2)/(2-r_1-r_2)$, or if $r_1 = r_2$, the equation becomes meaningless; these values satisfy the azeotropic condition, when we would expect F to become constant in $Z_{(z)}$.

A curve fitting procedure is used to determine the reactivity ratios. C, r_1 and r_2 are varied to fit equation (9) to the experimentally determined values of F and $Z_{(z)}$. All sources of error must be considered during curve fitting to obtain reliable values and confidence intervals. When using equation (3) to determine the reactivity ratios of solutions, for instance, linear least-square fits are invalid[15] because the errors in F and f are approximately equivalent. Computer programs for valid curve-fitting procedures in solution are commercially available; this model requires similar software[16]. As shown in the experimental section, equation (9) properly predicts the shape of F vs. $Z_{(z)}$ data. However, in the absence of a statistically valid curve fitting procedure, our estimates of r_1 and r_2 must be considered tentative at best. More importantly, we are unable to provide intervals of confidence at this time.

EXPERIMENTAL

The reactor. All samples were grown in a cylindrical chamber designed for obtaining a wide range of data. A schematic of the self-built reactor is given in figure 2. The deposition tube was 35cm long and 7.62cm in diameter; temperature uniformity was ensured by wrapping the entire length tightly with 0.25 inch diameter copper tubing connected to the chamber by thermally conductive epoxy. Water pumped through the copper tubing from a constant temperature water circulating bath allowed various deposition temperatures. Thermocouples were attached to the outer wall of each chamber to monitor temperature.

Homopolymers. Cyclo-di-paraxylylene, cyclo-di-parachloroxylylene and cyclo-di-paradichloroxylylene, the three commercially available dimers, were purchased from Specialty Coatings and used to grow homopolymers of PPX, PPX-C and PPX-D. The compounds were used as received but outgassed at 0.28 Torr for two hours before use. The thickness of the films was kept low because our method of measuring thickness, variable angle spectroscopic ellipsometry, is more accurate at lower thicknesses. Each homopolymer was grown on a clean, polished silicon strip, 10cm x 3cm, placed near the downstream end of the reactor. At the downstream end, deposition rates are

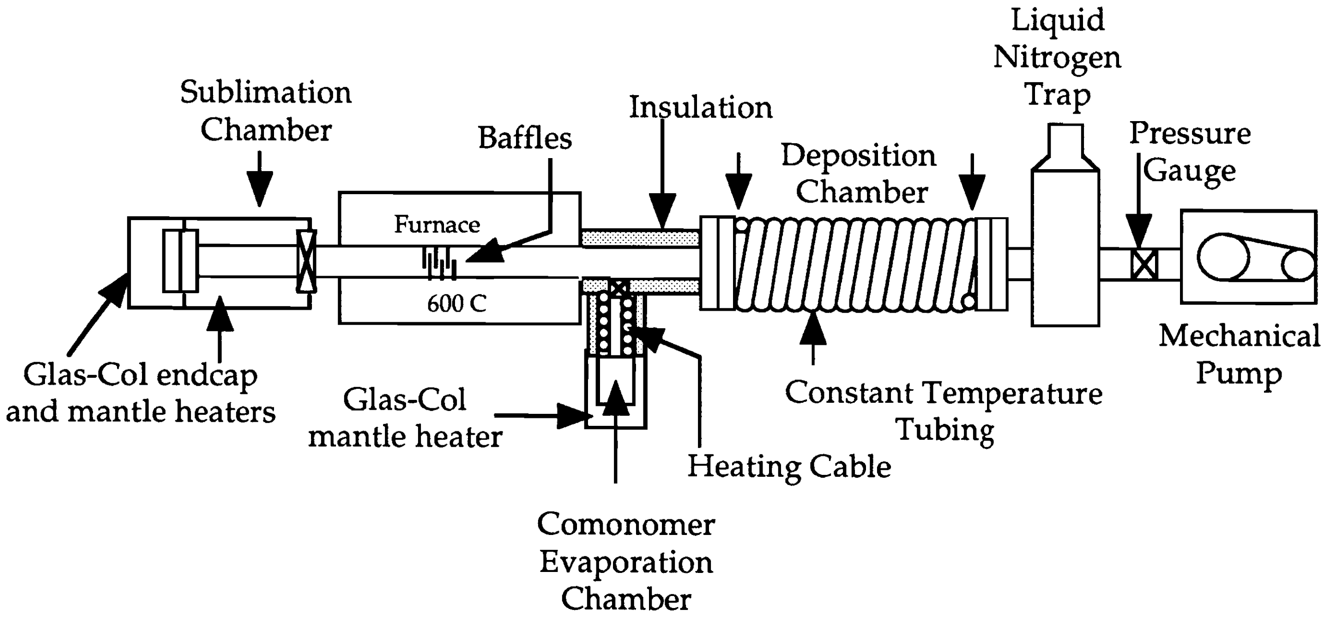

Figure 2. Reaction chamber used for homo- and copolymerization

low and the monomer is completely cooled. The substrates were blown dry with compressed air before use and handled with gloves at all times. The base pressure during each deposition was 0.275 ± 0.005 Torr.

The cyclo-di-paraxylylene sublimation temperature was maintained at 138.5° ± 0.5°C, the thermal cleavage furnace was maintained at 620°C and the temperature between the furnace and the deposition chamber was maintained above 60°C. The temperature of the deposition pipe was 23.2±0.3°C throughout the deposition. The cyclo-di-parachloroxylylene sublimation chamber was maintained at 133.5±0.5° C; the thermal cleavage furnace was maintained at 620°C and the temperature between the furnace and the deposition pipe was maintained above 125°C. The temperature of the deposition chamber was 26.6±0.4°C throughout the deposition. The cyclo-di-paradichloroxylylene sublimation chamber was maintained at 139.5±0.5°C, the thermal cleavage furnace was maintained at 620°C and the temperature between the furnace and the deposition pipe was maintained above 150°C. The temperature of the deposition chamber was 38.6° ± 0.2°C throughout the deposition. Each deposition lasted 60 minutes.

After growth, each film was annealed for twelve to fifteen hours at 106°C and 0.28 Torr; the temperature was returned to room temperature over a period of two hours before returning the sample to atmospheric pressure. Annealing was performed to rid the film of unreacted monomer and other impurities.

Copolymers of PPX-C and PFOMA. The copolymer films were thicker than the homopolymer films to ensure the electron beam used for elemental analysis would not penetrate the sample, causing erroneous readings.

PFOMA (>99%) was purchased from Monomer Polymer. PFOMA and PPX-C were chosen because of the ease with which chlorine and fluorine are resolved in an electron probe and because we predict they form random copolymers. Finally, high growth rates are achieved at relatively high deposition temperatures for PPX-C; high deposition temperature ensured the range of composition would be small. Three runs were performed at deposition temperatures of 20°C, 24°C and 28°C. Three clean silicon substrates, each 10cm x 1cm, were placed end-to-end in the deposition chamber before each run. In each case, the cyclo-di-parachloroxylylene sublimation chamber was maintained at 115°C, the PFOMA sublimation temperature at 54°C and the furnace at 620°C.

For each run, approximately 4 grams of cyclo-di-parachloroxylylene and 3 grams of PFOMA were weighed into ceramic boats, placed in their appropriate chambers and a vacuum immediately pulled. Valves between the sublimation chambers and main reactor were closed after the pressure in the chamber reached its base pressure, which required about one minute. During this minute, we assume the amount of monomer entering the deposition chamber was negligible because the boats require more than one minute to reach thermal equilibrium with the sublimation chamber walls. All temperatures were then allowed to stabilize for twenty minutes before the valves were opened, starting deposition. Deposition times were 60 minutes at 20°C, 75 minutes at 24°C, and 90 minutes at 28°C so that each run would result in similar film thicknesses. The unsublimated cyclo-di-parachloroxylylene and PFOMA were weighed after each deposition to determine the amount of each monomer which entered the chamber. Each sample was annealed as described in the homopolymer section.

Analysis. Absolute elemental compositions were determined by wavelength dispersive analysis with a Cameca SX-50 electron probe. Electrical conductivity was ensured with a 25nm thick sputtered coating of carbon. A 5nA, 8kV beam, about 500nm in diameter, was rastered through an area of 30μmx30μm. Poly(tetrafluoroethylene), poly(chlorotrifluoroethylene), and a PPX-C homopolymer were used as calibration standards. Measurements points were at 1 cm intervals, with three measurements made at each point. The films darkened somewhat during the measurements, each of which lasted 40 seconds.

Film thicknesses and refractive indices were determined with a variable angle spectroscopic ellipsometer, purchased from J. Woollam Company. The use of variable angle spectroscopic ellipsometry for measuring CVP films is discussed in more detail elsewhere[17]. Samples were measured in the wavelength range 500-1000 nm in 2 nm increments and at angles from 65 to 80 degrees in five degree increments from a line normal to the plane of the film. The homopolymers were measured in 0.5cm increments, and the copolymers in 1cm increments. The instrument measures the ellipsometric parameters psi and delta; each point was the average of ten measurements. The measurement spot was about 1mm x 3mm. For modeling the data, each film was assumed to be birefringent and transparent; the dispersion relations both perpendicular and normal to the film were assumed to fit Cauchy's equation. The birefringent Cauchy model was in excellent agreement with the experimental data; a typical example is shown in figure 3. The largest

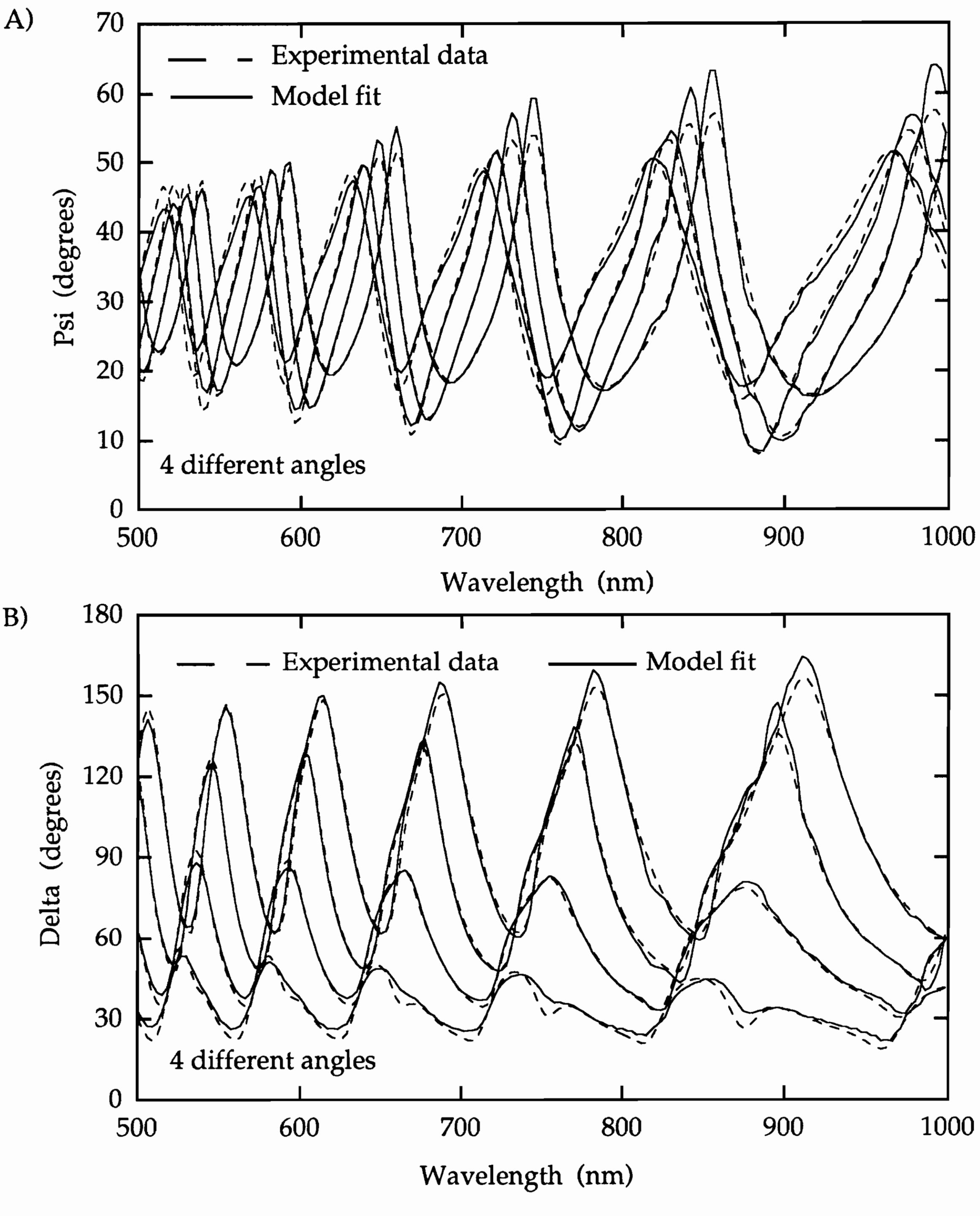

Figure 3. Typical match between variable angle spectroscopic ellipsometry data and model, yielding film thickness.

systematic error was found to be from placement of the sample in the ellipsometer; for this reason, each homopolymer thickness determination is the average of five measurements, with the sample being removed and replaced between measurements. The largest standard deviation for any sample was 0.41%; typical standard deviations were 0.20%.

The copolymer films were only measured once; the same anisotropic Cauchy model was used for curve fitting. As film thicknesses exceeded about five microns, the data became too noisy for reliable thickness determination. Only points with good agreement between the model and the experimental data were considered in determining the constants A and B.

RESULTS AND DISCUSSION

Order of initiation Figures 4 through 6 shows thickness vs. position for CVP homopolymers. Error bars are not shown due to extremely small standard deviations (≈0.2%) in the measurements. Four different fits are shown for each material as indicated; the values of λ and the root mean square error are presented on each graph. The best fit for PPX, shown in figure 4, is obtained for $\lambda = 3$. We conclude polymerization is initiated by three paraxylylene molecules combining to form a trimer diradical, in accordance with prediction[3].

The PPX-C film data also most closely matched the curve obtained from $\lambda = 3$, as shown in Figure 5. The data for PPX-D, shown in figure 6, best matched the curve obtained from $\lambda = 4$. This suggests four paradichloro-

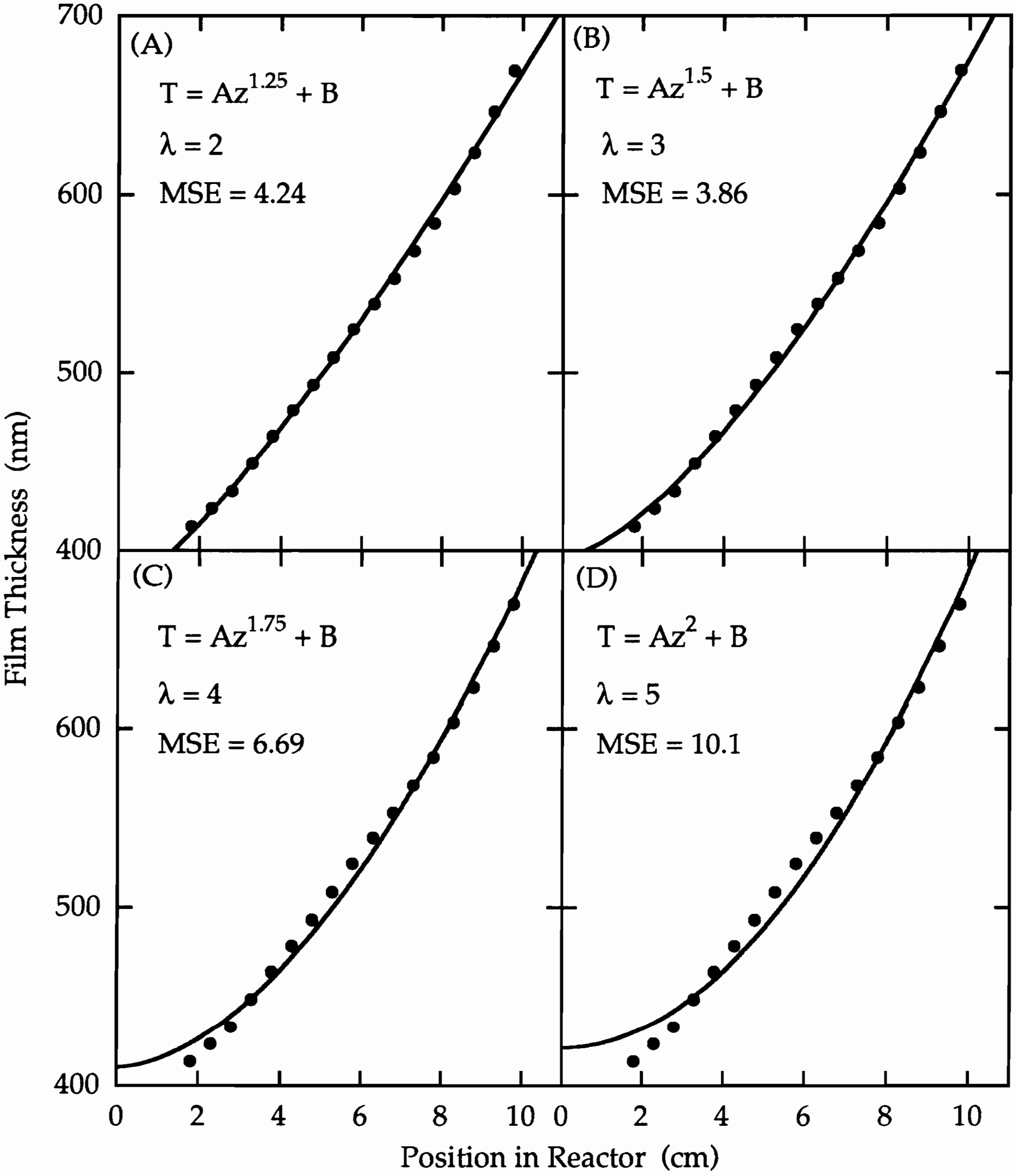

Figure 4. Film thickness vs. position in reactor for polyparaxylyene. Each quadrant employs a different curve fit as indicated.

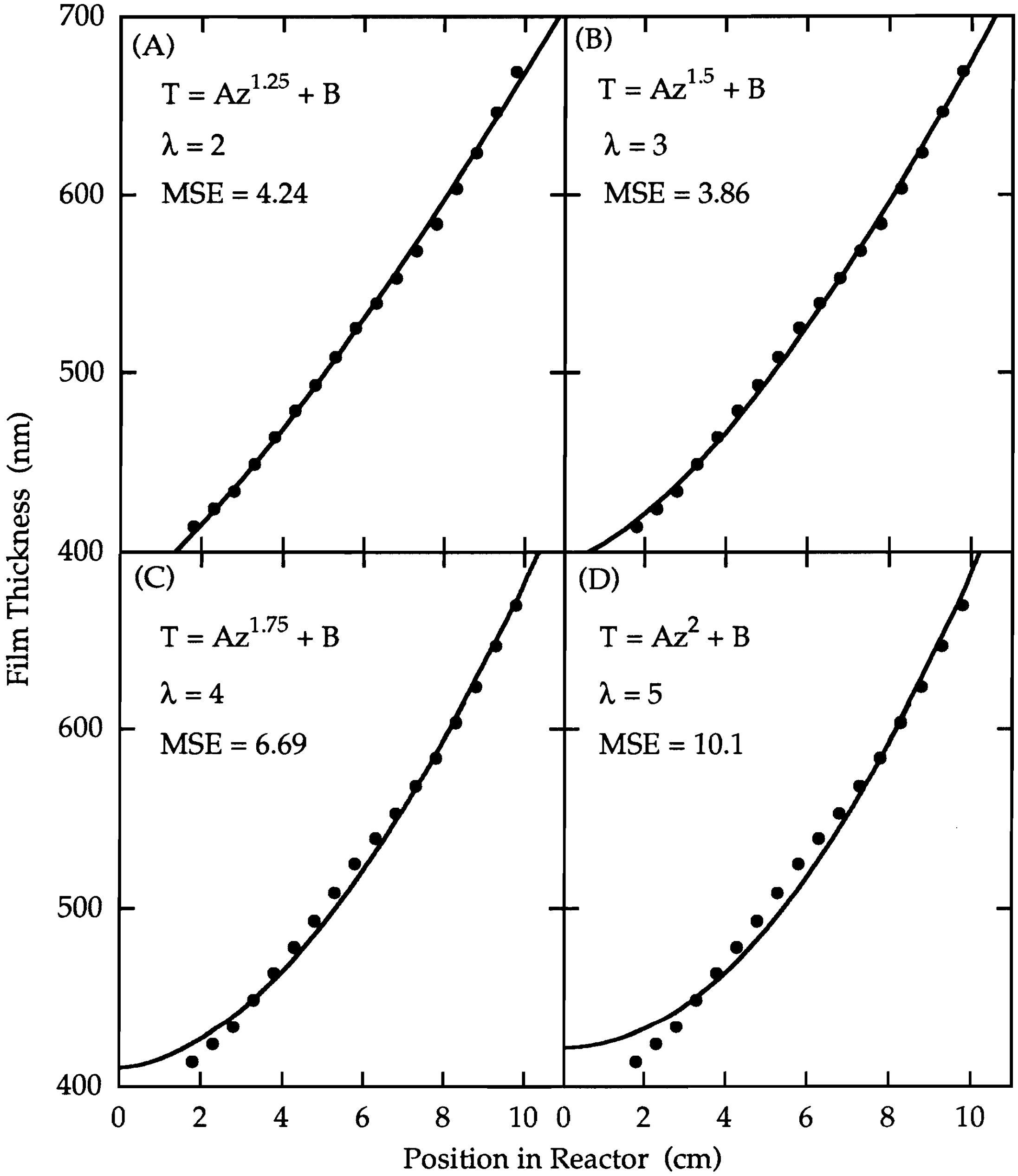

Figure 5. Film thickness vs. position in reactor for polychloroparaxylylene. Each quadrant employs a different curve fit as indicated.

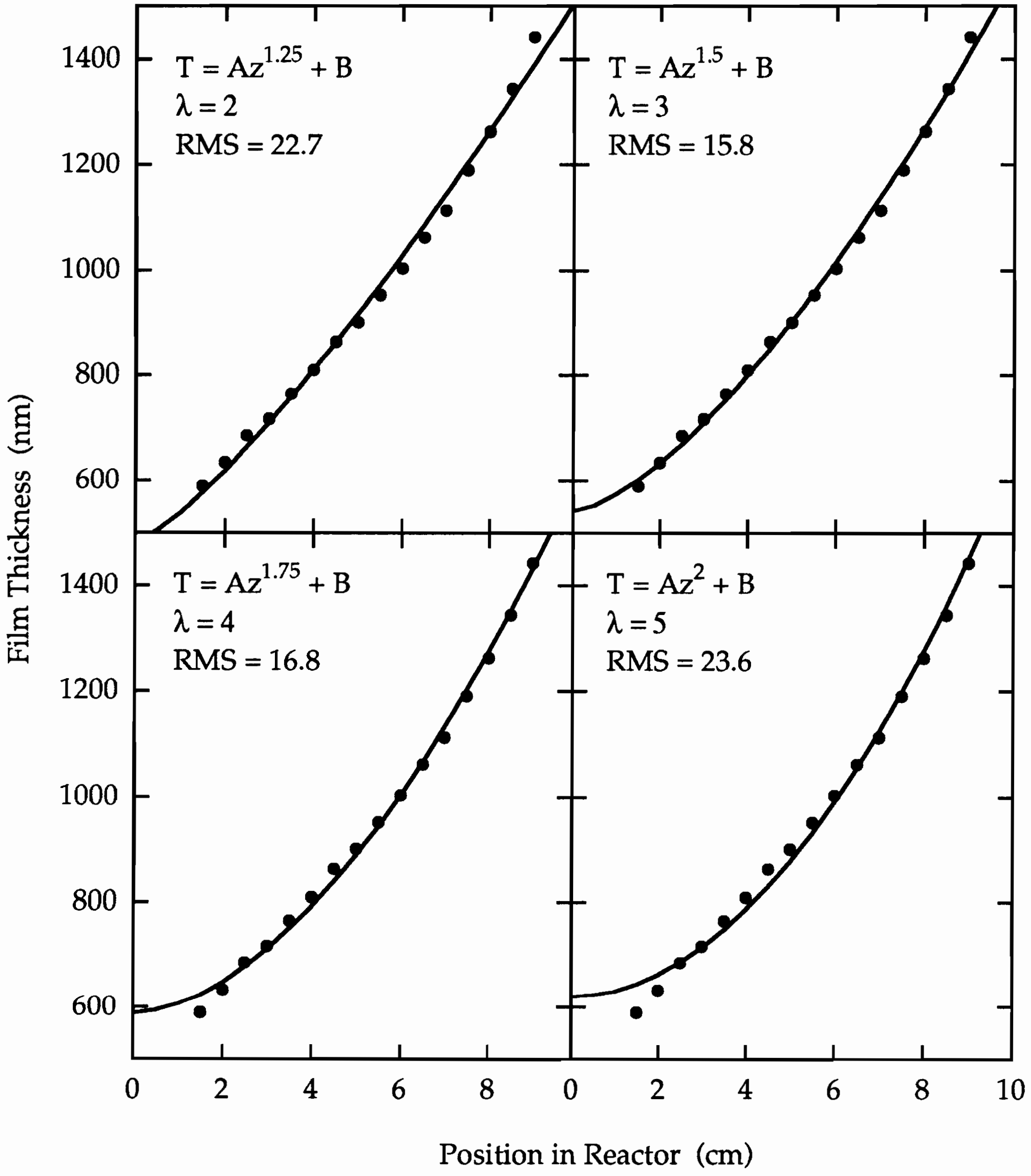

Figure 6. Film thickness vs. position in reactor for polydichloroparaxylylene. Each quadrant employs a different curve fit as indicated.

xylylene molecules were required to initiate polymerization, forming the tetramer diradical. Recent molecular orbital calculations suggest chlorine acts as a mildly deactivating electron donor in the monomer[18]; perhaps two chlorines sufficiently reduce the polarizability of the monomer that initiation requires four monomers rather than three. The exact role played by substituents during initiation, however, remains to be determined.

Reactivity Ratios The value for r_1 was found to increase with increasing temperature: 13.04 at 20°C, 19.07 at 24°C and 33.99 at 28°C. Both r_1 and its temperature dependence are very high in the deposition temperature range studied. This is not surprising; PX is extremely reactive and the deposition temperatures were very close to the PFOMA sublimation temperature, suggesting the residence times on the walls of PFOMA were very short. At each temperature, r_2 was found to be approximately zero ($\approx 10^{-8}$), though always positive. Figure 7 shows the thickness-vs.-z data from which A and B were calculated for each run. Figure 8 shows each of the three sets of data along with the curve fit obtained from the reactivity ratios listed above.

As discussed earlier, we have not yet developed a statistically valid curve fitting method for obtaining reactivity ratios, nor can we calculate regions of joint confidence. However, we have shown the curve generated by equation 9 provides a satisfactory fit to the experimental data. In addition, the values obtained for r_1 and r_2 are not unreasonable. We note that the precision with which film thickness can be measured is often better than the precision of composition measurements; if the difference in precision is

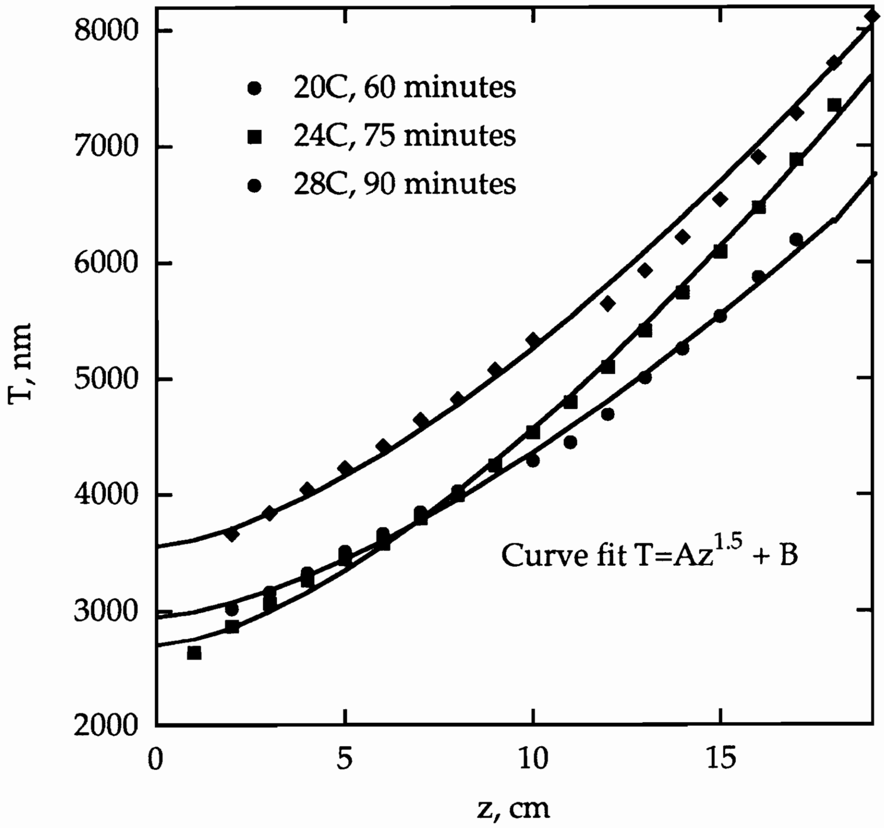

Figure 7. Thickness vs. distance for copolymer films, from which $Z_{(z)}$ is calculated.

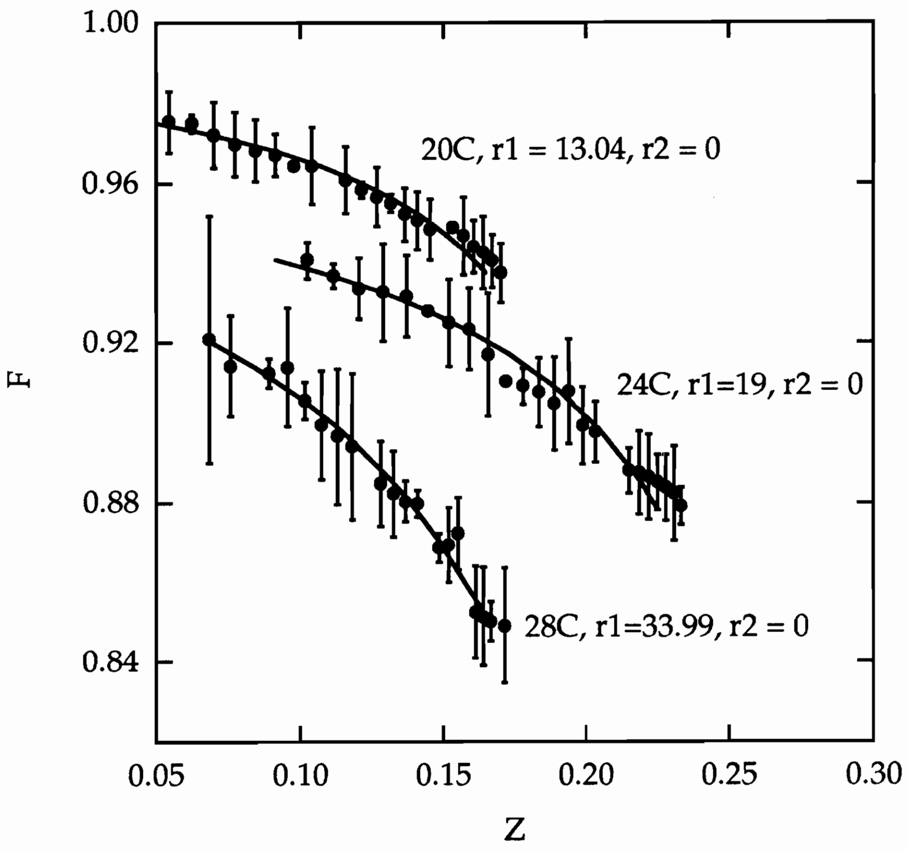

Figure 8. Composition of copolymer films grown at different temperatures vs. $Z_{(z)}$, along with curves predicted by equation 9.

significant, linear least square fitting will give acceptable "initial guess" values of the reactivity ratios, though no information about joint confidence regions[16].

SUMMARY

A model for chemical vapor polymerization in two dimensions is presented which allows determination of the order of initiation and reactivity ratios for random copolymers. We assume that monomer pressure is determined primarily by a linear pressure gradient which forces gas through a cylindrical reaction chamber. This assumption suggests the thickness of a film will vary as $z^{(\lambda+3)/4}$ if z is the flow direction and λ is the number of monomers required for spontaneous initiation. Our experimental results suggest that $\lambda = 3$ for PPX and PPX-C, while $\lambda = 4$ for PPX-D.

If PPX is grown in the presence of a reactive vinylic comonomer, a copolymer film will result with a composition gradient in the z direction. We equate the monomer conversion as a function of reactivity ratios to the monomer conversion as a function of film volume. This yields an equation which satisfactorily describes experimentally determined composition gradients. The reactivity ratios can be varied to obtain the best fit of composition vs. a function of position in the reactor. Until a statistically valid curve fitting algorithm is developed, reactivity ratios can only be estimated.

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CHAPTER 3

Room Temperature Copolymerization to Improve the Thermal and Dielectric Properties of Polyxylylene Thin Films by Chemical Vapor Deposition

(Journal of Materials Research, 9(12), 3125-30, 1994.)

Justin F. Gaynor and Seshu B. Desu

ABSTRACT

Polyxylylene thin films grown by chemical vapor deposition (CVD) have long been utilized for uniform, pinhole-free conformal coatings. Homopolymer films are highly crystalline and have a glass transition temperature around room temperature. We show room temperature copolymerization with previously untested comonomers during the CVD process. Samples were studied with wavelength dispersive analysis, FTIR, scanning variable angle ellipsometry and x-ray diffraction. Copolymerizing chloro-p-xylylene with perfluorooctyl methacrylate results in dielectric constants at optical frequencies as low as 2.19, compared to 2.68 for the homopolymer. Copolymerizing p-xylylene with 4-vinylbiphenyl resulted in films whose onset of weight loss in TGA measurements was 450°C, compared to 270°C for the homopolymer.

Room Temperature Copolymerization to Improve the Thermal and Dielectric Properties of Polyxylylene Thin Films by Chemical Vapor Deposition

Justin F. Gaynor and Seshu B. Desu

INTRODUCTION

Vacuum polymerization of cyclo-di-p-xylylene is a unique polymerization reaction which requires no catalyst and creates no reaction byproducts, resulting in extremely pure material with exceptional conformity. Here, we report on a copolymerization method which leads to increased thermal stability, reduction in refractive index and lowered crystallinity. This may increase the suitability of this method for producing intermetallic dielectrics for the electronics industry or low-loss planar waveguides.

The first report[1] of room-temperature copolymerization during CVD of xylene monomers was with maleic anhydride as the comonomer. The successful copolymerization of 9-vinylanthracene, 4-vinylbiphenyl and perfluorooctyl methacrylate (PFOMA) with paraxylenes has been reported earlier, and is discussed in detail here [2]. Several vinylic monomers have been reported which were copolymerized at temperatures below 0°C, but resulted in poor topography due to the inability of the polymer to achieve its most stable configuration during the growth process[1,3]. The low vapor pressures of the comonomers listed above allows their use at room temperature.

Parylene films grow by a free-radical mechanism, as shown in figure 1. Initiation requires three or more molecules to be close enough together to form the more stable diradical, which is only likely to occur after the monomer has adsorbed on the substrate[4,5]. Additional monomer adds to the diradical, propagating the polymer outward from the surface. The rate of initiation is proportional to the third power of monomer concentration and the propogation rate is proportional to the monomer concentration, leading to high molecular weights. This polymerization mechanism, unique to cyclo-di-paraxylylenes, is largely responsible for the utility of these films; the conformity and purity of films grown by this method exceed any other type of thin film polymer processing technique. The polymerization mechanism has been widely studied and the reader is referred to excellent reviews to supplement this brief introduction[3,6].

The major drawback to this process is the limited number of compounds which can be polymerized, and the consequent limits to property tailoring. Many substituted monomers have been synthesized and studied, and most form linear polymers whose properties are in accordance with prediction. However, only three compounds are commercially available: cyclo-di-p-xylylene; cyclo-di-*p*-chloro- xylylene, which has an average of one chlorine atom substituted on each carbon ring; and cyclo-di-*p*-dichloroxylylene, which has two chlorine atoms substituted on each carbon ring. The goal of this research is to significantly alter the properties of the films with commercially available materials while retaining the high purity and conformality of CVD processing.

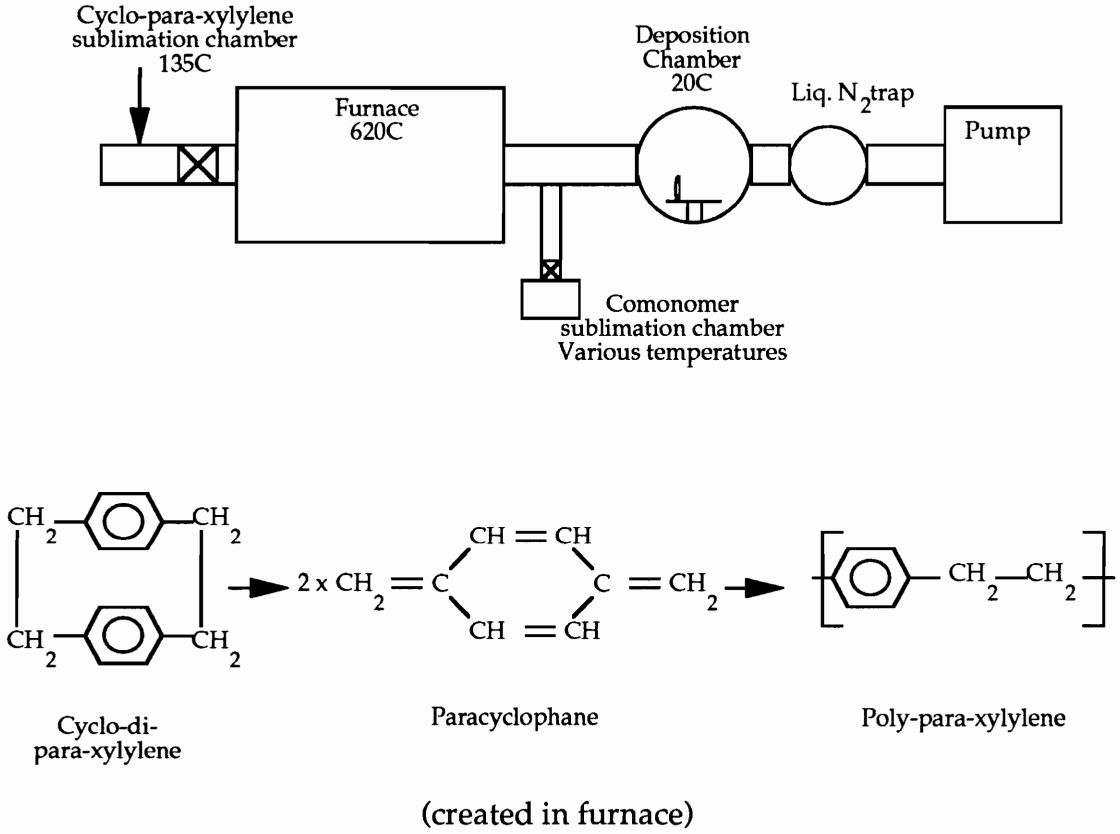


Figure 1. Vacuum deposition equipment and reaction path.

The commercial uses of these films are based upon the extremely high purity inherent to the processing method. Desirable properties include low dielectric constants, high electrical resistance, high breakdown voltages, conformal deposition, low processing temperatures, low stresses, hydrophobicity, biocompatibility and solvent resistance. Many of these properties vary with the degree of crystallinity. Because the degree of crystallinity in a polymer is greatly dependent on its thermal history, the properties may change significantly during use. The substitution in the backbone with comonomers, as discussed here, often inhibits the ability to crystallize. The copolymerization method results in properties which are less temperature or thermal history dependent and can be used where high crystallinity is not required.

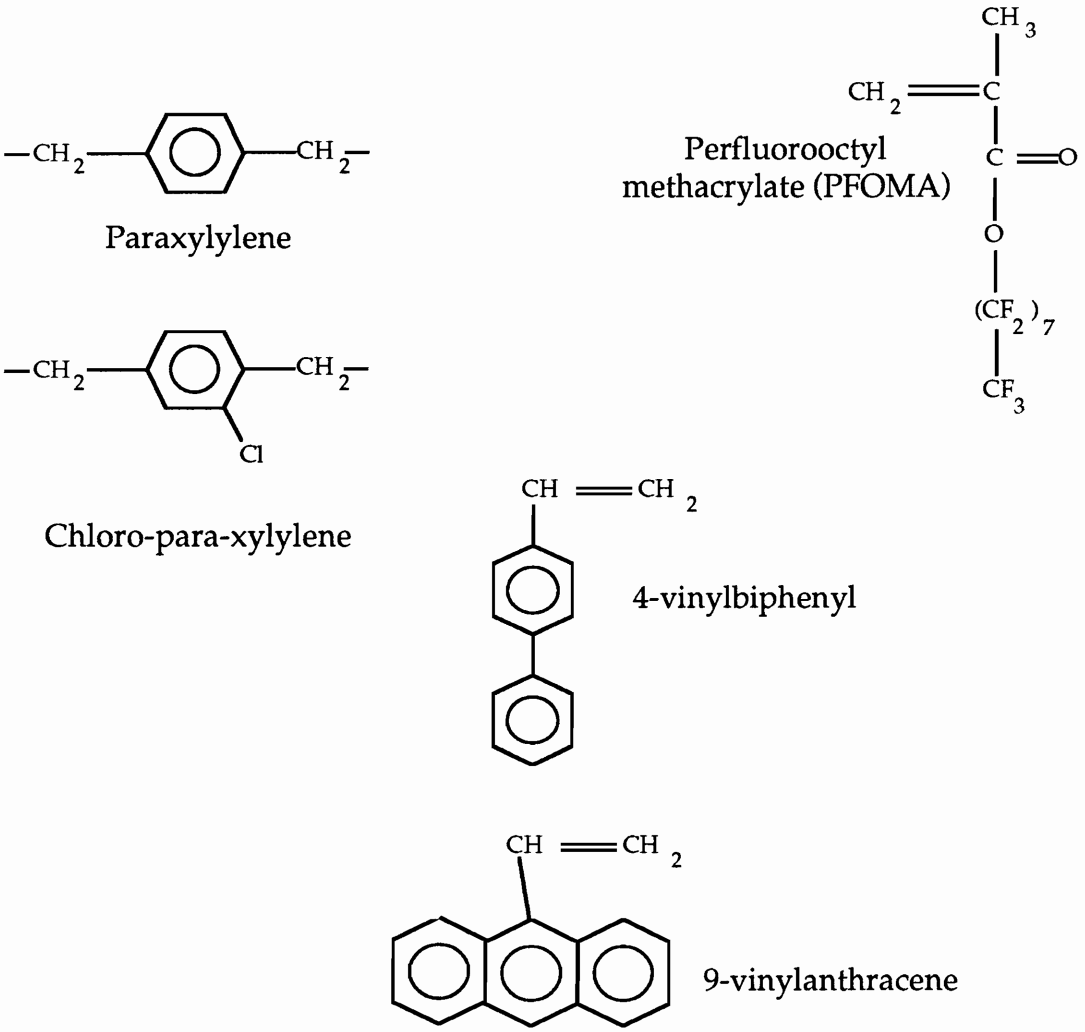
EXPERIMENTAL

Fabrication All samples were prepared according to the Gorham method[7] in a homemade reactor modified to allow for the addition of comonomers to the gas mixture downstream from the hot furnace. Sublimation temperatures for cyclo-p-xylylene and cyclo-*p*-chloro-xylylene were 135°C when homopolymers were grown; when a comonomer was used, the sublimation temperature was reduced to 128°C to prevent the total monomer partial pressure from being high enough to allow gas-phase polymerization. Sublimation of perfluorooctyl methacrylate was at 64°C; 9-vinylanthracene at 165°C; and 4-vinylbiphenyl at 160°C. Partial pressures within the reactor were not measured due to the tendency of the reactants to form films on all cooled surfaces, damaging pressure sensors. The base pressure in the reactor was 0.28 ± 0.01Torr throughout each deposition, about six times higher than in commercial equipment but well within the limits described by Gorham[7].

The thermal cleavage furnace was held at 620°C. The comonomer feeder tube was maintained at 130°C for homopolymers and for copolymers with PFOMA; this was increased to 180°C when copolymerizing with 4-vinylbiphenyl and 9-vinylanthracene. The reaction chamber was maintained between 20-23°C for homopolymers and copolymerization with 4-vinylbiphenyl and 9-vinylanthracene, and at 20°C for copolymerization with PFOMA. Because the reaction took place at room temperature, the entire reaction chamber was coated, rather than the substrate alone. This led to rapid depletion of the monomers, and consequently the thickness rapidly decreased with distance into the chamber. Growth rates at the entrance to the reactor, where growth was fastest, were about 6nm/minute. The copolymer films' compositions also varied with position in the reactor.

Cyclo-di-*p*-xylylene, trade name DPXN, and cyclo-di-p-chloroxylylene, trade name DPXC, were purchased from the Nova Tran corporation. PFOMA, 9-vinylanthracene and 4-vinylbiphenyl were purchased from Lancaster Synthesis. Their structures are shown in Figure 2.

Characterization FTIR spectra were obtained on a Perkin-Elmer 1710 with a MCT detector operating at liquid nitrogen temperature. Samples were grown on 25 mm diameter by 4 mm thick single crystal disks of CaF_2,



Paraxylylene

Chloro-para-xylylene

Perfluorooctyl methacrylate (PFOMA)

4-vinylbiphenyl

9-vinylanthracene

Figure 2. Chemical structures of paraxylylenes and comonomers.

purchased from International Crystal Laboratories. Spectra were averaged over 64 measurements, with a bare CaF_2 crystal run as a background. The sample chamber and detector chamber were purged with dry nitrogen before and during data collection.

Refractive indices and thicknesses were determined with a variable-angle spectroscopic ellipsometer purchased from J. Woollam Company. Samples were deposited on <111> Si with a 1.3nm layer of SiO2. Samples were scanned from 400 to 1000nm wavelength light in 2nm increments and at $\theta = 70, 75$ and 80 degrees. Data points were the average of 25 measurements per wavelength.

TGA analysis was performed with a Seiko Thermal Analysis System. Samples were deposited on a detergent-smeared silicon wafer, and removed with running tap water. Samples were then thoroughly rinsed in alcohol and distilled water before being dried in a vacuum oven for 12 hours at 105C. Sample weights were between 10 and 20 mg. The heating rate was 10C/min. Samples were tested in an air environment.

X-ray diffraction scans were performed with a Scintag Automated X-Ray Diffraction System. Samples were deposited on CaF_2 and annealed at 105°C under vacuum for sixteen hours. The incident beam was held at 5^{o} above the plane of the film, and the position of the detector scanned.

Absolute compositions of the PFOMA/cyclo-di-p-chloroxylylene samples were determined by wavelength dispersive analysis with a Cameca SX-50 electron probe. Samples were grown on B-doped <111> Si. Electrical conductivity was ensured with a sputtered coating of carbon. 5nA and 10nA beams were used with voltages of 9kV and 10kV. Samples were grown on two 10cm long strips of B-doped <111> Si placed lengthwise in the reactor with 0.5cm between them. The temperature of the reaction chamber was 20°C. Samples were annealed at 110°C and 0.3Torr for twelve hours to remove any unreacted monomer. Each data point is the average of two sixty second measurements, during which the sample remained stable. Data was taken every 0.5cm along the strips until a sudden decrease in fluorine was detected, followed by the detection of silicon. Because the samples grew thinner with increasing distance into the reactor, this indicated that the analytical volume was exceeding the actual thickness of the sample.

The extreme structural similarity of 4-vinylbiphenyl and 9-vinylanthracene to paraxylylene precluded determination of their compositions by this method, though copolymerization was indicated by FTIR. Attempts to determine film composition by peak height ratios were unsuccessful. 9-vinylanthracene-co-paraxylylene films were brittle and yellow and showed poor adhesion. They were not analyzed further.

RESULTS AND DISCUSSION

Composition vs. Position. As noted earlier, the composition of the copolymer films changed with distance into the reactor, reflecting the differing gas composition as one species was consumed preferentially to the other. Figure 3 shows the raw wavelength dispersive analysis results when measured at 10nA and 9kV. The increase in perfluorooctylmethacrylate with distance is clearly linear. From this data, the mol fraction of PFOMA monomer in the copolymer is easily determined. The results are shown in

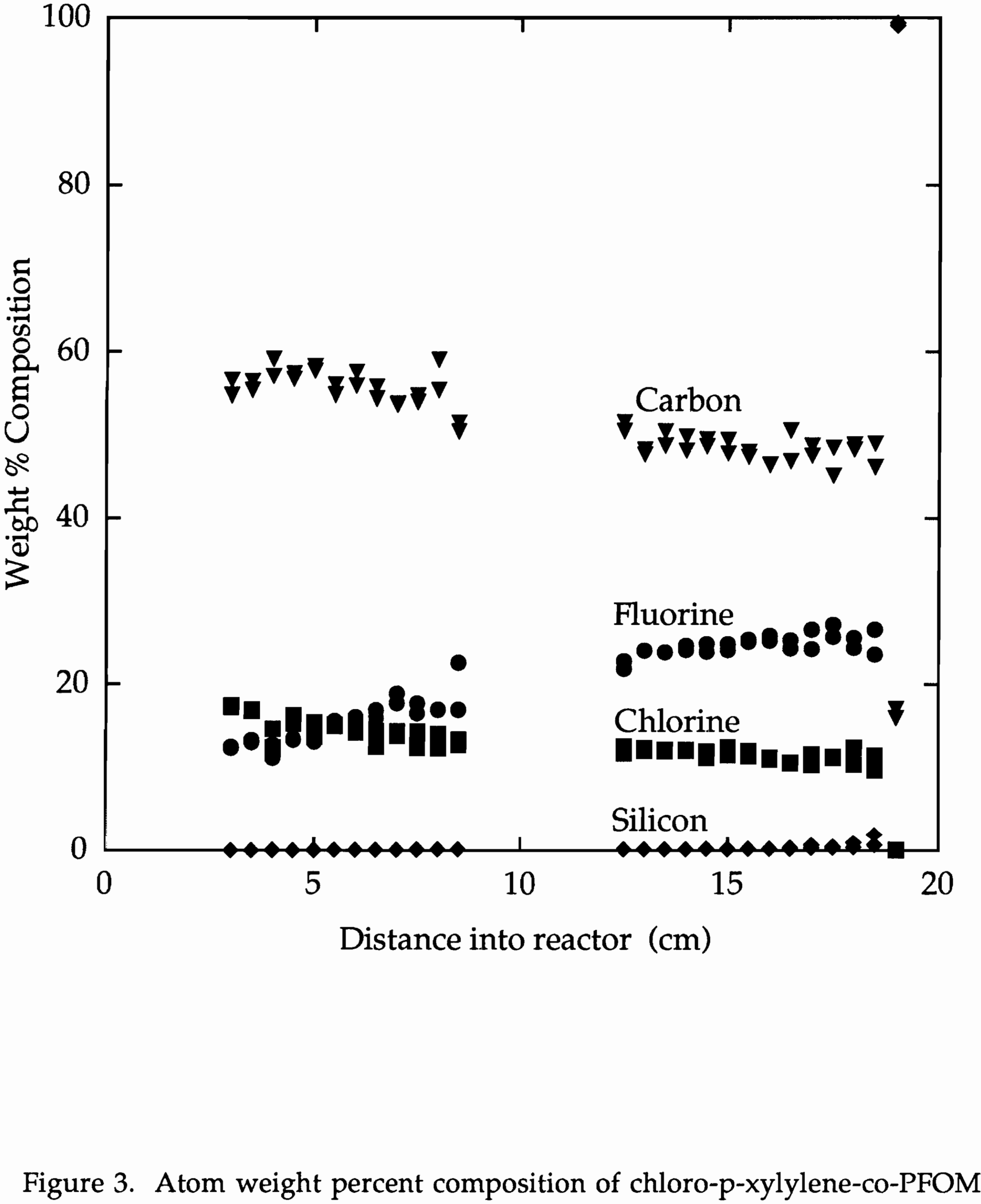


Figure 3. Atom weight percent composition of chloro-p-xylylene-co-PFOMA vs. position in reaction chamber (two measurements).

figure 4. At the entrance to the reaction chamber, about 7% of the polymer is perfluorooctyl methacrylate, increasing to a maximum of 20%. Individual samples measured under different processing conditions (sublimation temperature of perfluorooctyl methacrylate = 66°C, reaction chamber = 15°C) indicate that at least 35 mol% perfluorooctyl methacrylate can be incorporated into the polymer. A model to account for the linear change in composition is currently under development.

Thermal Stability It has been reported previously[8,9] that poly-p-xylylene and poly-p-chloroxylylene begin losing weight at temperatures around 270°C in air, and is nearly completely charred at 500°C. When heated in nitrogen, however, it is stable to about 480°C, where it rapidly decomposes. When the hydrogen atoms in the CH_2 groups are replaced by fluorine, the polymer is degrades above 500°C in both air and nitrogen when heated at 10°C/minute. It has been proposed that the decomposition of poly-*p*-xylylene occurs through the formation of peroxy radicals which attack the CH_2 bonds, resulting in chain scission[9]. Finally, when poly-p-dichloroxylylene is heated in air, it does not gain weight before decomposing, and the onset of decomposition does not occur until about 320°C. Thus, the formation of peroxy radicals appears to be inhibited. It has been speculated that the additional chlorine atom on each ring may sterically hinder oxygen from attacking the CH_2 bonds, or that electron density may be withdrawn near the hydrogen atom by the strongly electronegative Cl atom, stabilizing the bond[9]. A similar phenomenon is noticed in the poly-p-xylylene-co-vinylbiphenyl

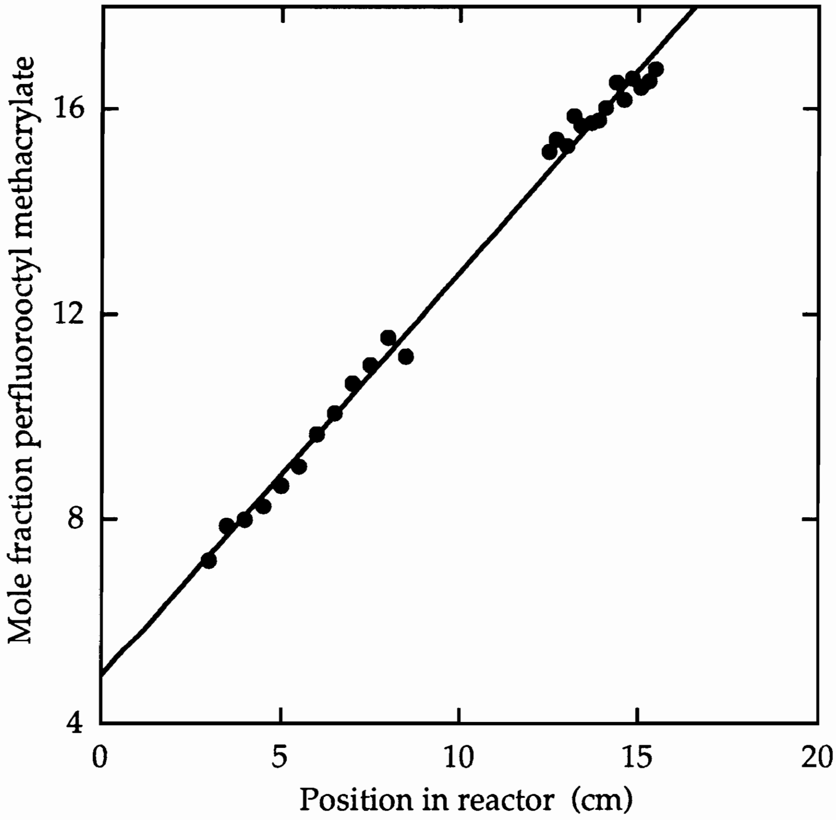


Figure 4. Mole fraction PFOMA in chloro-p-xylylene-co-PFOMA vs. position in reaction chamber.

samples. In Figure 5, it can be seen that the homopolymer decomposes in the same manner reported earlier. However, as the amount of vinylbiphenyl in the sample is increased, the thermal stability increases. The sample with the highest vinylbiphenyl concentration behaved nearly the same in air and nitrogen. The structure of vinylbiphenyl suggests that it could either sterically shield the CH_2 groups or electronegatively stabilize them. Unfortunately, the chemical similarity of vinylbiphenyl to poly-p-xylylene did not allow for the determination of actual chemical composition in these samples.

Dielectric Constant The dielectric constant of poly-p-chloroxylylene is about 3 in the range 60Hz-1MHz, and 2.7 in the gigaherz region[3]. Two strategies to reduce this would be to lower the density of the material by making it amorphous, and lowering it chemically by the introduction of carbon-fluorine bonds. With the copolymerization method, both of these strategies can be implemented simultaneously. Cyclo-di-p-chloroxylylene was copolymerized with PFOMA. As expected, an increase in the amount of PFOMA resulted in a reduction in crystallinity (Figure 6) after samples were annealed at 110°C for 12 hours. The major x-ray diffraction peaks cited in the literature for polyparaxylylene are the 020 (16.7°), -111 (17.7°) and 110 (22.7°); polychloro-para-xylylene has the same crystal structure, and it is expected that the peaks occur in similar positions. Additional evidence for reduction in crystallinity was provided by scanning variable angle ellipsometry. No appreciable change in either refractive index or sample thickness in the copolymers was noted after annealing. In contrast, a homopolymer

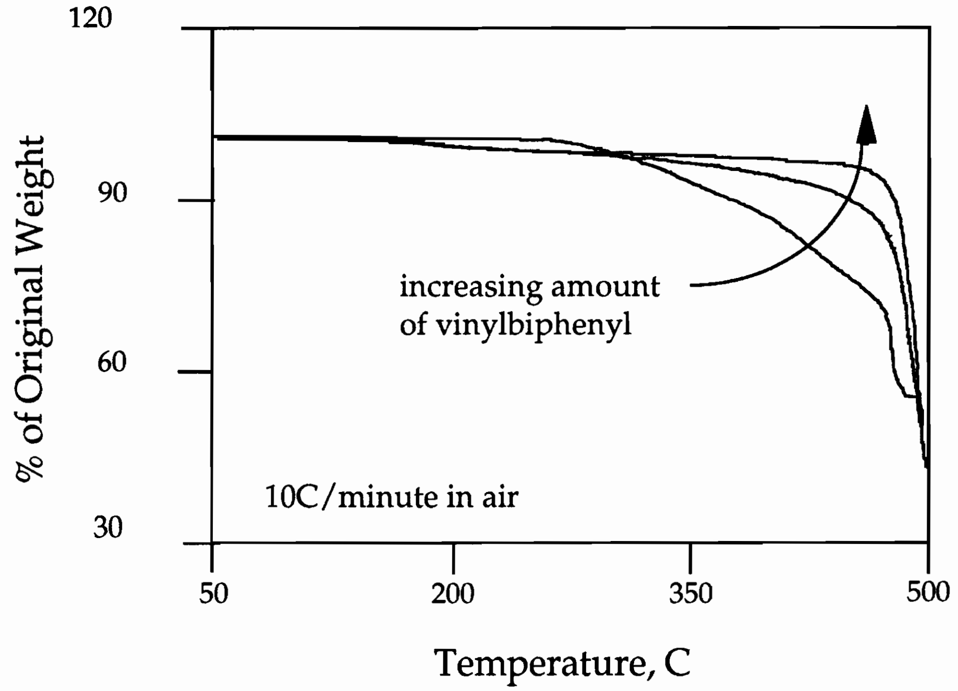


Figure 5. Thermal stability in air of p-xylylene-co-vinylbiphenyl films vs. composition.

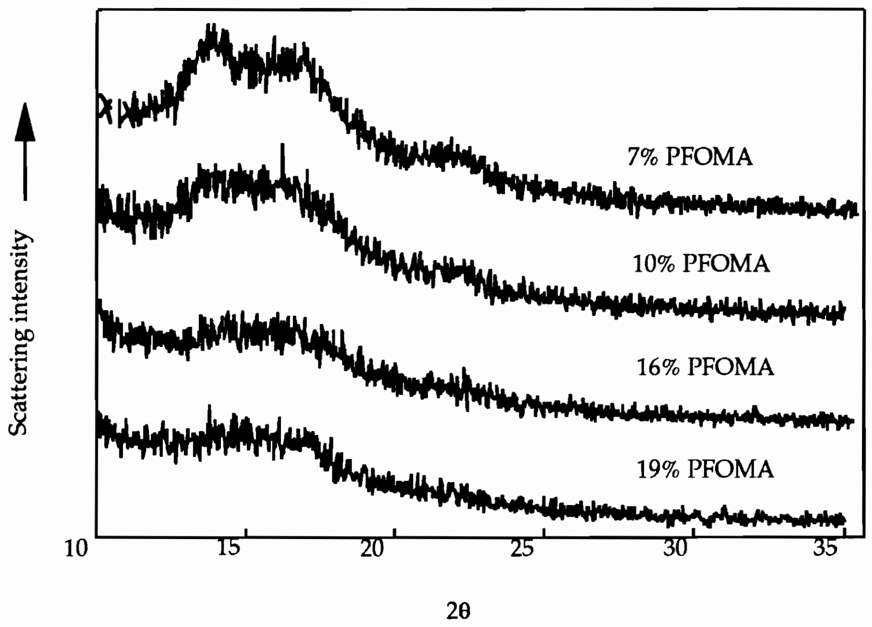


Figure 6. X-ray diffraction peaks of annealed chloro-p-xylylene-co-PFOMA, showing supression of crystallinity with increasing comonomer concentration.

undergoing the same annealing treatment showed a 4% reduction in thickness and an increase in refractive index (wavelength = 589nm) from 1.628 to 1.636, indicating densification through increase in crystallinity. Figure 7 shows the refractive index and absorption constant as a function of wavelength for the homopolymer. A Cauchy dispersion relation was assumed. The model from which the data were obtained is in excellent agreement with the experimental data, as shown in Figure 8.

A decrease in refractive index vs. composition was observed by ellipsometry. In the optically nonabsorbing region, the dielectric constant is simply the square of the refractive index. Figure 9 shows the refractive index and dielectric constant, as determined by ellipsometry, as a function of perfluorooctyl methacrylate concentration. A sample with 35% PFOMA had a refractive index of 1.48.

CONCLUSIONS

The use of comonomers to change the properties of cyclo-p-xylylenes has been demonstrated. The conditions for growing different types of copolymers are described. The high purity, highly conformal processing combined with significant changes to refractive index allow for the production of efficient waveguides. The higher temperature stability of one copolymer may allow for its wider use as a dielectric layer in integrated circuits.

Copolymers which can be grown at room temperature include p-xylylene with 4-vinylbiphenyl and 9-vinylanthracene and p-chloroxylylene

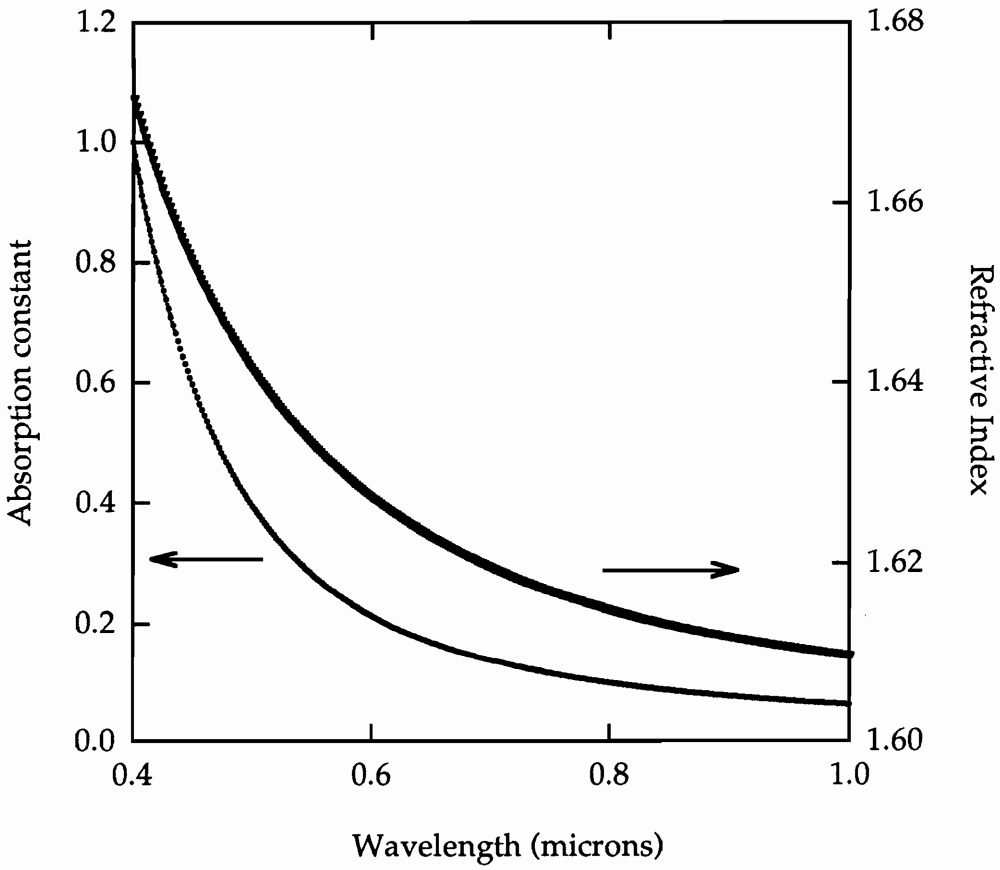


Figure 7. Refractive index and absorption constant vs. wavelength for chloro-p-xylylene.

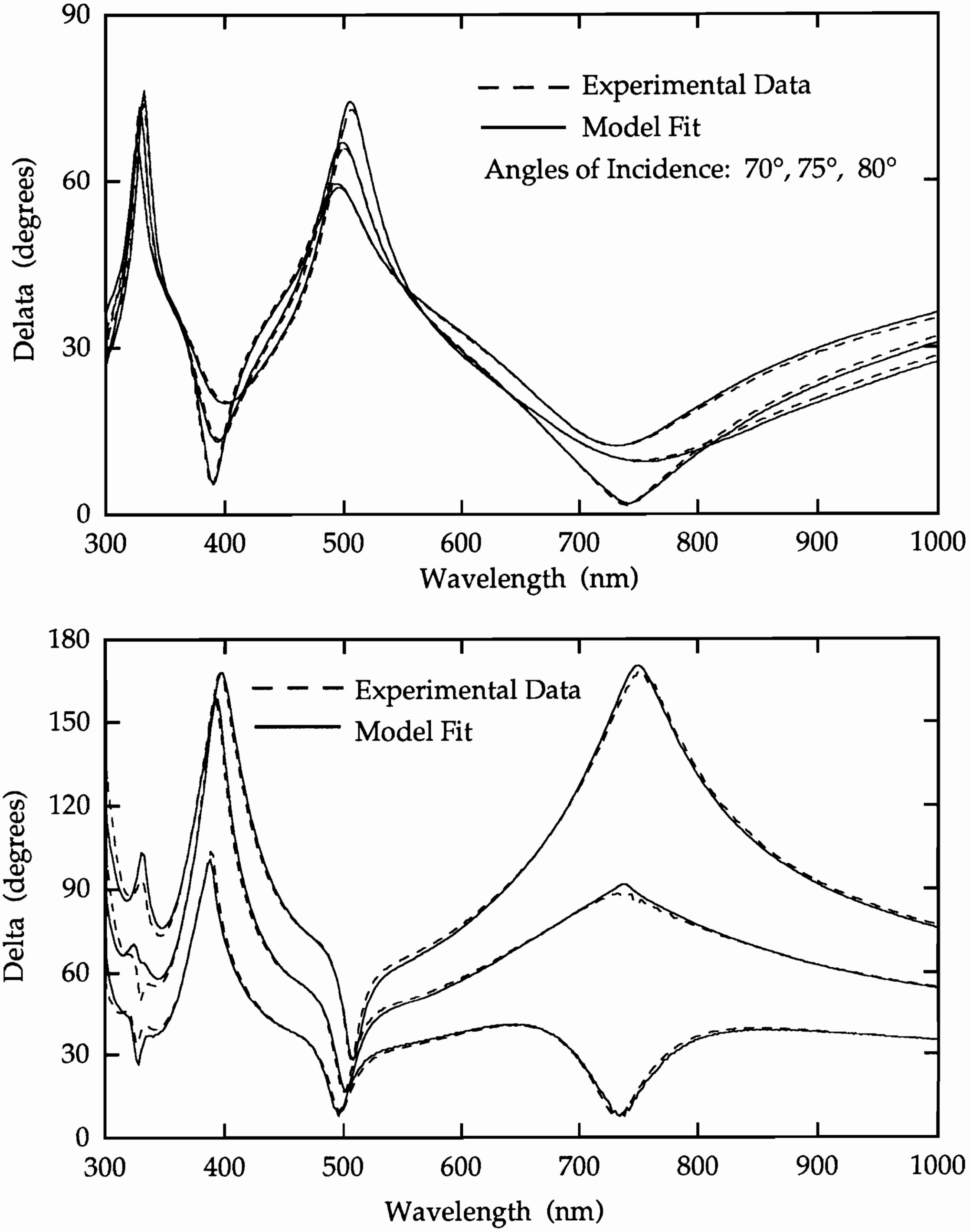


Figure 8. Experimental and model psi and delta from variable angle scanning ellipsometry.

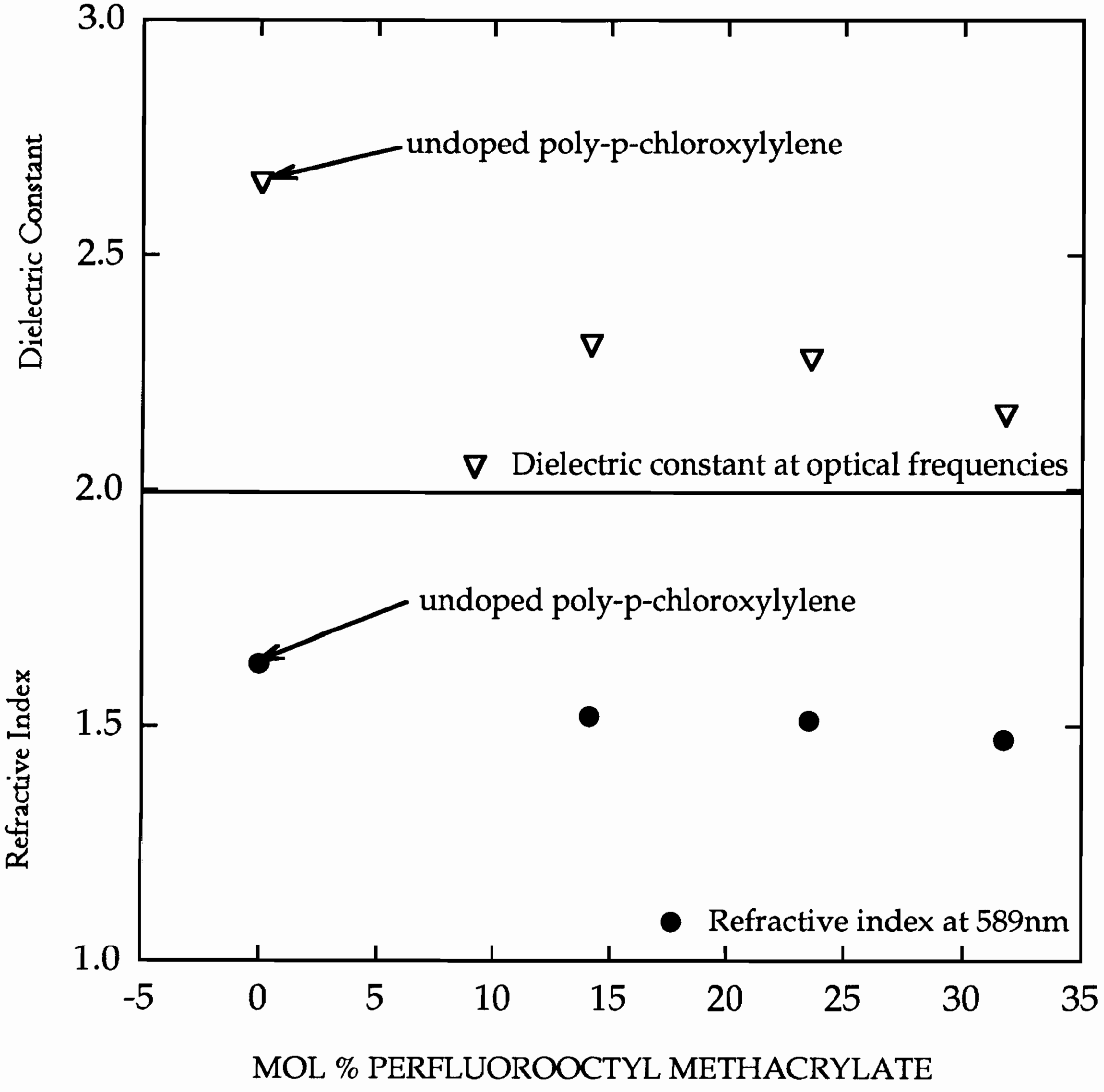


Figure 9. Dielectric constant and refractive index of chloro-p-xylylene-co-PFOMA vs. composition, assuming dielectric constant = n^2.

with PFOMA. The addition of 4-vinylbiphenyl to p-xylylene significantly increases its oxidative stability. When heated in air at 10°C/minute, the undoped material starts to decompose around 270°C, while the copolymer doesn't degrade until above 450°C. The crystallinity and refractive index of p-chloroxylylene can be lowered; the lowest refractive index achieved was 1.48 at a wavelength of 589nm.

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CHAPTER 4

Optical Properties of Polymeric Thin Films grown by CVD

(To appear in Journal of Materials Research, Jan. 1996)

Justin F. Gaynor and Seshu B. Desu

ABSTRACT

For the first time, the refractive index of polyparaxylylene films, the only polymers grown commercially by chemical vapor deposition (CVD), are reported throughout the visible spectrum. This information is required if optical components such as antireflective coatings or waveguides are to be fabricated with CVD polymers. These properties are compared to a low-index CVD copolymer, poly(parachloroxylylene-co-perfluorooctyl methacrylate), invented in our laboratory. The ellipsometric constants psi and delta were measured for wavelengths between 400nm and 1000nm using variable angle spectroscopic ellipsometry; many samples of each film were deposited to improve statistics. The data was modeled assuming a birefringent film following Cauchy dispersion both parallel and perpendicular to the film plane; excellent agreement between models and experimental data were obtained. The refractive index (λ = 632.8nm) of the copolymer in the film plane was 1.389, compared to 1.645 - 1.665 for the homopolymers. PPX, PPX-C and the copolymer showed negative birefringence, while PPX-D showed positive birefringence. The optical properties of PPX showed little thickness dependence for films ranging from 36nm to 2100nm thick.

Optical Properties of Polymeric Thin Films grown by CVD

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INTRODUCTION

Polyparaxylylene (PPX), polyparachloroxylylene (PPX-C) and polyparadichloroxylylene (PPX-D) have achieved modest commercial importance due to their unique ability to form polymeric thin films by CVD[1]. Recently, the use of these films in planar thin-film waveguides or optical filters has been proposed[2]. The films are transparent throughout the visible spectrum, tough, easily patterned, hydrophobic, resistant to solvent attack and pinhole-free even when very thin. They can be grown on any substrate, including liquids and powders. There are small differences in the indices of refraction (**n**) of PPX, PPX-C and PPX-D. A much greater range of properties is available if the process of chemical vapor copolymerization is employed[2,3]; here, we present a low-index copolymer, poly(parachloroxylylene-co-perfluorooctyl methacrylate), or PPX-C/PFOMA, which would significantly increase the efficiency of a waveguide. This copolymer, which retains all the advantages of CVD processing, may also prove useful for antireflective coatings or as a low dielectric constant material for the microelectronics industry. The structures of the three homopolymers and copolymer are shown in figure 1.

Until now, information about the homopolymers' optical properties has been limited to UV/visible/IR transmission spectra, refractive indices of the three films at wavelengths of 589.9 and 632.8nm, and birefringence of PPX.

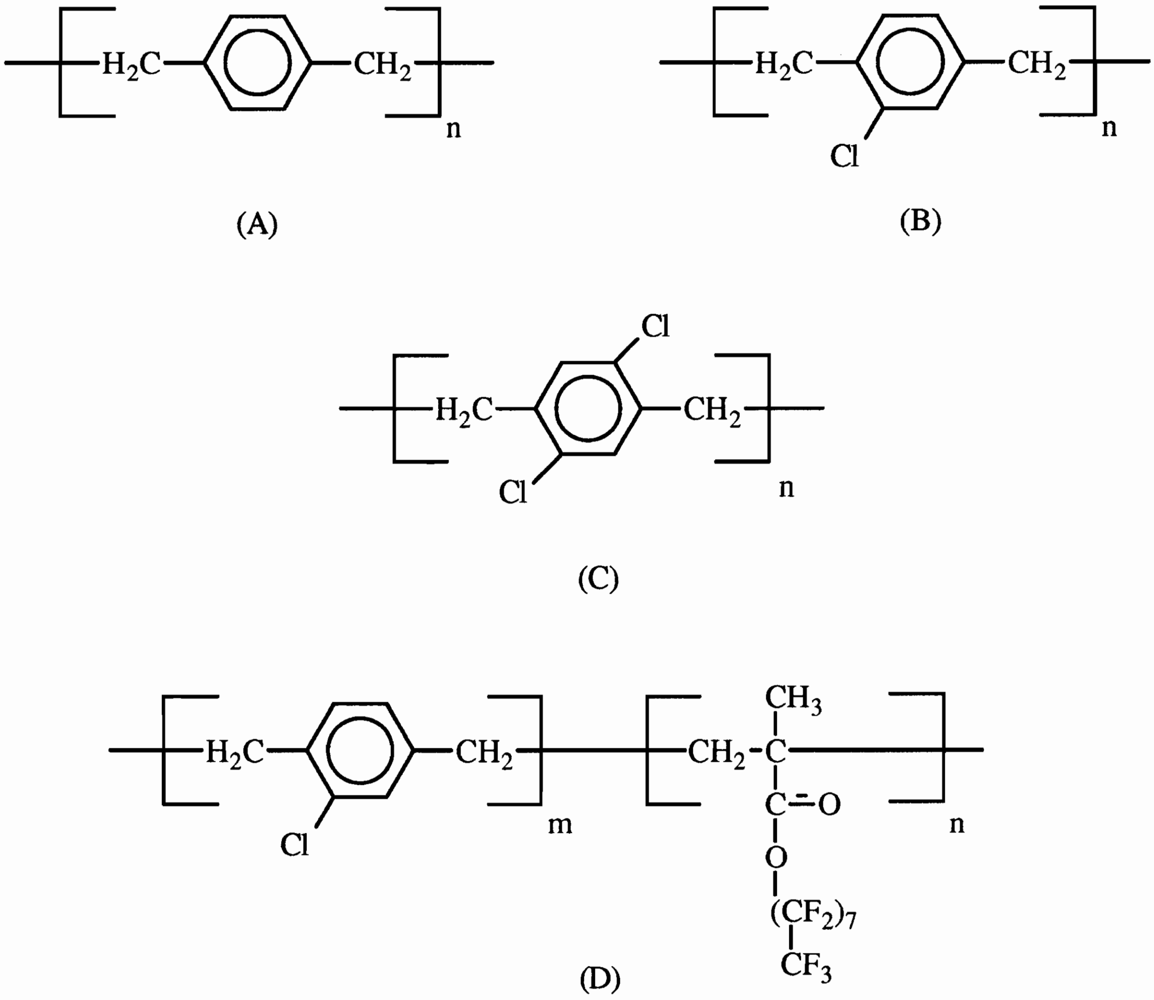


Figure 1: Chemical structures of:

A) polyparaxylylene, or PPX

B) polyparachloroxylylene, or PPX-C

C) polyparadichloroxylylene, or PPX-D

D) polyparachloroxylylene-co-perfluorooctyl methacrylate, or PPX-C/PFOMA

Here, the refractive indices of annealed films are reported through the wavelength spectrum from 400-1000nm. Because the films are birefringent, the indices in both the film plane and perpendicular to the film plane are presented. PPX has been reported as having negative birefringence, meaning the refractive index is higher perpendicular to the film plane than parallel to the film plane. Isoda reports enhanced molecular ordering in PPX films thinner than 100nm[4] grown on cleaved alkali halide crystals. We grew a series of ultrathin PPX films (36-100nm thick) on silicon to determine whether this ordering, if present on the native oxide layer, has any effect on the refractive index and birefringence.

While the properties of the polyparaxylylenes are not exceptional, the CVD process is often advantageous. The chemical vapor deposition of thin films of polyparaxylylenes from dimeric precursors has been thoroughly discussed in the literature[1,5-7]; the reaction pathway and deposition equipment are shown in figure 2. It is a unique room-temperature polymerization reaction which requires no catalyst and creates no byproducts, leading to highly crystalline, low stress films of exceptional purity and conformity. The films have found commercial use as passivation coatings for circuit boards[1], dielectric layers for capacitors[8], chemically resistant coatings for rubber gaskets in the alternative fuels industry[9], document preservatives[10], biocompatible coatings[11,12] and encapsulants of moisture sensitive or corrosive chemicals[6], among other applications.

Refractive index vs. wavelength were measured by variable angle spectroscopic ellipsometry (VASE). In this technique, linearly polarized light

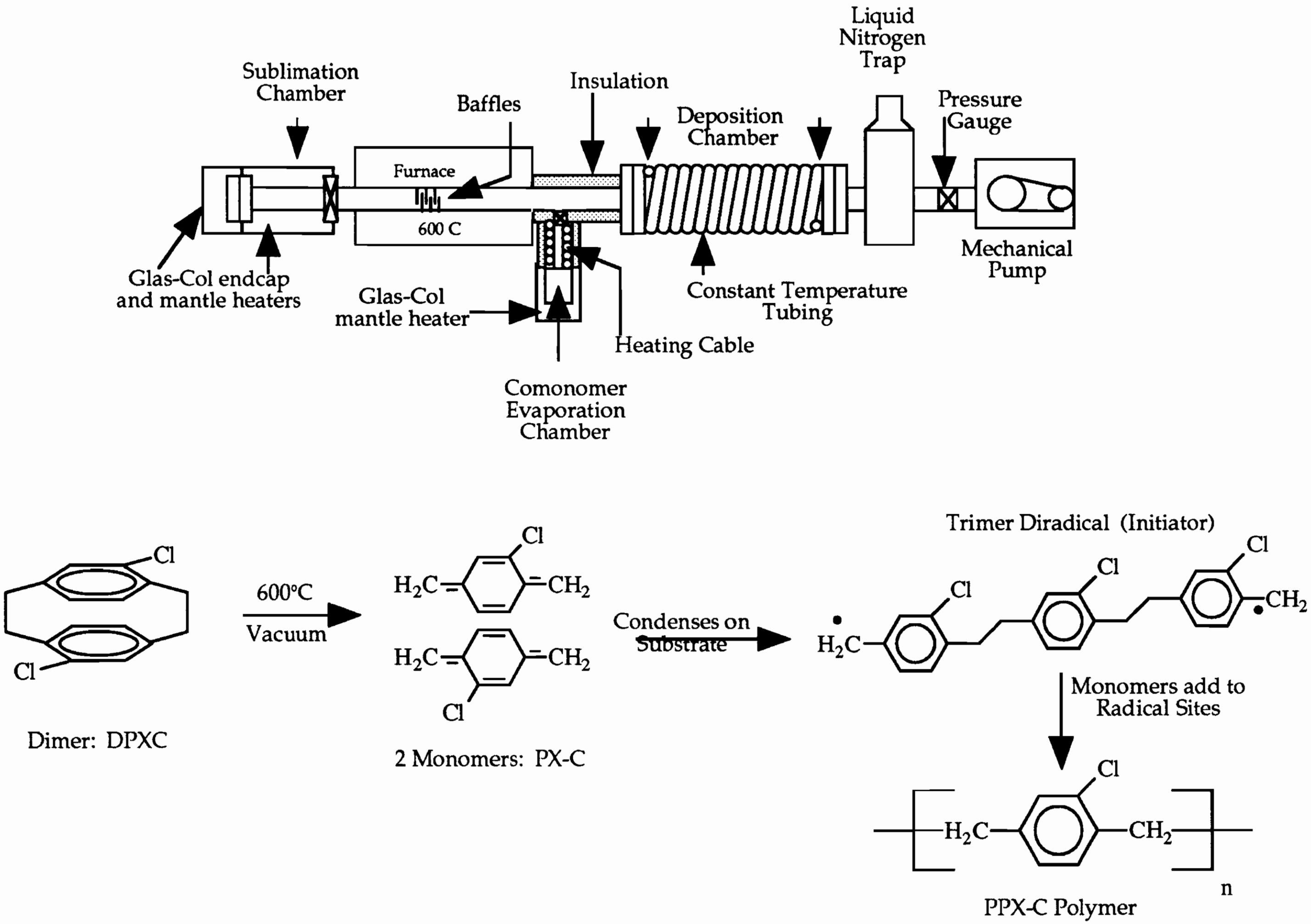


Figure 2: Reaction pathway and deposition equipment for chemical vapor polymerization

strikes a sample and is reflected into a rotating polarizer. After interaction with films and reflection, the outgoing beam will, in general, be elliptically polarized. Ellipsometry is a model-based technique; the refractive index is not measured directly. Instead, a model is proposed which assumes a certain index which, in turn implies values of psi and delta; these parameters describe the elongation and tilt of the ellipse, respectively. If the implied values closely match the experimental values, confidence is placed in the model. In single-wavelength ellipsometry, the model assumes a homogeneous, nonscattering layer; thickness must be determined independently. From the measured values of psi and delta at various angles of incidence, an equation is solved to obtain the refractive index.

VASE allows for more detailed modeling, allowing incorporation of thickness, voids, thickness inhomogeneities, graded index layers and surface roughness into the model. Commercially available software allows an approximate model to be constructed; selected parameters can then be fed into an iterative curve fitting program and varied to obtain the best match with the experimental data. Values obtained in this way must be physically realistic and not be excessively correlated with other curve fitting parameters.

EXPERIMENTAL

Sample preparation Films of medium thickness (0.2-2μm) were grown to determine effects of wavelength and angle of incidence on **n**. Silicon substrates were chosen for their high reflectivity in the visible region, large refractive index mismatch with the polymer films, well characterized optical properties, and ready availability of highly-polished samples. 2cm x 2cm squares of <111> p-type were flown clean with dry nitrogen before use. The thickness of the native oxide layer on each substrate was measured by spectroscopic ellipsometry at ten different points; the average thickness of the oxide layers in these experiments ranged from 1.8nm to2.5nm, with a standard deviation in each case of about 0.3nm.

Parylene N, Parylene C and Parylene D, the three commercially available precursors, were purchased from Specialty Coatings, Inc. and used to grow PPX, PPX-C and PPX-D, respectively. About four grams of the precursor were weighed and packed into a ceramic boat, then degassed at 0.28 Torr for one hour before use. Each deposition lasted thirty minutes; monomer partial pressures varied from run to run, yielding a range of final film thicknesses. The base pressure during each deposition was 0.275 ± 0.005 Torr. The homemade deposition chamber was a 75mm diameter cylinder wrapped in tubing attached to a constant temperature bath. Samples were clamped vertically in the center of the tube, with the polished side perpendicular to the flow direction. Thirty-two samples of PPX were grown, including several samples thinner than 100nm; these were used for refractive index vs. thickness studies in the region where substrate effects cannot be ignored. Film thicknesses ranged from 36nm to 1556nm. Seventy-one samples of PPX-C were grown with thicknesses ranging from 580nm to 1453nm. Thirty-nine samples of PPX-D were grown with thicknesses ranging from 201nm to 842nm.

Before beginning a deposition, the thermal cleavage furnace was allowed to heat up while the deposition chamber stabilized at a chosen temperature. A vacuum was then pulled and the liquid nitrogen cold trap filled. A valve between the dimer sublimation chamber and the thermal cleavage furnace was kept opened to reduce the pressure in the sublimation chamber; the valve was then reclosed until the proper sublimation temperature was reached, at which point the valve was opened and deposition began. The depositions of PPX were carried out at sublimation temperatures from 95°C to 138°C. The thermal cleavage furnace was maintained at 620°C; the temperature between the furnace and the deposition pipe was maintained above 120°C. The deposition temperature was 18°C. Growth rates varied from 1.20nm/min to 51.9nm/min. PPX-C was grown at sublimation temperatures from 110°C to 138.5° ± 0.5° C. The thermal cleavage furnace was maintained at 620°C; the temperature between the furnace and the deposition pipe was maintained above 150°C. The deposition temperature was 27°C; growth rates varied from 19.3nm/min to 48.4nm/min. PPX-D was grown at sublimation temperatures of 110°C to 145°C; the thermal cleavage furnace was maintained at 620°C and the temperature between the furnace and the deposition pipe was maintained above 150°C. The temperature of the deposition pipe was 40°C throughout the deposition. Growth rates varied from 6.7nm/min to 28.1nm/min.

Perfluorooctyl methacrylate (PFOMA) was purchased from Monomer Polymer and sublimed at 54°C with varying partial pressures of DPXC, resulting in copolymers with varying compositions. As expected, lower partial pressures of PX-C monomer resulted in polymers with higher PFOMA concentrations and lower refractive indices. Lower-index copolymers were grown at the expense of growth rates, which are determined by the partial pressure of PX-C; decreasing the PX-C partial pressure allowed more PROMA to be incorporated into the film while reducing the rate of initiation. Even small amounts of PFOMA in the films reduced the refractive index; x-ray scattering measurements demonstrate they reduce the crystallinity of the films, thereby reducing optical density^2. Here, we present only the results from our lowest-index film. The DPXC sublimation temperature was 95°C and deposition lasted one hour. The deposition temperature was 16°C and the growth rate 4.2 nm/min, yielding a final thickness of 252nm.

After growth, each film was annealed for twelve to fifteen hours at 106°C and 0.28 Torr; the temperature was then allowed to fall back to room temperature over a period of two hours before the sample was returned to atmospheric pressure. The annealing step was performed to rid the film of unreacted monomer and other impurities as well as reducing local variations in density and thickness. Lower growth rates could lead to higher crystallinity or ordering of the system; the annealing step presumably reduced variations in ordering due to growth rate as well.

Analysis Films were measured in a variable angle spectroscopic ellipsometer, purchased from J. Woollam Company. Samples were measured in the wavelength range 400-1000 nm in 2nm increments at incident angles from a line normal to the plane of the film ranging from 30 to 80 degrees in ten degree increments. The instrument measures the ellipsometric parameters psi and delta; each data point was the average of twenty measurements. The measurement spot was about 1mm x 3mm, though dependent on the angle of incidence. Each homopolymer sample was measured at one point. We grew several different compositions of the copolymer; only the sample with the lowest index is presented here. This sample was measured four times in order to gather statistics.

RESULTS AND DISCUSSION

Several models were attempted for each material. Both birefingent and isotropic models were attempted, as were thickness nonuniformities, surface roughness, and interfacial layers between the SiO_2. Most models were rejected due to either poor fit to the experimental data and/or excessively correlated variables. For all films, the best results were from a simple model: a bottom layer of polished silicon, with optical constants as reported by Palik[14]; above that was layer of SiO_2 whose thickness was determined before depositing the films, again with optical constants reported by Palik; and an uppermost layer assumed to be a birefringent, homogeneous, nonuniform layer of polymer which followed Cauchy dispersion relations both parallel to and perpendicular to the plane of the film. The Cauchy relation is a phenomenological equation:

$$\mathbf{n} = A_1 + A_2/\lambda^2 + A_3/\lambda^4 + \ldots$$

where the A_i are constants and λ is the wavelength. Because of excessive correlation (absolute value > 95%) between the values of A_2 and A_3, we used only the first two terms in the Cauchy equation, assuming $A_{3,4,\ldots\infty} = 0$. We assumed there was no absorption in this wavelength range. This assumption is valid; transmission spectra in the literature show immeasureably small absorption or scattering for wavelengths longer than 360nm[1,13]. Thickness nonuniformities determined by curve fitting were usually less than 3%.

Approximate values for the thickness, Cauchy constants and thickness nonuniformity were fed into the curve fitting program. Different sets of starting parameters were used for each model to ensure that the curve fitter was falling into an absolute, rather than local, minimum in mean squared error. The models were in excellent agreement with the experimental data; an example is shown in figure 3. The mean squared error (MSE) in psi and delta between the model and experimental data in this figure is approximately twenty; most fits were better than this. Any spectrum which had a MSE > 20 was rejected. None of the fit parameters showed excessive correlation.

Refractive index vs. wavelength Each model generated two sets of extrapolated Cauchy dispersion constants, for light parallel and perpendicular to the film. Figure 4 shows the refractive indices in the film plane of the three annealed homopolymers as a function of wavelength; figure 5 shows the same information perpendicular to the film. Error bars in each figure represent 95% confidence levels. The Cauchy constants obtained are listed in Table 1. Values of **n** for wavelengths of 589.9nm and 633nm are listed in Table 2; the values are close to other reports in the literature[1, 15].

Figure 6 shows the indices of the PPX-C/PFOMA copolymer both in the film plane and perpendicular to the film plane. Figure 7 shows typical ellipsometric data and fit for the copolymer; the mean squared error in this example was 7.13. The composition of the copolymer was not measured, as the film was too thin for accurate readings by wavelength dispersive analysis.

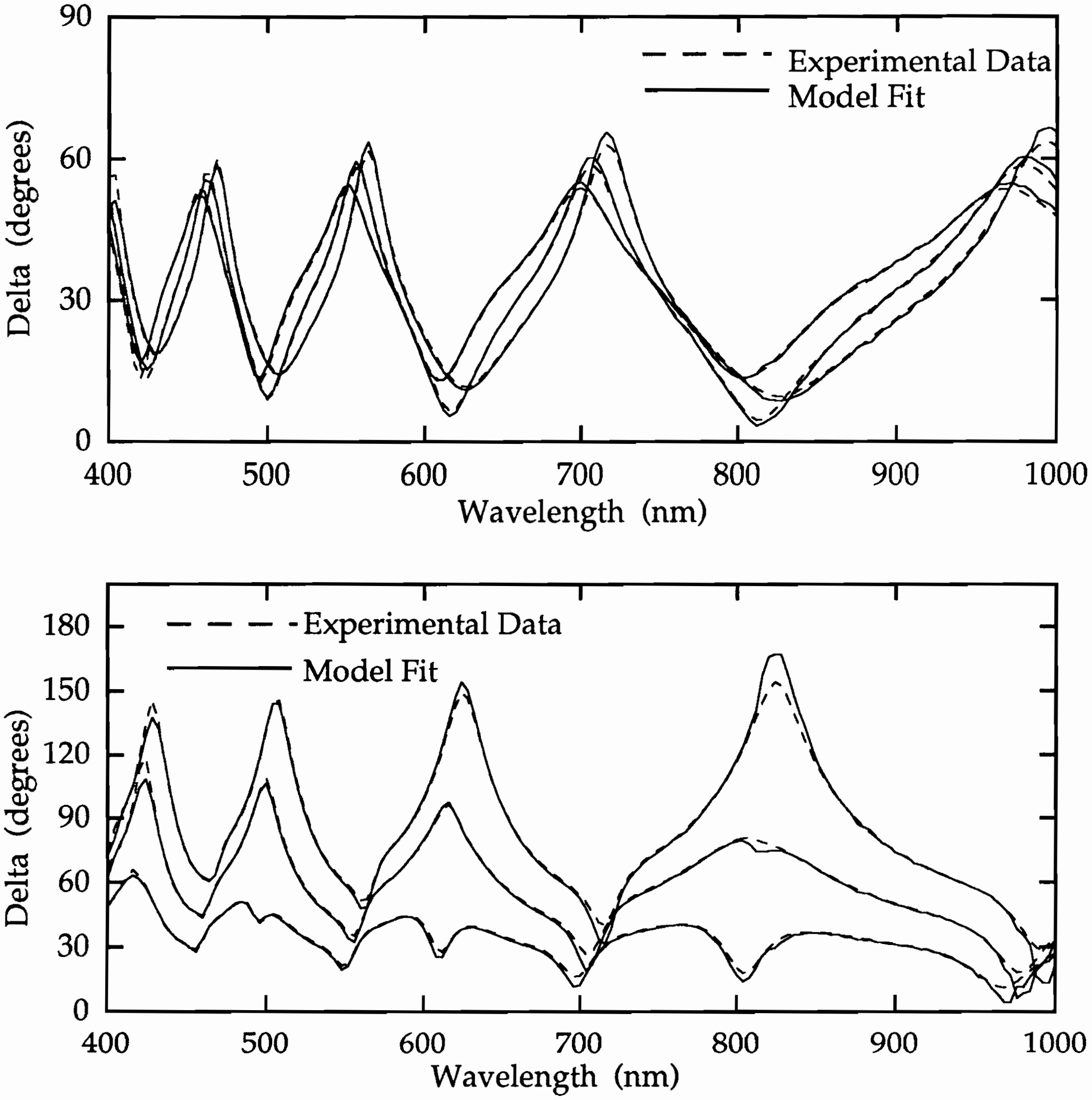


Figure 3: Typical match of ellipsometric model to data; mean squared error of 19.84 in this example. Top graph: Psi; Bottom graph: Delta. Curves correspond to angles of incidence of 60°, 70° and 80°. Solid lines: Model; Dashed lines: Experimental data.

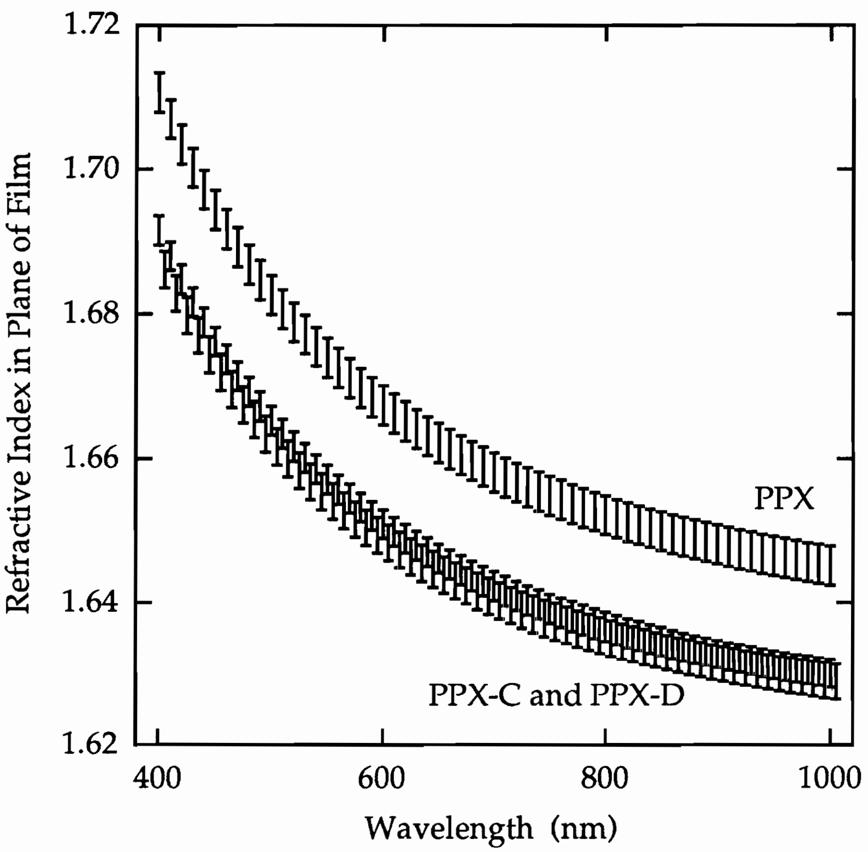


Figure 4: **n** vs. wavelength for PPX, PPX-C and PPX-D in plane of film; error bars are 95% confidence levels.

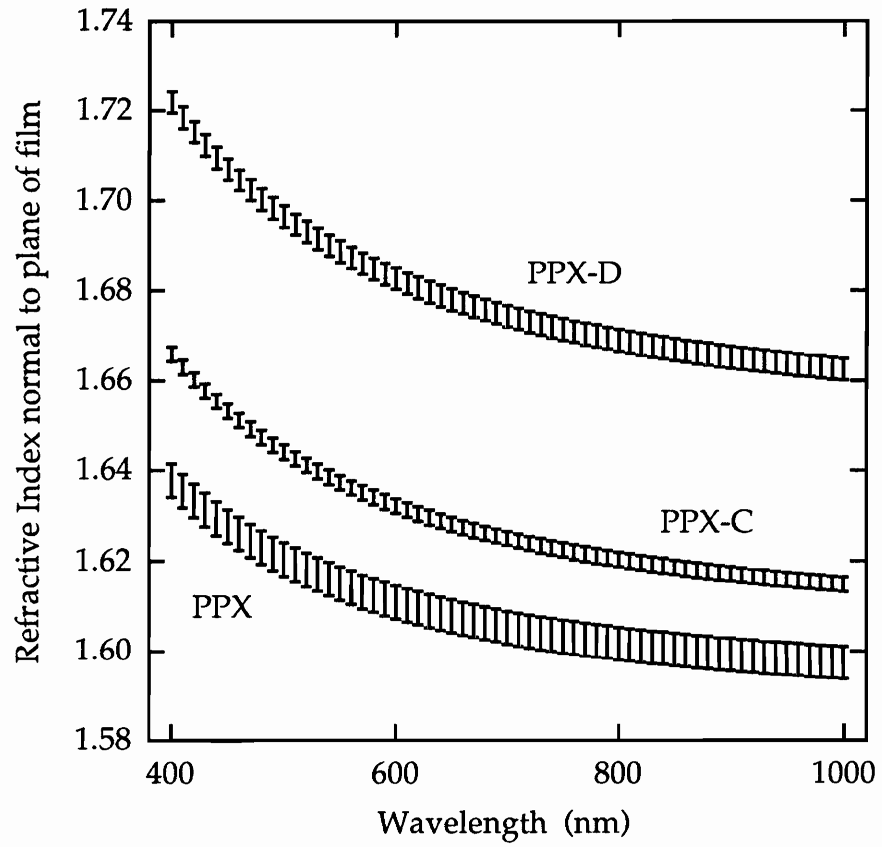


Figure 5: **n** vs. wavelength for PPX, PPX-C and PPX-D perpendicular to plane of film; error bars are 95% confidence levels.

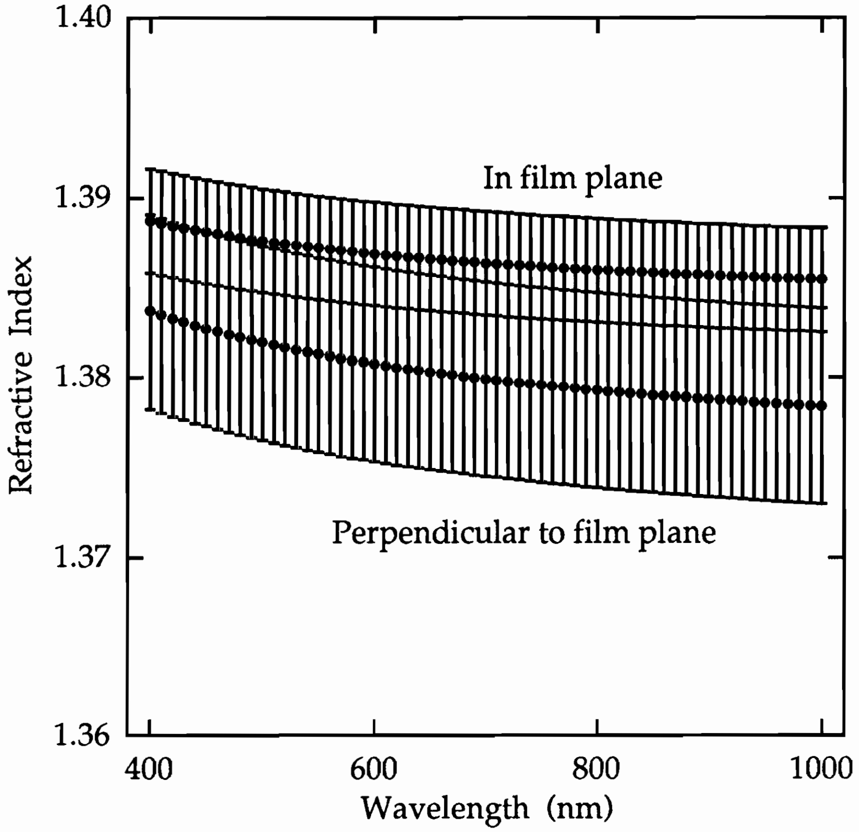


Figure 6: **n** vs. wavelength for PPC-C/PFOMA copolymer, in plane of film and perpendicular to plane of film. Error bars are 95% confidence levels.

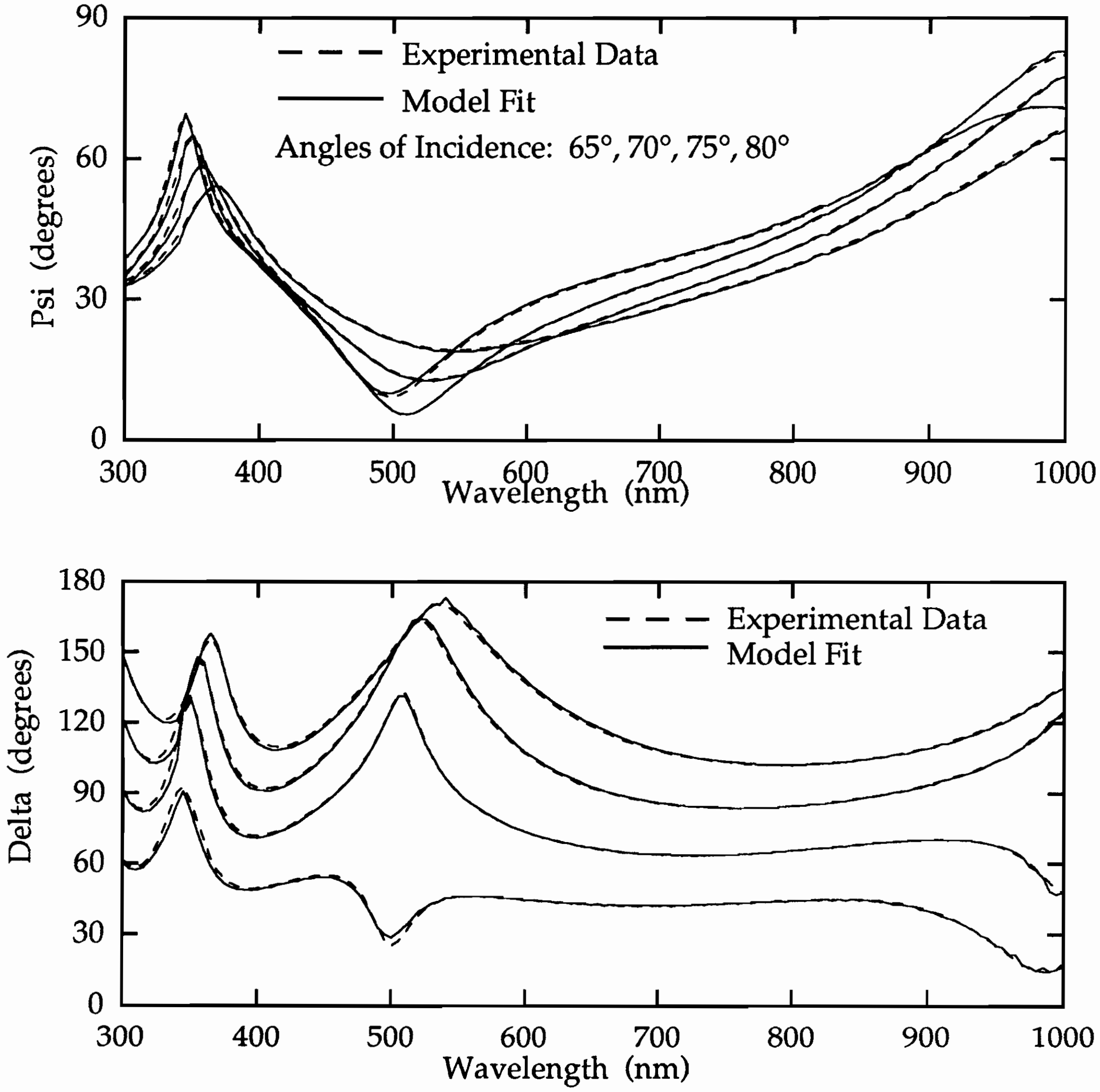


Figure 7: Ellipsometric data and model for typical PPX-C/PFOMA scan. Mean squared error of 7.81. Top graph: Psi; Bottom graph: Delta. Curves correspond to angles of incidence of 50°, 60°, 70° and 80°. Solid lines: Model; Dashed lines: Experimental data

In previous studies of 2 micron thick samples, however, a film with 32 mol% PFOMA had a refractive index at 589.9nm of 1.482[2]. Therefore, we conclude that the mole fraction of PFOMA in the films presented here was well in excess of 32%. We also note the thicker films were somewhat cloudy; the thinner film in this study was highly transparent. Further studies of these films are being carried out.

The similarities in **n** shown in figure 4 demonstrate that the polyparaxylylenes alone are poor candidates for the fabrication of visible-region waveguides. Although there are small differences in index, they are much smaller than the values published previously for incident beams perpendicular to the film plane. The extremely low values of refractive index for the copolymer, on the other hand, demonstrate the wide range of properties achievable by chemical vapor copolymerization. Successful fabrication of polymeric waveguides or antireflection coatings by CVD almost certainly requires chemical vapor copolymerization.

Refractive index vs. angle of incidence The values listed in Table 2 were extrapolated during curve fitting to angles of 0° and 90° from a line normal to the plane of the film; the actual measurements were made at angles intermediate to the two extremes. The only previously reported birefringent behavior was for PPX[15]; the values reported for **n** in the plane and perpendicular to the plane of the film were 1.668 and 1.592, respectively, at 589.9nm. This is confirmed by our study, though we found slightly higher values normal to the film plane. PPX-C and the copolymer show a weak birefringence and PPX-D exhibits a strong positive birefringence. We believe this is the first report of the positive birefringence of PPX-D.

Refractive index vs. thickness Figure 8 shows the refractive indices of PPX at 632.8nm as a function of film thickness. For film thicknesses ranging from 44nm to 1556nm, there was no statistically significant refractive index dependence on film thickness. The two thinnest samples, with approximate thicknesses of 38nm and 36nm, showed poor matches between the experimental data and models. The films were examined under SEM and found to be continuous; this is consistent with earlier work from Spivak and Ferrante, who found films as thin as 29nm were pinhole-free[16]. Figure 9, an SEM photograph of the thinnest film sputtered with gold and peeled from the substrate, shows the film is continuous. We cannot explain the poor ellipsometric results at this time. Though we only studied PPX, it is reasonable to assume the other materials do not have significant thickness dependence on optical properties.

SUMMARY

A new copolymer is introduced which greatly extends the range of optical properties available by chemical vapor deposition of polymeric films. Variable angle spectroscopic ellipsometry was used to determine the optical dispersion and birefringence of the copolymer and the three commercially available homopolymers. The refractive indices perpendicular to the film plane are in agreement with earlier published reports; however, the refractive indices in the film plane are very similar among the three commercially available homopolymers. This does not allow the fabrication of efficient waveguides. The refractive index of the copolymer is much lower than for

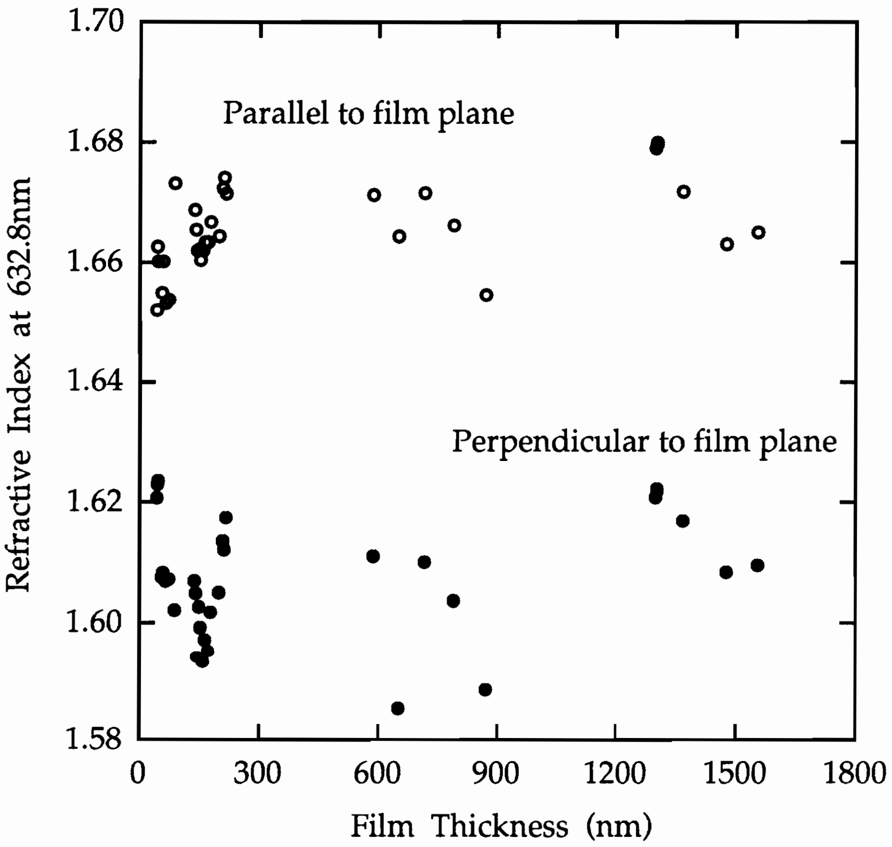
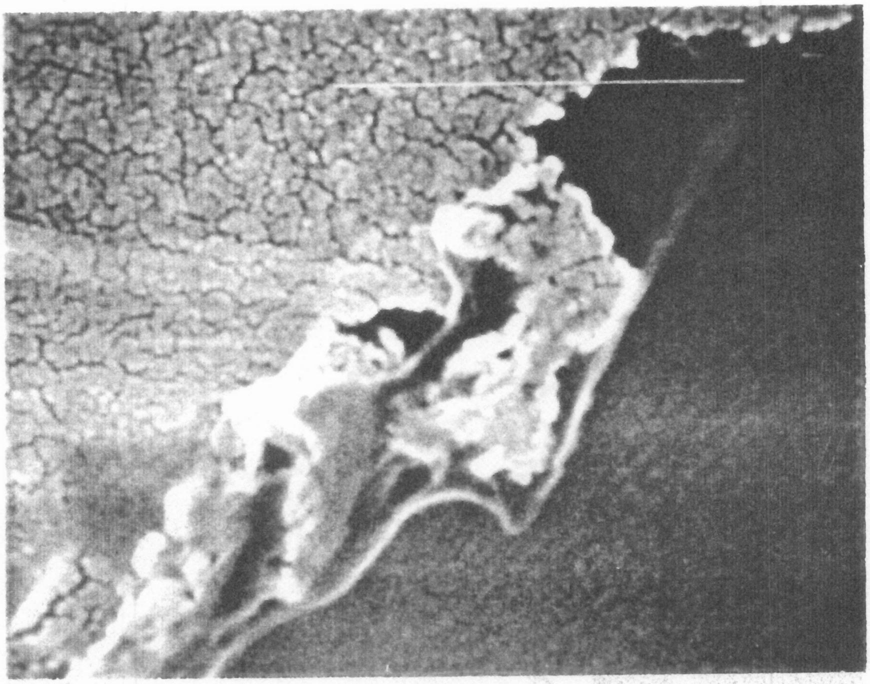
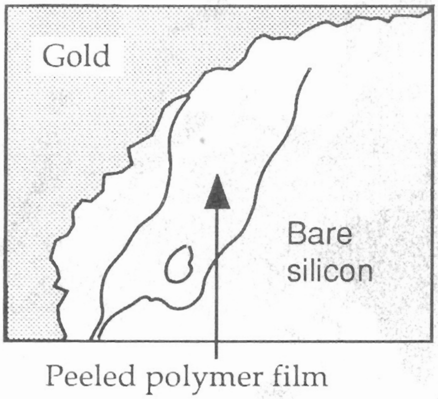


Figure 8: **n** vs. thickness in PPX

Figure 9: SEM micrograph of gold-coated, peeled 36nm thick PPX film; photo shows film is continuous when very thin.





the homopolymers, however, which would allow large gains in device performance. The birefringence is in agreement with earlier reports for PPX; the birefringence of PPX-C and PPX-D are reported for the first time. PPX-D, unlike the other three materials, exhibits positive birefringence. Refractive index was independent of thickness for PPX samples measured in the thickness range 44-1556nm.

ACKNOWLEDGEMENT

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Table 1

Cauchy dispersion constants of annealed films

$\mathbf{n} = A + B/\lambda^2$, λ in μm

Errors are 95% confidence intervals

	In plane of film		Perpendicular to plane of film	
Material	A	B	A	B
PPX	1.632 ± .0044	.013 ± .0010	1.592 ± .0051	.0070 ± .0011
PPX-C	1.618 ± .0018	.0117 ± .0001	1.605 ± .0016	.0097 ± .0001
PPX-D	1.618 ± .0022	.0109 ± .0003	1.651 ± .0047	.0113 ± .0009
Copolymer	1.383 ± .0044	.002 ± .0011	1.375 ± .0056	.0035 ± .0009

Table 2

Refractive indices, **n**, at λ =632.8nm

Errors are 95% confidence intervals

Material	In plane of film		Perpendicular to plane of film	
	λ=589.9nm	λ=632.8nm	λ=589.9nm	λ=632.8nm
PPX	1.665 ± .0031	1.669 ± .0031	1.609 ± .0037	1.612 ± .0037
PPX-C	1.647 ± .0020	1.652 ± .0020	1.629 ± .0016	1.633 ± .0016
PPX-D	1.645 ± .0025	1.649 ± .0025	1.678 ± .0024	1.683 ± .0024
Copolymer	1.389 ± .0029	1.389 ± .0029	1.384 ± .0054	1.385 ± .0054

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CHAPTER 5

A New Method for Fabricating High Performance Polymeric Thin Films by Chemical Vapor Polymerization

Justin F. Gaynor, J. Jay Senkevich and Seshu B. Desu

ABSTRACT

A vacuum deposition method is presented in which polymeric films are grown from paraxylylene and a vinylic comonomer chosen for desirable properties. The concentration of paraxylylene in the final copolymer is negligibly small if proper deposition conditions, presented here for the first time, are employed. Films deposited above the "ceiling temperature" of paraxylylene with n-phenyl maleimide, for example, showed thermal stability and FTIR spectra nearly identical with homopolymers of poly(n-phenyl maleimide). Different rate limiting steps are proposed to explain film composition; paraxylylene is under surface reaction control, while the comonomer obeys mass flow control. This results in a deposition environment extremely rich in comonomer. Growth rates and compositions were consistent with predictions. The initiation reaction did not appear different than for homopolymerization of paraxylylene. The general method presented here, with proper choice of comonomer, allows fabrication of films limited above all by the comonomer employed.

A New Method for Fabricating High Performance Polymeric Thin Films by Chemical Vapor Polymerization

Justin F. Gaynor, J. Jay Senkevich and Seshu B. Desu

INTRODUCTION

The chemical vapor deposition (CVD) of inorganic films has attained great technological and commercial importance. The inherent advantages of CVD, along with the growing importance of thin polymer films for diverse applications, suggest a general scheme for chemical vapor polymerization (CVP) would find rapid acceptance in industry. In this paper, the requirements for chemical vapor polymerization are briefly reviewed, as is the single class of polymers, the polyparaxylylenes, which have been deposited this way. A method is proposed for chemical vapor copolymerization (CVcP) in which the resultant film is composed predominantly of comonomer. The method makes testable predictions, which are confirmed experimentally.

CVP has many advantages over other methods of polymer film deposition[1-7]. Because of the high surface mobility of monomer compared to high polymer, better penetration into troughs or porous surfaces can be achieved. The absence of solvents allows the deposition of smooth, pinhole free coatings of exceptional purity. There is no liquid intermediate phase between the gas and solid, so problems due to surface tension, such as pulling away from corners, are avoided. Finally, CVP, which is carried out in an isolated vacuum environment, eliminates the environmental hazards associated with solvent-based processing.

CVP of chain type polymers requires the following:

1) Initiation must occur exclusively on the surface.
2) The rate of propagation must greatly exceed the rates of initiation and termination.
3) The mobility of monomers on the surface must be high.
4) Monomers must be stable under deposition and sublimation conditions.

Despite the seeming simplicity of these requirements, CVP of only one class of polymers, polyparaxylylene (PPX) and its substituted analogues, has thus far been reported. The reaction pathway of the commercially employed Gorham method is shown in figure 1, and is described in detail in the literature[3,4,6,8-10]. The starting material, di-cyclo-paraxylylene, is sublimed under vacuum and flows down a pressure gradient into a furnace at 600°C, where the molecule cleaves into two paraxylylene (PX) monomers. The monomers then enter a reaction chamber near room temperature. Initiation occurs when three monomers react to form a trimer diradical, so:

$$\text{rate of initiation} \propto K_i[M]^3$$

where K_i is the initiation rate constant and [M] is monomer concentration[11,12]. The concentration is high enough for appreciable initiation only after adsorption (often misnamed "condensation" in the

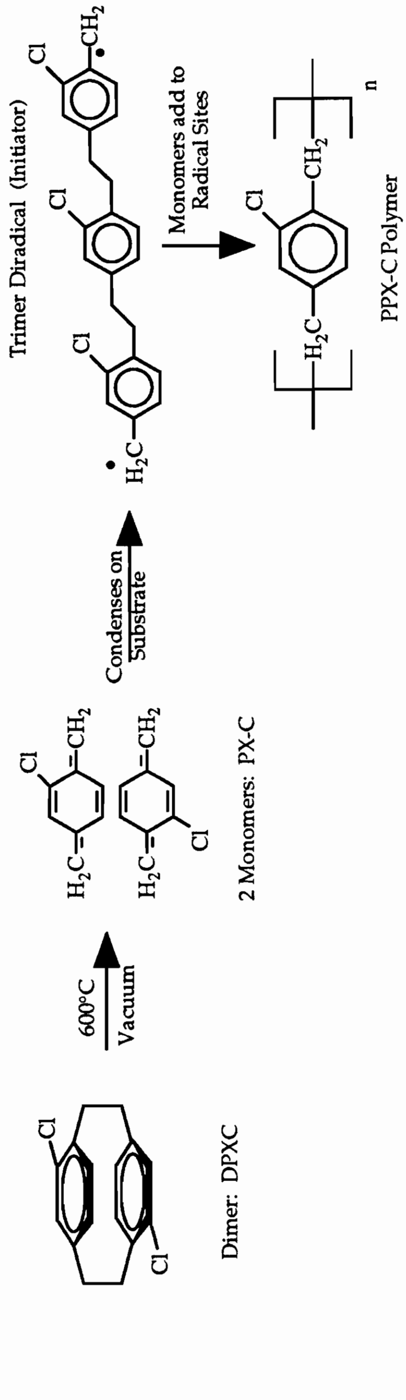


Figure 1: Reaction pathway for parachloroxylylene (PX-C) polymerization.

literature) on the substrate, ensuring no polymerization occurs in the gas phase. Once the diradical is formed, simple radical addition takes place at a rate proportional to monomer concentration, so propagation occurs much more rapidly than initiation. Typical deposition conditions result in high polymer with about 2000-3000 repeat units per molecule[3]. The polymerization terminates when the free radical reactive site is buried too far in the film for unreacted monomer to reach it. There are no reaction byproducts and side reactions are insignificant.

Recent experiments have demonstrated the addition of a comonomer to the reaction chamber can yield a copolymer; this process may significantly change the properties of the films[12-15]. Polymerization is still initiated by the creation of PX trimer diradicals; either PX or the comonomer, however, can participate in propagation. This process will be referred to as chemical vapor copolymerization, or CVcP. The method to be presented here is a variation of CVcP.

The copolymerization of chain-type molecules has been studied in detail, primarily in solution. In most cases, the final composition of the copolymer is dependent on the composition of the monomer feed and the relative reactivity of the two species. Most comonomer pairs obey the Mayo-Lewis equation, which allows the composition of a copolymer to be predicted from the feed composition[16]:

$$F_1 = \frac{f_1(1+[r_1-1]f_1)}{(r_1+r_2-2)f_1^2+2(1-r_2)f_1+r_2} \qquad (1)$$

where F_i is the mol fraction of monomer *i* in the final polymer, f_i is the mol fraction of monomer *i* in the reaction mixture, and the r_i are the reactivity ratios. These are defined as:

$$r_1 = \frac{K_{11}}{K_{12}}; \qquad r_2 = \frac{K_{22}}{K_{21}} \qquad (2)$$

where the K_{ij} are propagation rate constants. In the general case that $r_1 \neq r_2$, f_i, and thus F_i, change as the reaction progresses. This composition drift does not occur during CVcP, as the monomer feed is in steady state flow; this simplifies the task of growing films uniform in composition. Throughout this paper, we will use the convention that the subscript 1 refers to PX and the subscript 2 refers to the comonomer.

For many applications, most notably those in which high temperature stability is required, high concentrations of comonomer in the film are desirable. Two ways to grow copolymers rich in comonomer are evident in equation 1: either choose a comonomer such that $r_1 << r_2$, or make $f_2 >> f_1$. PX, which is exothermic by approximately 77 kJ/mol during the propagation reaction, is one of the most reactive monomers known through a wide temperature range; there are few, if any, monomers for which $r_2 >> r_1$[17-18].

For most comonomers, then, creating a copolymer with F_2 approaching 1, requires an extremely small fraction of PX in the reaction mixture. This can be accomplished by simply reducing the partial pressure of PX in the reaction vessel. The growth rate is proportional to [PX partial pressure]$^{3/2}$, however, so reducing PX partial pressure reduces growth rates[11].

Another method would be to create an extremely high concentration of comonomer at the growth interface. This could be accomplished, in principle, by using an extremely high partial pressure of comonomer. As the total pressure of gas in the reaction vessel increases, however, the diffusion rate of reactive species from the gas to the surface is reduced; as a result, thickness uniformity, step coverage, pinhole density and defect density suffer. Finally, large, closely-spaced batches become more difficult to process[19]. The approach described in the next section allows a feed ratio extremely rich in comonomer without greatly increasing the total gas pressure or reducing the growth rate.

A NEW METHOD

The number of PX molecules which strike the growth interface is a factor of three to four higher than the number which are consumed; the remainder reenter the gas[11]. The rate limiting step for deposition is the rate at which monomer is consumed by initiation or propagation reactions; this is known as surface reaction control. In many commercial CVD processes, by contrast, the rate limiting step is the rate at which reactive species diffuse to the surface, where they are rapidly and efficiently consumed by reaction[19]. This is known as mass flow control.

If the deposition temperature is below about -60°C, PX will condense on the surface whether it reacts or not[20-27]. Under such conditions, the monomer is obeying mass flow control. The molecules do not rely on surface reactions to adhere to the surface, and the rate at which they deposit is directly proportional to their concentration in the gas. When grown at this temperature, the monomer deposits and is subsequently consumed in either initiation or propagation reactions; some monomer remains unreacted. There is a transition from mass flow control to surface reaction control as the deposition temperature is increased; this is in contrast to most inorganic CVD, where raising the deposition temperature brings about mass flow control.

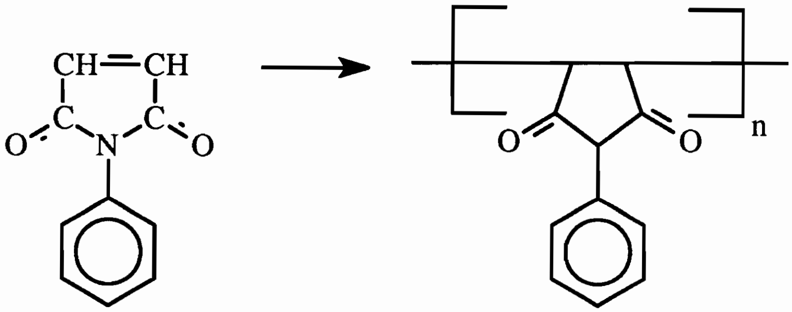
The method presented here is to choose a combination of comonomer and deposition temperature such that PX obeys surface reaction control while the comonomer obeys mass flow control. Under such conditions, the comonomer will condense on the surface, while PX strikes the surface and mostly reevaporates. Some PX, however, will form initiation sites which quickly attack the condensed comonomer. If the deposition temperature exceeds the "ceiling temperature" of PX polymerization, there will be negligibly small amounts of PX in the final film. (The "ceiling temperature," as used here, is not a true ceiling temperature but rather the temperature at which the residence time of monomers on the surface is so small the rate of polymerization becomes impractically small. We follow the temperatures suggested by Gorham[3].) Under such conditions, PX can also participate in propagation reactions, of course, but its relative concentration on the surface is very small; the final polymer will be composed almost entirely of the comonomer. If the comonomer is deposited too quickly, though, a large fraction of it will be unable to polymerize. In practice, it is necessary to optimize conditions such that the final copolymer is rich in comonomer while allowing almost all the comonomer to react.

Limitations The lightest of the paraxylylenes is unsubstituted PX; this has a "ceiling temperature" of about 30°C. Growth of films very rich in comonomer is limited, then, to comonomers which condense above 30°C at the deposition pressure employed. Most common monomers are too volatile to form films by this method. In many cases, however, heavier analogues of a chosen monomer can be synthesized without greatly affecting the desired properties of the final polymer.

To demonstrate the method, a copolymer extremely rich in comonomer was synthesized with very little unreacted comonomer at 40°C, using n-phenyl maleimide (NPMI) as a comonomer. The structures of NPMI and poly(NPMI) are shown in figure 2.

EXPERIMENTAL

A copolymer where the comonomer adds by mass flow control is readily distinguishable from copolymers in which both monomers obey surface reaction control. The presence of unreacted comonomer, anomalously high growth rates and anomalously high comonomer content



n-phenyl maleimide (NPMI)

Figure 2: Structures of n-phenyl maleimide (NPMI) and poly(NPMI).

are all consistent with comonomers obeying mass flow control. In this section, experiments to measure growth rate and composition profiles in a long reaction chamber are described; this method has been described in more detail elsewhere[12]. The purpose of each experiment is presented in Results and Discussion.

The reactor All samples were grown in a cylindrical chamber designed for obtaining a wide range of data. A schematic of the homemade reactor is given in figure 3. The deposition tube was 35cm long and 7.62cm in diameter; temperature uniformity was ensured by wrapping the entire length tightly with 0.25 inch diameter copper tubing connected to the chamber by thermally conductive epoxy. The tubes leading into and out of the deposition chamber were both 5.04cm in diameter. Water pumped through the copper tubing from a constant temperature circulating bath allowed various deposition temperatures. Thermocouples were attached to the outer wall of all sublimation, furnace and deposition chambers to monitor temperature.

Homopolymers. Cyclo-di-paraxylylene and cyclo-di-parachloroxylylene were purchased from Specialty Coatings and used to grow homopolymers of PPX and PPX-C. The difference in molecular weight of the two species allows different deposition rates at a given temperature; PPX-C can be grown at temperatures up to about 90°C, while PPX cannot be grown at temperatures above about 30°C. The compounds were used as received but outgassed at 0.28 Torr for two hours before use. For ellipsometric studies, each homopolymer was grown on three clean, polished silicon strips, 10cm x 3cm, placed horizontally end-to-end through the length of the reactor. For FTIR studies, samples were grown on 2cm x 2cm squares of clean, undoped silicon,

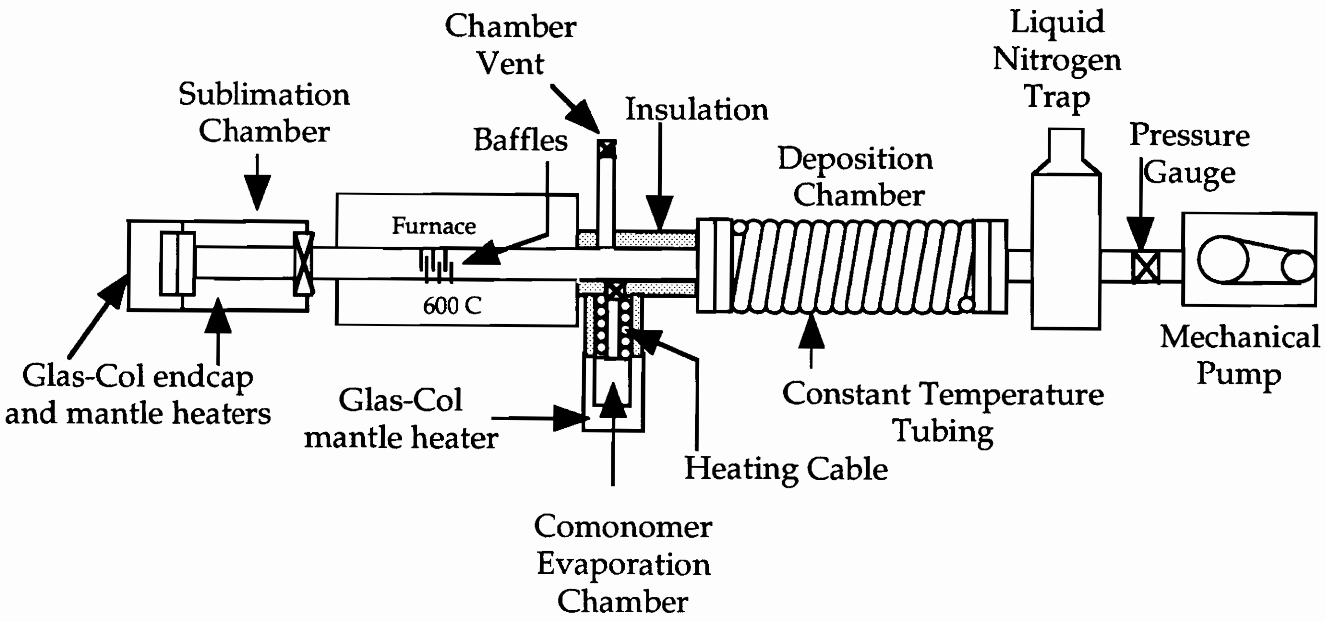


Figure 3: Deposition equipment for chemical vapor copolymerization.

polished on both sides. All substrates were blown dry with compressed dry nitrogen before use.

Typical deposition conditions for PPX were a dimer sublimation temperature of 120°C, with deposition temperatures as indicated in the Results and Discussion section. Dimer was packed and weighed in ceramic boats; approximately four grams of dimer was loaded into the sublimation chamber per run. Substrates were loaded onto an aluminum sample holder with the same length as the interior of the deposition chamber. After loading the samples in the chamber, the furnace and water bath were heated to 620°C and the deposition temperature, respectively. The sublimation chamber was heated to 70°C. These temperatures were held for 90 minutes to allow thermal equilibrium before pulling a vacuum and filling the liquid nitrogen trap. The base pressure during each deposition was 0.103 ± 0.005 Torr. After vacuum was pulled, a valve isolating the sublimation chamber was opened, evacuating the sublimation chamber, and closed again. The sublimation chamber was then warmed to the desired temperature. The sublimation valve was opened, beginning deposition. Deposition ended when the valve was closed. Temperatures were allowed to fall back to near room temperature before the vacuum pump was isolated and the reaction chamber vented.

Copolymers of PPX-C and NPMI NPMI (>98%; main contaminant n-phenyl succinimide) was purchased from Lancaster. NPMI was chosen because of its high temperature stability, low vapor pressure and ready availability. Though the NPMI was not purified, the polymerization process is, in addition, a distillation process; contaminants are unlikely to deposit under the same conditions as the monomer. A clean silicon substrates, 10cm x 1cm, was placed in the center of the deposition chamber before each run. In each case, the cyclo-di-parachloroxylylene sublimation chamber was maintained at 115°C, the NPMI sublimation temperature at 85°C and the furnace at 620°C.

For each run, approximately 4 grams of cyclo-di-parachloroxylylene and 3 grams of NPMI were weighed into ceramic boats. The NPMI was melted at 100°C and resolidified immediately after placement in the reactor; this was to prevent the vacuum from pulling powder into the chamber at an uncontrolled rate. The same warmup procedure was followed as for homopolymers; the comonomer sublimation chamber was cooled to 50°C after the melting step. After vacuum was pulled and the sublimation chambers evacuated and re-isolated, sublimation temperatures were raised to 120°C for PX dimer and 85°C for NPMI. All temperatures were then allowed to stabilize for twenty minutes before the valves were opened, starting deposition. Deposition times were typically twenty minutes. The unsublimated PX dimer and NPMI were weighed after each deposition to determine the amount of each monomer which entered the chamber.

Analysis Relative elemental compositions for PPX-C-co-NPMI films were determined by wavelength dispersive analysis using a Cameca SX-50 electron probe. The concentrations of chlorine, oxygen, and nitrogen were measured. Electrical conductivity was ensured with a 25nm thick sputtered coating of carbon. A 5nA, 8kV beam, about 500nm in diameter, was rastered through an area of 30μmx30μm. Measurements points were at about 0.5 cm intervals, with five measurements made at each point. The films darkened somewhat during the measurements, each of which lasted 40 seconds. Signal intensities were compared to films of polyvinylchloride, PPX-C homopolymer, and poly(vinyl pyrrolidone). Pressure in the measurement chamber was approximately 1×10^{-10} Torr.

Film thicknesses and refractive indices were determined with a variable angle spectroscopic ellipsometer from J. Woollam Company. Details of the procedure have been published elsewhere, and will be briefly reviewed here[15]. Samples were measured in the wavelength range 400-1000 nm in 2 nm increments and at angles from 65 to 80 degrees in five degree increments from a line normal to the plane of the film. All samples were measured in 0.5cm increments. In this technique, linearly polarized light is incident on the sample; after interaction with the sample, the reflected beam is generally elliptically polarized. The instrument measures the ellipsometric parameters psi, which describes the elongation of the ellipse, and delta, which describes its tilt with respect to the optical axis. Each point was the average of ten measurements. The measurement spot was about 1mm x 3mm. For modeling the data, each film was assumed to be birefringent and transparent; the dispersion relations both perpendicular and normal to the film were assumed to fit the empirical Cauchy equation:

$$\mathbf{n} = A + (B/\lambda^2) + (C/\lambda^4) + \ldots$$

where $\mathbf{n}$ is the refractive index, A, B, C,... are empirically determined constants, and λ is the wavelength. In modelling the data, we used only the first two terms in the series. A birefringent Cauchy model was in excellent agreement with the experimental data. The use of variable angle spectroscopic ellipsometry for measuring CVP films is discussed in more detail elsewhere[15]. The largest systematic error in film thickness was found to be from placement of the sample in the ellipsometer; for this reason, each thickness determination is the average of five measurements, with the sample being removed and replaced between measurements. Standard deviations in thickness among the five measurements were less than 1% in all reported data.

RESULTS AND DISCUSSION

Anomalous growth rate Beach's model for PPX deposition, which assumes surface reaction control, predicts growth rate is proportional to PX partial pressure to the 3/2 power[11]. This has been confirmed in subsequent experiments[12]. Growth rates are limited by the rate at which trimer diradical initiation species are created. If both PX and the comonomer obey surface reaction control, and assuming comonomer does not participate in initiation, then growth rates should still be proportional to the [partial pressure of PX]$^{1.5}$, if differences in molar volumes of the two species are neglected. If the comonomer obeys mass flow control, growth rates should be much higher.

It is difficult to measure the partial pressure of monomer in the reaction chamber due to the tendency for polymer to form on all surfaces. Measuring growth rate profiles for gas flowing through a long uniform cylinder is a more accurate method of determining growth rate dependence on pressure. In this method, reactive gases are fed into a long tube; under surface reaction control, the growth rate profile is determined by the pressure profile within the tube. The radial pressure gradient is negligible, so the pressure profile is produced by the sublimation chamber on one side of the reaction chamber and pump on the other. Pressure can be assumed linear with distance far from the ends of the chamber, so growth rates are expected to decrease with distance, Z, in the tube as $Z^{1.5}$ during homopolymerization. This has been confirmed experimentally[12]. Growth rates of copolymers growing under surface reaction control should not differ from homopolymerization, assuming the molar volumes of the two monomers are approximately the same. If the copolymer obeys mass flow control, growth rates should be much higher in the upstream end of the furnace; further down the tube, after the comonomer has been largely consumed, it will resemble the profile of surface reaction control.

In one experiment, copolymers of PPX-C and NPMI were grown on three silicon substrates at deposition temperatures of 70°C and 40°C; homopolymers of PPX-C were grown at the same temperatures. In figures 4 and 5, the thickness profiles of these four depositions are shown. Three things are immediately recognizable:

1) None of the thickness profiles decrease as $Z^{1.5}$. The assumption that the pressure gradient is linear is valid only far from the ends of the cylinder; in these experiments, data was taken throughout the length of the chamber. The substrate in the center of the tube does show $Z^{1.5}$ dependence.

2) The thickness profiles of the homo- and copolymers are essentially identical at 70°C. This suggests both monomers obeyed surface reaction control.

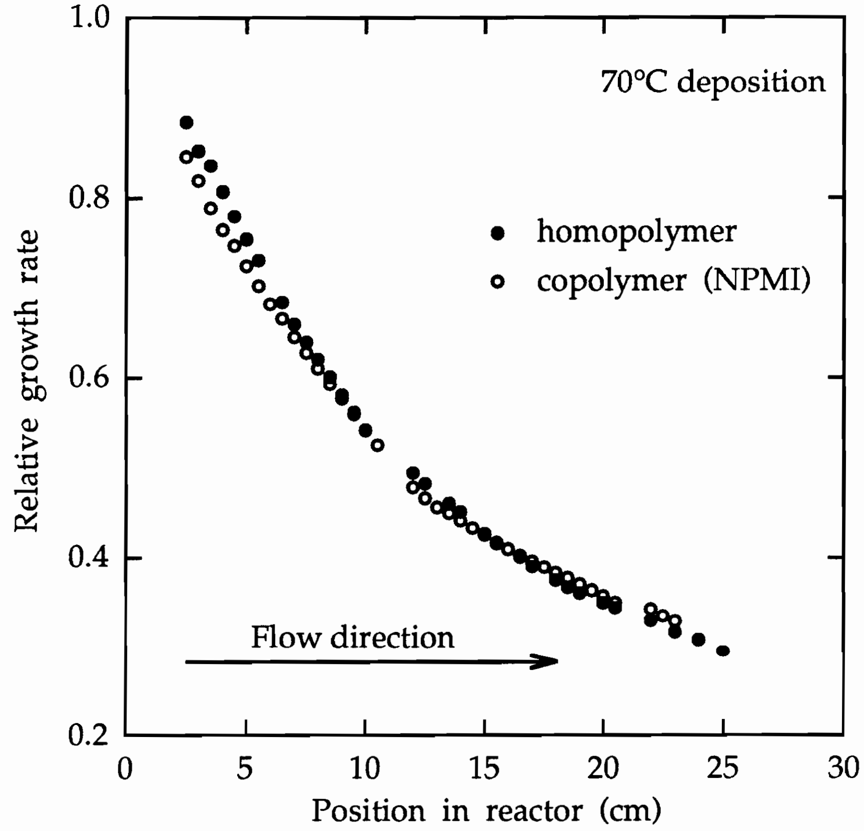


Figure 4: Growth rate profiles of PX-C/NPMI grown at 70°C along length of deposition chamber. Curves are normalized at 23 cm. position.

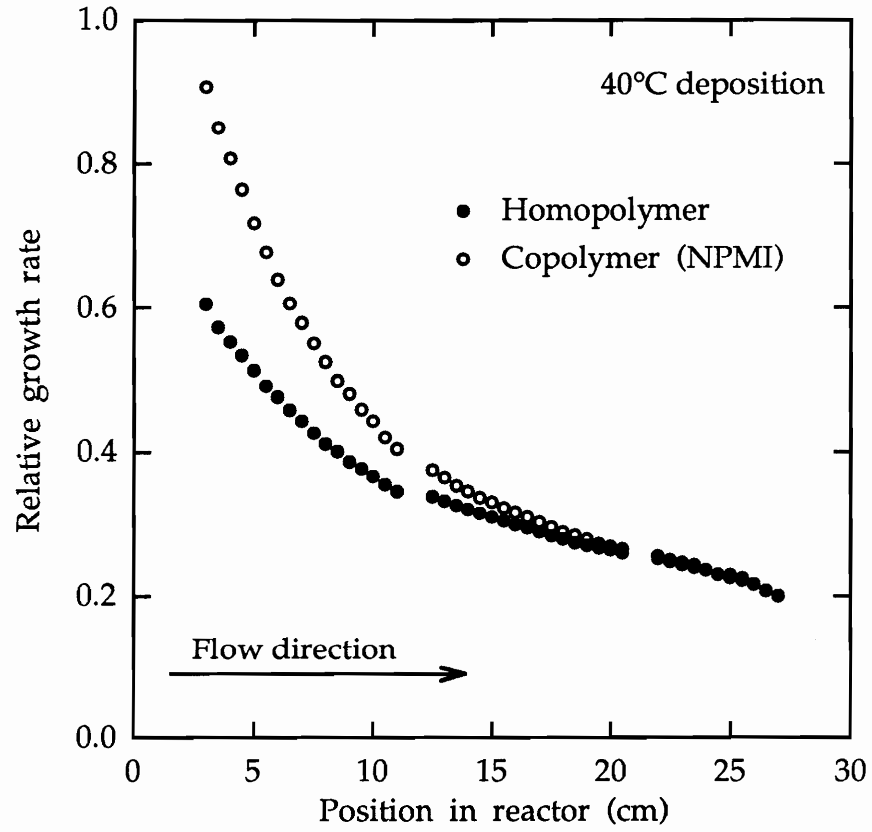


Figure 5: Growth rate profiles of PX-C/NPMI grown at 40°C along length of deposition chamber. Curves are normalized at 25 cm. position.

3) The growth rate of the copolymer upstream is greatly enhanced at a deposition temperature of 40°C, though growth rates downstream are practically indistinguishable from the homopolymer. This suggests the comonomer obeys mass flow control at this temperature.

This interpretation assumes the initiation reaction is the same as in PX homopolymerization. The double bonds in PX, however, have a high electron density, while the double bond in NPMI is very electron deficient. In solution, such monomer pairs may form perfectly alternating copolymers and, in extreme cases, even spontaneously initiate. The composition of such copolymers is approximately independent of feed composition. The considerable composition gradient of these films under surface reaction control, to be discussed in the following section, suggests they are not perfectly alternating. If the electron density effect is not strong enough to induce perfectly alternating copolymerization, it certainly isn't strong enough to create charge transfer complexes, which would be a second initiation mechanism. Therefore, our assumption that NPMI does not change the initiation reaction is probably valid. Additional evidence is provided by figure 4. An increase in initiation rate would be reflected by an increase in growth rate, but the presence of NPMI had no influence on the growth rate profile.

Anomalous comonomer concentration profile Relative composition profiles of the films grown at 70°C and 40°C are shown in figures 6 and 7, respectively. Error bars represent 95% confidence levels. Because absolute compositions could not be determined due to difficulty of obtaining reliable

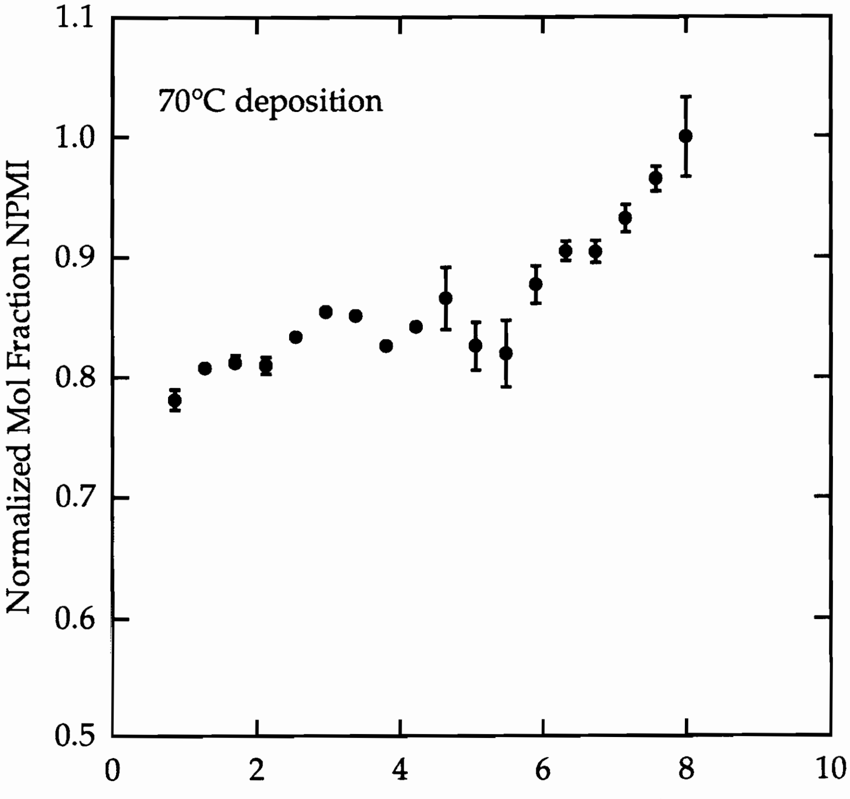


Figure 6: Composition profiles of PX-C/NPMI grown at 70°C along length of deposition chamber. Curves are normalized to maximum NPMI content.

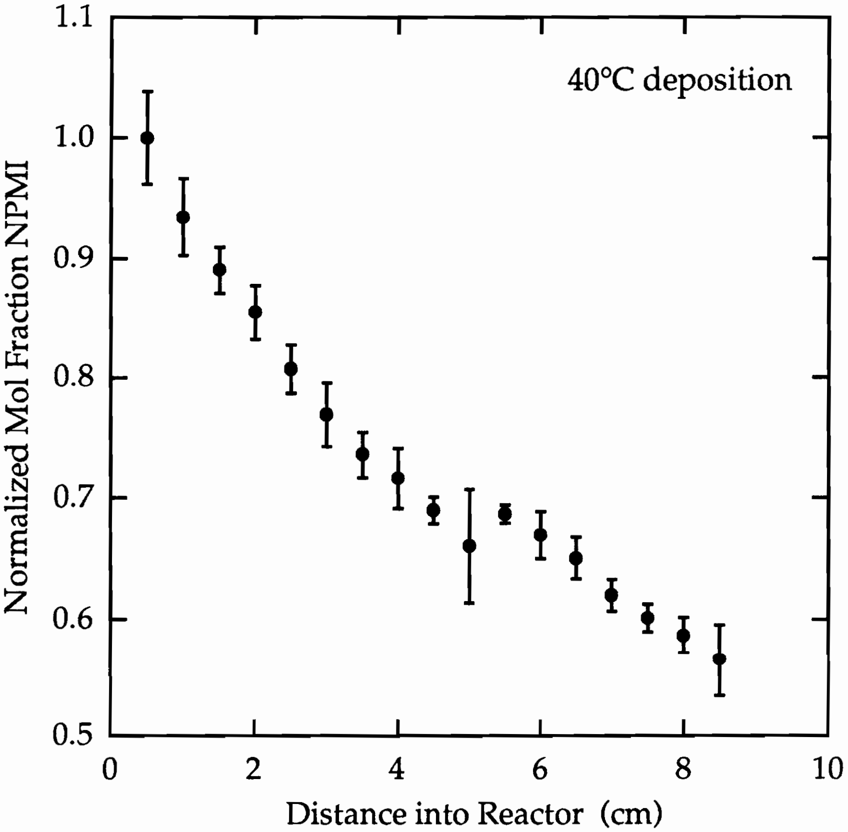


Figure 7: Composition profiles of PX-C/NPMI grown at 40°C along length of deposition chamber. Curves are normalized to maximum NPMI content.

standards and weakness of nitrogen and oxygen signals, they are normalized to maximum NPMI concentration.

The sample grown at 70°C shows an increase in NPMI content with distance into the reactor. This implies the relative concentration of NPMI at the surface increased with distance, which further implies PX-C was consumed more rapidly. This behavior is consistent with the extremely high reactivity of PX-C.

In the sample grown at 40°C, the amount of NPMI in the films drops rapidly with distance. It is extremely unlikely the 30°C decrease in deposition temperature had such a large influence on reactivity ratios; instead, this is further evidence the comonomer condensed under mass flow control before reacting.

Presence of unreacted comonomer FTIR can be used to determine whether NPMI is present in CVcP films, and also whether the NPMI is present as copolymer or unreacted monomer. Strong absorptions at wavenumbers around 1707, 1597, 1500, 1384, and 1183 indicate the presence of NPMI. Earlier reports indicate two large differences in the spectra of unreacted monomer and poly(NPMI). A strong, sharp peak at about 830 wavenumbers disappears; unfortunately, this peak is obscured by a PPX peak at 826 wavenumbers. A smaller but still significant peak at 1147 disappears upon polymerization, while a broader peak appears around 1185 wavenumbers. Films grown under mass flow control should show both the broad peak at 1185 wavenumbers and the narrower peak at 1147 wavenumbers, indicating unreacted monomer amid the copolymer; films grown under surface reaction control should not display the 1147 wavenumbers peak.

Figure 8 shows an FTIR spectrum of a PPX/NPMI film grown at 40°C. The peaks around 3008, 2922, 2854, 1513, 1448 and 1050 wavenumbers can be attributed to PPX. There is a peak at 1147 wavenumbers, as predicted. This film was annealed at 0.275 Torr and 100°C for two hours after measuring the spectrum; these conditions are well below the vapor pressure of NPMI monomer. The spectrum of the annealed film is shown in figure 9. Although the spectrum is largely unchanged, the peak at 1147 wavenumbers has vanished. This provides further evidence the film, though essentially a copolymer, contained unreacted monomer before annealing.

Figure 10 shows a portion of the FTIR spectrum of an unannealed PPX-C/NMPI film deposited at 70°C. At so high a deposition temperature, it was necessary to use PPX-C rather than PPX to obtain reasonable growth rates. The major peaks in the spectrum indicate the presence of both PPX-C and NPMI; it qualitatively confirms NPMI was present in smaller concentrations than the films grown at 40°C. Peaks at 1147 wavenumbers, indicating unreacted NPMI, and at 1185 wavenumbers, indicating adjacent NPMI units in a polymer chain, were both nearly indistinguishable from noise. This suggests a small amount of reacted NPMI, and negligible unreacted NPMI, both predicted by surface reaction control.

Properties of compolymers grown under mass flow control Having shown copolymers can be grown in which the two monomers follow different rate limiting steps, it remains to demonstrate copolymers extremely rich in comonomer are possible. In the profile experiments described in the

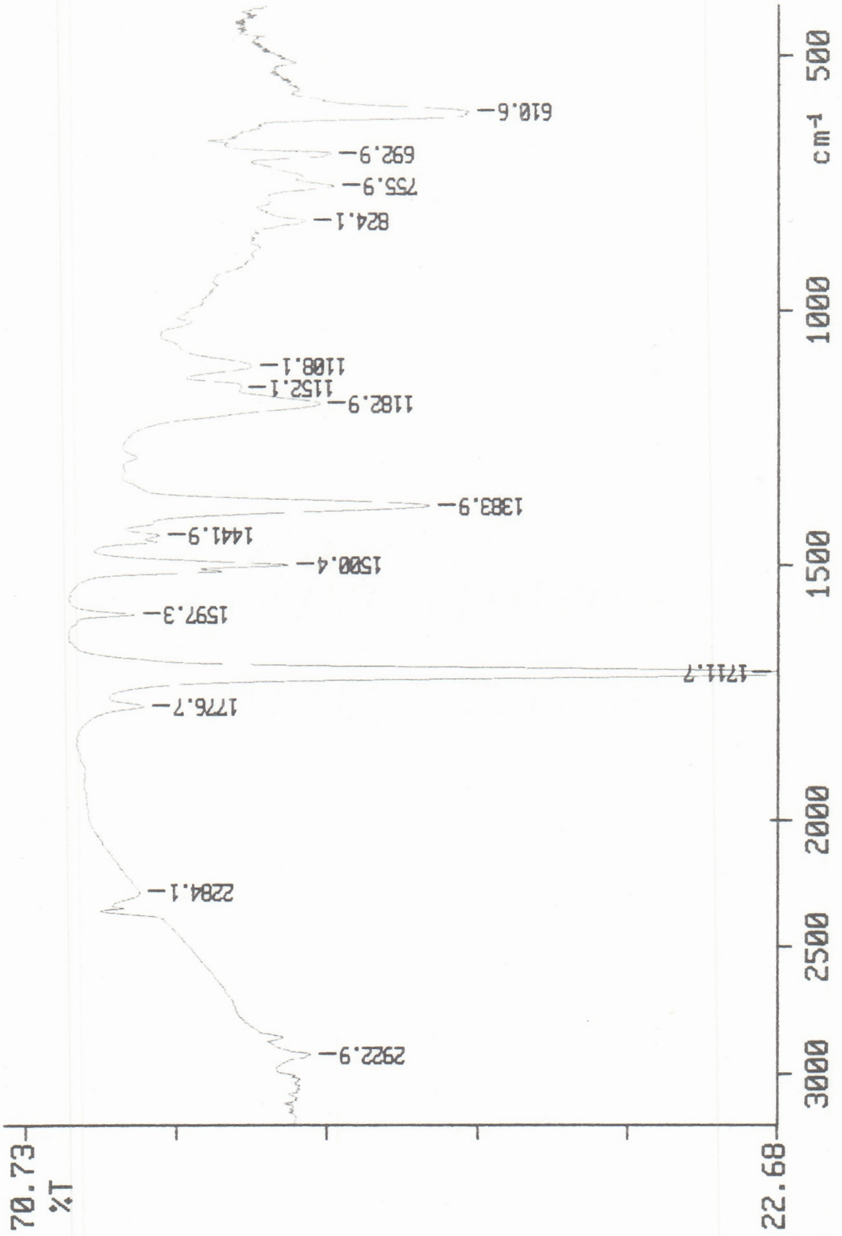


Figure 8: FTIR spectrum of as-deposited PX-C/NPMI film grown at 40°C. Peak at 1152 wavenumbers indicates unreacted NPMI monomer.

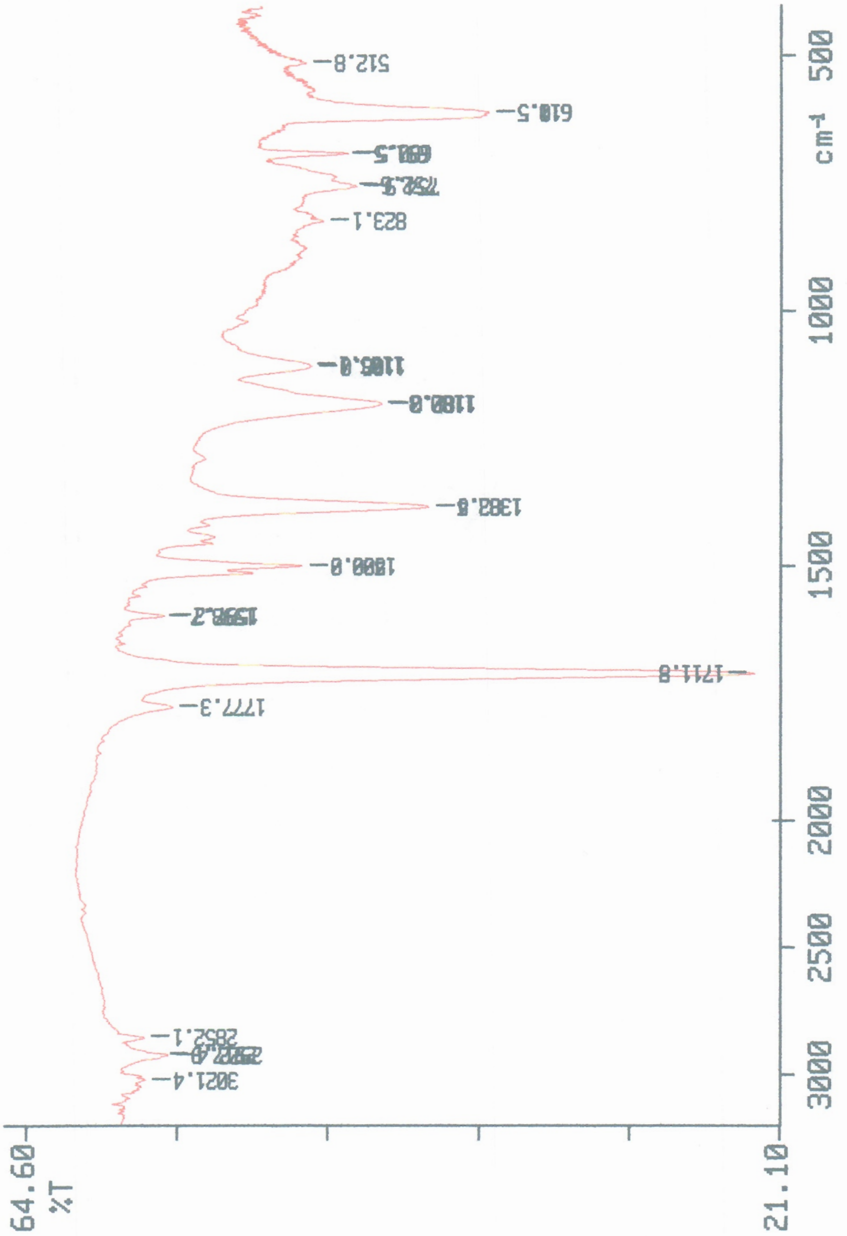


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Figure 9: Same film as in figure 8 after annealing. Peak at 1152 wavenumbers has vanished.

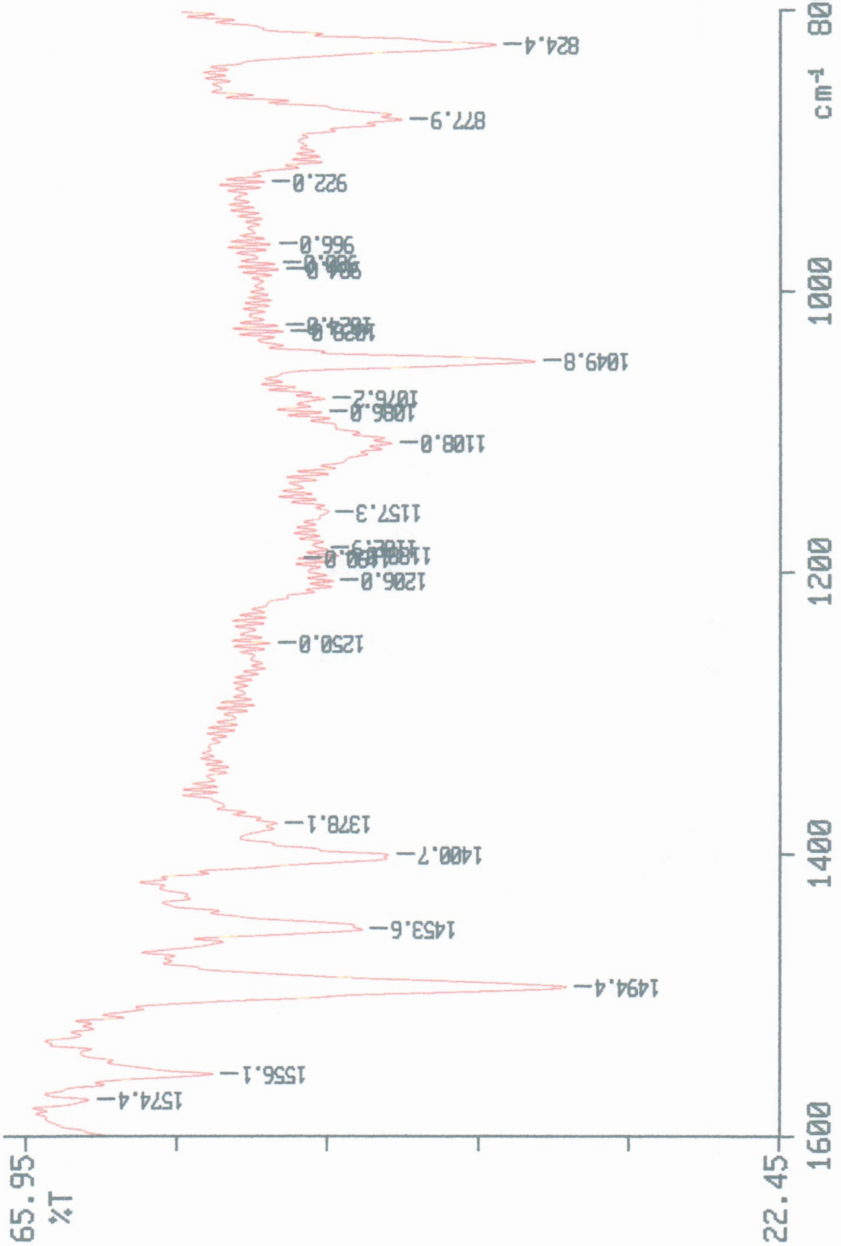

Figure 10: FTIR spectrum of as-deposited PX-C/NPMI film grown at 70°C.

preceding paragraphs, both monomers deposited at an appreciable rate, despite their differing rate limiting steps. To grow copolymers with minimal PX content, it is necessary to reduce the residence time of PX. The "ceiling temperature" of PX polymerization is generally considered 30°C; although not a true ceiling temperature, growth rates are impractically slow and a low molecular weight, grainy material results when it is exceeded[3]. Despite this, we achieved high growth rates (up to 70nm/min) and smooth, conformal films when copolymerizing at 40°C. The highest growth rate of PPX homopolymer under the same conditions was 4.4nm/min, and the resultant material was porous.

The molecular weight of these films was not measured. The data provided here, though, suggests high molecular weight material was produced. First, the rate of PX initiation is very low above the "ceiling temperature"; the very high growth rates and small amount of unreacted monomer are consistent with high molecular weight. Finally, molecular weights could be reduced by chain transfer agents. The deposition environment in vacuum is extremely pure, however, and PX is an inefficient chain transfer agent[6]; therefore, only comonomers which can function as chain transfer agents could form low molecular weight materials.

As mentioned previously, absolute composition could not be measured. The FTIR spectra in figures 8 and 9, though, suggest the film is very rich in NPMI. Although refractive indices of the films were measured, they yielded no insight into composition: The refractive index of the copolymer film at a wavelength of 632.8nm was 1.623 ± .0015 in the film plane and 1.592 ± .0016 perpendicular to the film plane, based on 131 ellipsometric measurements of films varying in thickness from 150nm to 1700nm. The only report of the refractive index of poly(NPMI) of which we are aware places the value at 1.62, although the frequency and orientation were not reported[28]. PPX homopolymer grown near room temperature has indices of 1.665 ± .0027 in the film plane and 1.608 ± .0037 perpendicular to the film plane; errors are 95% confidence levels[15].

The thermal degradation behavior of copolymers is very sensitive to composition. For this reason, we ran TGA spectra of PPX and PPX/NPMI in air. The results of these tests are shown in figure 11. The homopolymer begins losing weight at about 270°C; this behavior mirrors reports in the literature[29-30]. The PPX/NPMI copolymer, on the other hand, shows thermal behavior almost identical to NPMI homopolymer; reports in the literature cite an onset of weight loss at 370°C, with 10% weight lost by 390°C[27]. We cannot explain the small loss in weight between 100°C-150°C at this time, though it appears to be due to contamination after removal from the deposition chamber rather than polymer degradation. From this test, we conclude the copolymer was predominantly NPMI. It appears the method presented here can be employed to grow a wide variety of polymeric films by CVP.

SUMMARY

A method for growing polymeric films by chemical vapor deposition is suggested. Paraxylylene (PX) and a comonomer flow into a reaction chamber;

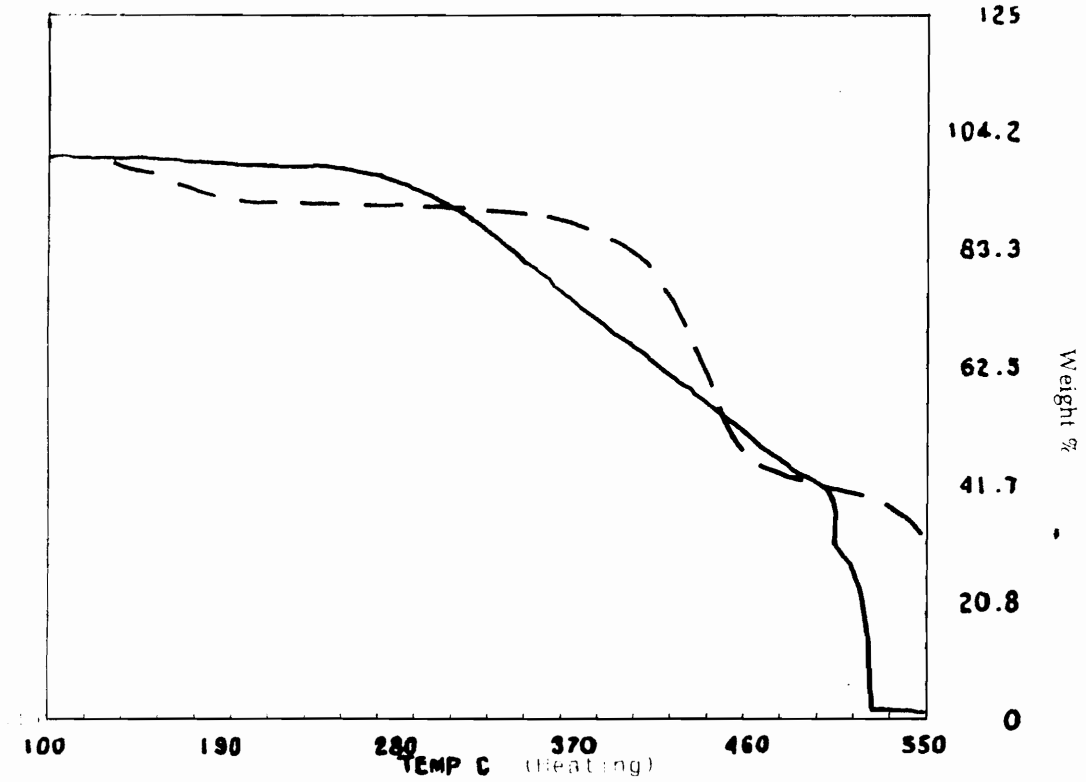

Figure 11: TGA spectra at 10°C per minute in air. Solid line: PPX Dashed line: PX/NPMI compolymer grown at 40°C

conditions are chosen such that PX only adheres to the surface when consumed by reaction, while the comonomer condenses. This leads to a deposition environment extremely rich in the comonomer. When polymerization is initiated by the PX molecules, the condensed comonomer is rapidly consumed in propagation reactions, yielding a copolymer rich in comonomer. A copolymer of PX-C and n-phenyl maleimide grown this way had growth rate and composition profiles which matched predictions for both mass flow control and surface reaction control, depending on deposition temperatures. If films are grown above the "ceiling temperature" of PPX growth, the resultant films are nearly indistinguishable from homopolymer films of the comonomer. A PX/NPMI film grown at 40°C, for example, shows thermal degradation indistinguishable from n-phenyl maleimide homopolymer; the amount of unreacted n-phenyl maleimide is small. This method greatly increases the range of available properties in polymer films grown by chemical vapor polymerization.

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CHAPTER 6

Summary

This dissertation has made two contributions to the literature of PX homopolymerization, and demonstrated chemical vapor copolymerization is a promising method for the fabrication of high quality thin films. For the first time since 1966, a method for the chemical vapor deposition of a new polymer has been developed. This new polymer is but one of many which could presumably be grown by the method presented here. These contributions are summarized in the following paragraphs.

The results of this research may be broken into the categories of homopolymers and copolymers. The homopolymer work addressed two issues not previously resolved in the literature. The first involved the chemistry of polymerization; more specifically, the number of PX monomers, λ, required to form the initiating diradical. Beach and Kubo, using thermodynamic data, argued the trimer diradical should be the smallest stable species. Beach's model for polymerization further predicted growth rate should depend on monomer partial pressure as $P^{((\lambda+3)/4)}$. If both the thermodynamic argument and Beach's model were correct, then growth rate should vary as $P^{1.5}$. The only experimental evidence suggested growth rate varied as P^2, implying $\lambda = 5$; in other words, a pentamer diradical was the smallest stable initiating species. In an experiment designed specifically to test growth rate vs. pressure, the work presented here confirmed the correctness of the thermodynamic prediction.

The conformal control with which PPX films can be grown make them attractive for the fabrication of optical components. Unfortunately, very little was known about their optical properties. For the first time, the three commercially available films were measured by variable angle spectroscopic ellipsometry. This technique allows highly detailed information about the optical properties of films to be extracted from raw data by modelling. The models must be physically realistic before modelling results can be believed. Using a very simple model, both the refractive index vs. wavelength and birefringence of these films were determined; the results were in agreement with earlier reports, while extending them through a greater wavelength and composition range. One consequences of this work was the discovery that PPX-D, unlike the other two polymers, has a higher refractive index perpendicular to the film plane than in the film plane. Also, the refractive indices in the film plane of all three polymers are much closer than perpendicular to the film plane. The refractive indices were previously measured perpendicular to the film plane, and suggested efficient waveguides could be formed with homopolymers. These new results show light trapping would be inefficient in the film plane using homopolymers alone.

The other results can be classified as chemical vapor copolymerization results. Very little has been published about CVcP. In 1976, Swarc reported this approach unlikely to be fruitful, as all previous attempts had failed due to the extremely high reactivity of PX monomer. Early attempts presented here showed even relatively small amounts of incorporated comonomer could greatly affect the crystallinity of the copolymers; many properties which are influenced by crystallinity could therefore be significantly affected.

A better theoretical understanding of the copolymerization was required to explain the experimental results. To quantify the relative reactivities of PX and a comonomer, a model was developed to measure reactivity ratios. The main problem the model had to overcome was the experimental impossibility of measuring the feed ratio in the deposition region. Experimental data obtained for demonstrating the reactivity ratio model confirmed Swarc's assertion of the high reactivity of PX monomer.

Perhaps the greatest property challenge for CVcP was the improvement of oxidative thermal stability, as PPX degrades at around 200°C in air. However, a method was found by which copolymers extremely rich in the comonomer could be formed; the FTIR spectrum, refractive index and thermal stability were essentially identical to homopolymers of the comonomer. This method has wide implications, as it suggests a great many polymeric films could be formed with properties dominated by a species other than PX. This work has generated industrial interest from microelectronics companies interested in developing alternatives to SiO_2 for interlayer dielectrics.

CHAPTER 7

Future Work

This dissertation raises more questions than it answers. The primary achievement of this work was the introduction of a new kinetic regime for the formation of polymeric films by chemical vapor copolymerization. In this scheme, a comonomer with a low vapor pressure is introduced into a reaction chamber with PX or a PX analogue. Under properly chosen conditions, the comonomer will condense on the substrate while PX will only remain on the substrate if consumed by initiation or propagation reactions. This results in polymer thin films composed almost entirely of the comonomer. The characterization performed in this dissertation, was limited to proof of concept. Almost nothing is known about the properties of films grown in this manner, nor those grown by surface reaction controlled CVcP.

The practical applications for this method are potentially enormous, but a great deal of research and development is required before the method is useful commercially. First, a suitable comonomer must be identified or synthesized for the selected application. Second, process parameters must be optimized for desired composition, growth rate, and "film quality", which is a catch-all phrase including topology, morphology, continuity, thickness uniformity, etc. Finally, performance evaluation must be performed on such properties as adhesion, stability under operating conditions, etc..

The second field of enquiry is the chance to study copolymers formed in the unique enviroment of CVcP. The absence of solvent, presence of a substrate and extremely high reactivity of PX are all important factors whose effects cannot be easily be predicted from the standpoint of conventional polymer relationships nor CVD of nonpolymeric materials. There have been virtually no reports on such standard polymer properties as conformation of homopolymers, for example; copolymerization makes such determinations even more complicated, and arguably more important. Copolymerization could lead to phase separation, for instance, which can drastically effect properties.

In Chapter 2, a model for surface reaction controlled polymerization was formulated. This is the first model of its kind to appear in the literature, and can undoubtedly be improved. A model to describe the deposition method presented in Chapter 5 would also serve both industry and academia.

In summary, this dissertation is the first of many steps required for the successful implementation of chemical vapor copolymerization in industry. It is hoped subsequent research will be pursued to help the methods introduced here serve the scientific and engineering communities.

APPENDIX I

The Reactor

Introduction During the three years in which this research was conducted, many permutations of the same basic reactor were employed. Some components, such as the furnace, pump and liquid nitrogen trap, remained constant. Several other features, such as the sublimation chambers, went through several design changes before reliable designs were produced. Finally, different reaction chambers were used for different experiments. The reactor described in detail here is the final design used in chapters two, four and five.

Most vacuum components were purchased either from Nor-Cal (1967 South Oregon Street, PO Box 518, Yreka, CA 96097, 800-824-4166) or MDC Vacuum Components (23842 Cabot Boulevard, Hayward, CA 94545-1651, 800-443-8817). Vacuum seals between components were achieved either with copper gaskets or rubber O-rings. Temperature controllers were purchased from Teco (108 Baywood Avenue, #100, Longwood, FL 32750, 407-767-8394). Short descriptions of assembly procedure are listed below; part numbers are listed with the drawings.

The final part of this appendix will be a rough sketch describing an "ideal" reactor, although this is solely the opinion of the author and has not been tested. It does, however, address a few shortcomings of the reactor used in this dissertation.

Pyrolysis furnace The pyrolysis chamber was custom-made by Nor-Cal. An Inconel® full nipple, 20″ long by 2″ in diameter, was made with four welded VCR fittings, two upstream and two downstream from the furnace. A set of baffles was placed in the center of the chamber to increase the residence time of the dimer in the hottest part of the reactor. The baffles were half-moon shaped pieces of Inconel® bolted together with successive flat ends at 90° angles, forcing gas into a spiral flow around them. A single k-type thermocouple was placed on the outer wall of the chamber. This was attached to a Teco 25A, 125V temperature controller.

The furnace was homemade from materials purchased from Thermcraft (3950 Overdale Road, PO Box 12037, Winston-Salem, NC 27117, 910-784-4800). Fiberglass insulation (0.25″ thick) was wrapped around the pyrolysis chamber to prevent electrical contact between the heating coils and chamber. Half-pipe heaters were placed on the insulation, then another layer of insulation was wrapped around the heaters, then half-pipe insulation placed around this insulation. Finally, a piece of sheet aluminum was wrapped around the entire assembly and bolted closed. 0.25″ thick fiberglass insulation was cut to cover the end faces of the furnace.

Sublimation chambers Both the dimer and comonomer chambers were 1.5″ diameter, 5″ long full nipples. Materials were loaded through swing doors with Viton® O-rings. K-type thermocouples were attached to the center of the outside chamber wall with metal hose clamps and attached to 15A, 125V Teco temperature controllers. Uniform heating was provided by custom heating mantles purchased from Glas-Col (711 Hulman Street, PO Box 2128, Terre Haute, IN 47802, 812-235-6167).

Reaction chamber The long reaction chamber was wrapped in 0.25″ diameter copper tubing attached via thermally conductive epoxy purchased from McMaster-Carr. The copper tubing was connected to 0.25″ inner diameter Nalgene® tubing purchased from Fisher Scientific, which led to a constant temperature circulating bath. The bath was filled with distilled water.

Substrate holder The substrates were placed on a 14″ x 1″ x 0.125″ strip of aluminum. The strip was designed so it could be broken apart, fed into the system through the liquid nitrogen trap and reassembled inside the reactor. Substrates were attached to the holder by placing a small piece of double-sided tape near the downstream end of the substrate.

Pumping system The pump was a Welch Duo-Seal mechanical pump with a base pressure in this system of about 0.11 Torr. In some chapters of this dissertation, the base pressure was erroneously listed as around 0.28 Torr due to false calibration. The pump required around one minute to pump the system to near its base pressure.

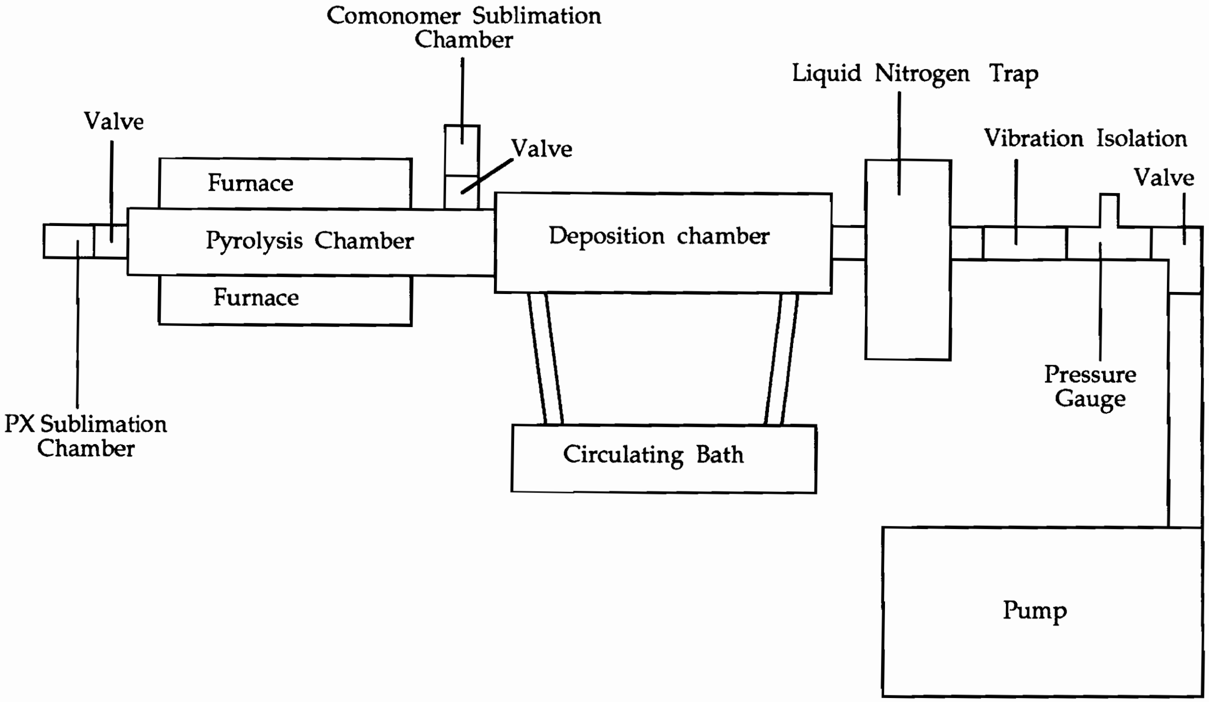
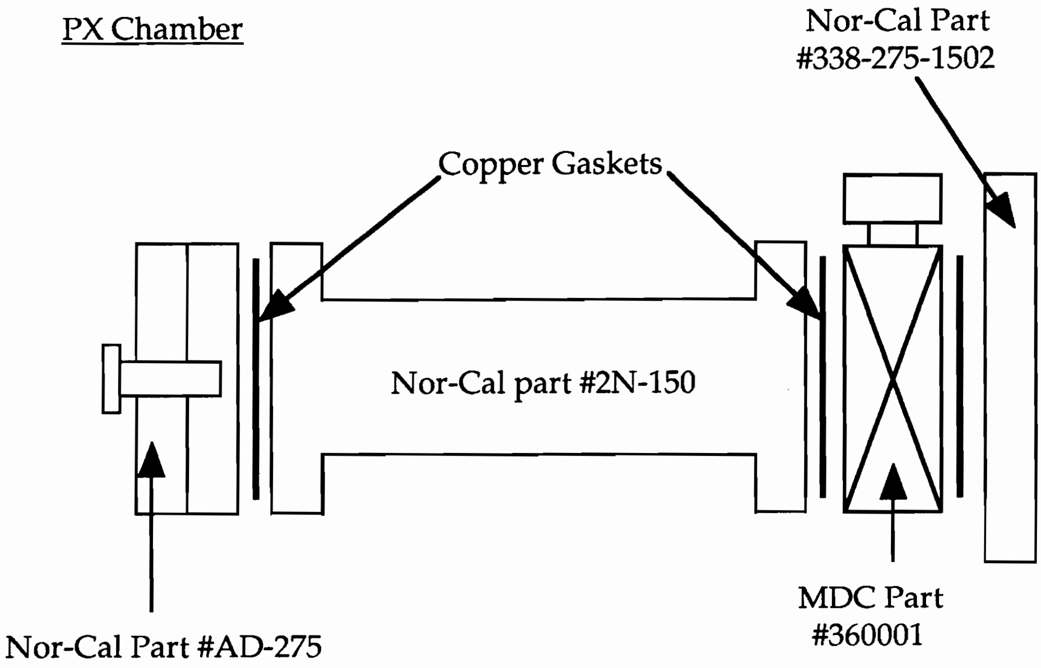


Figure 1: Overall View of Reactor

PX Chamber



Comonomer Chamber

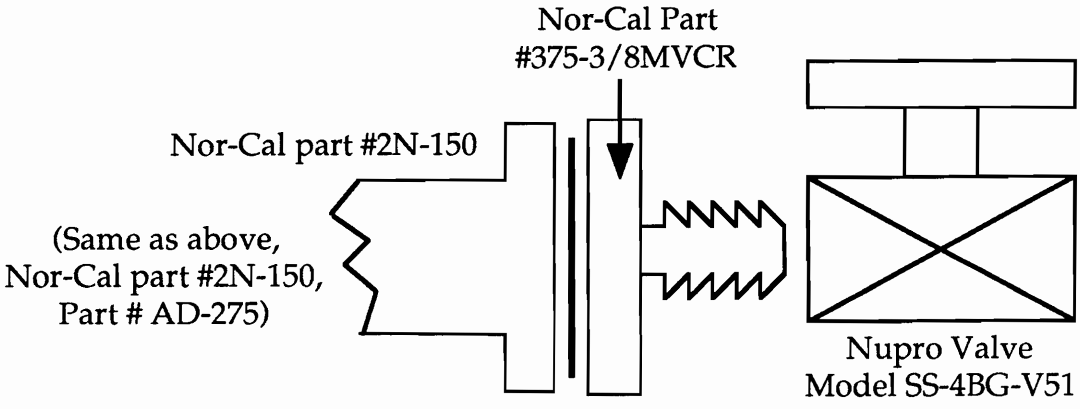


Figure 2: Exploded View of Sublimation Chambers

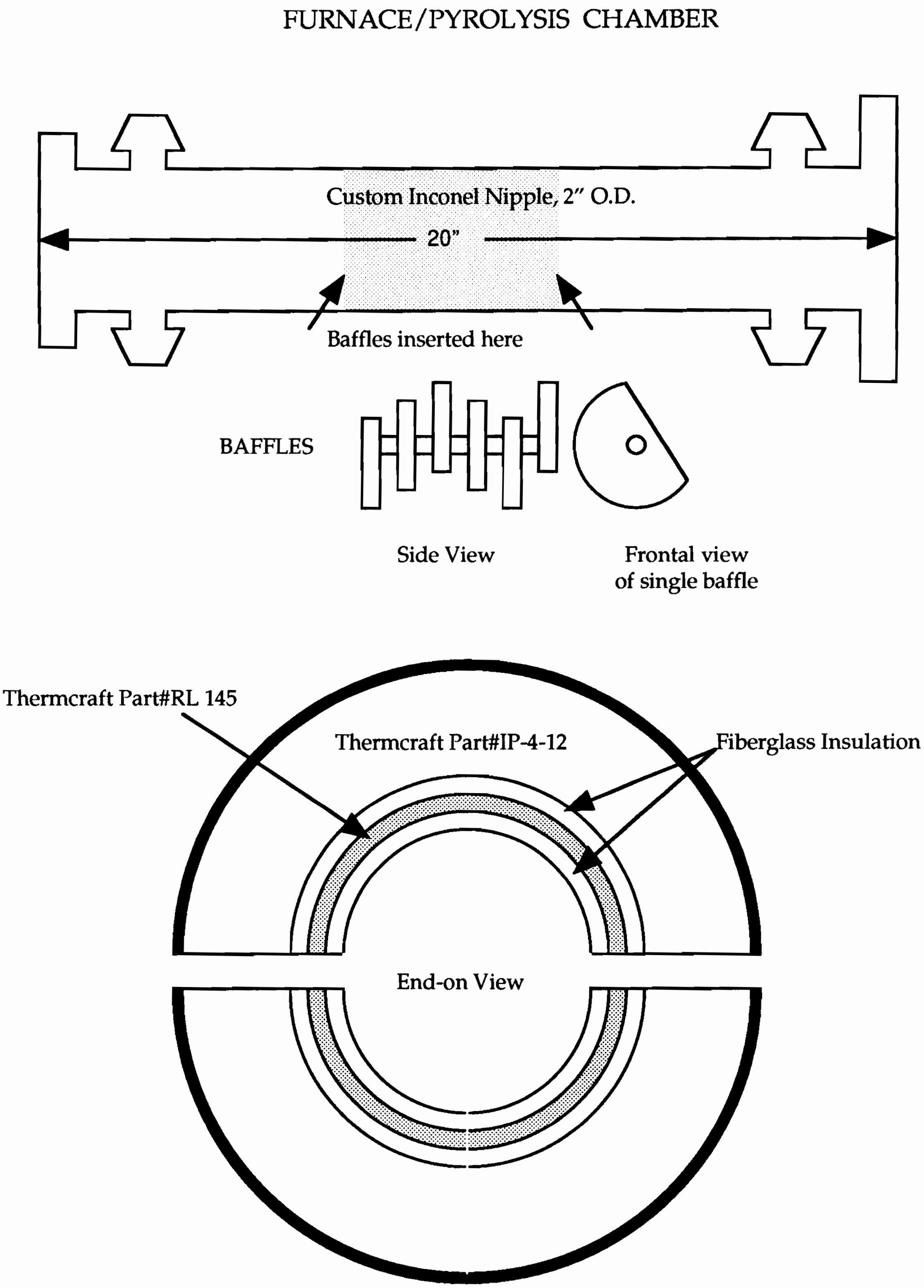


Figure 3: Pyrolysis Furnace Assembly

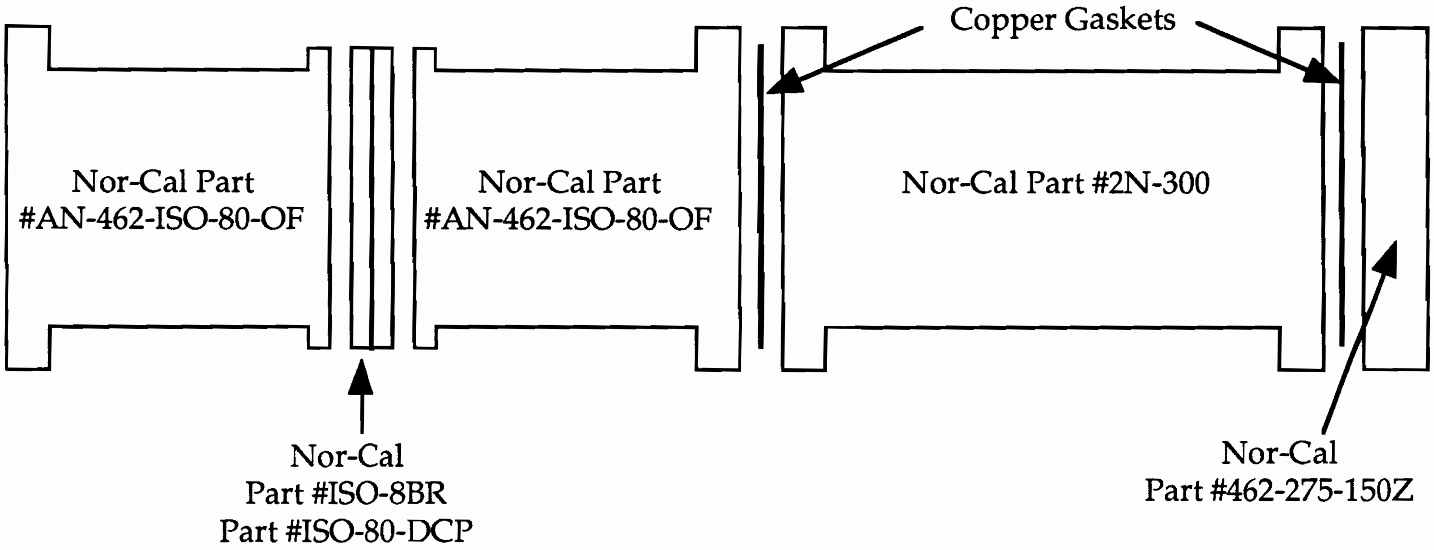


Figure 4: Exploded View of Deposition Chamber

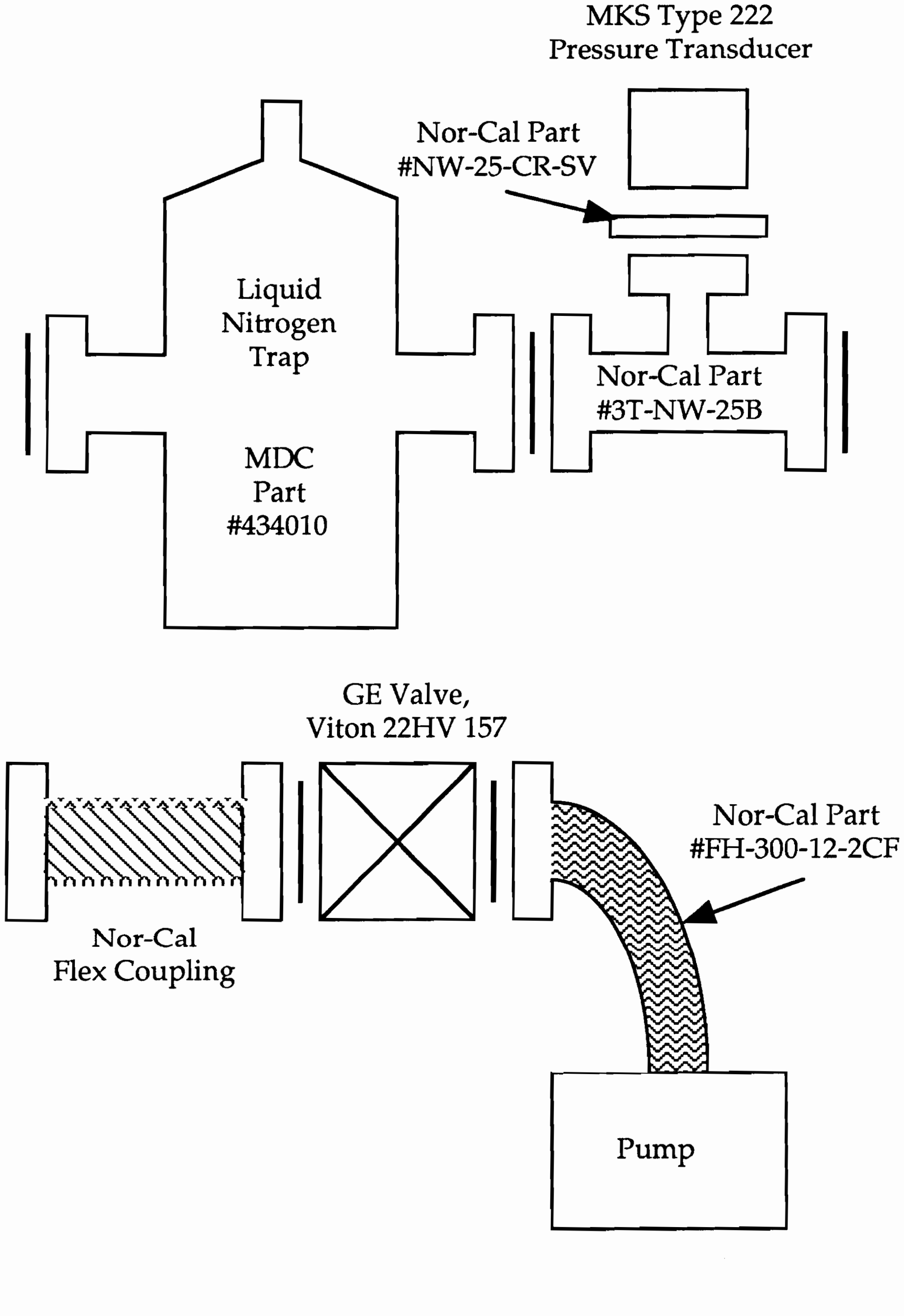
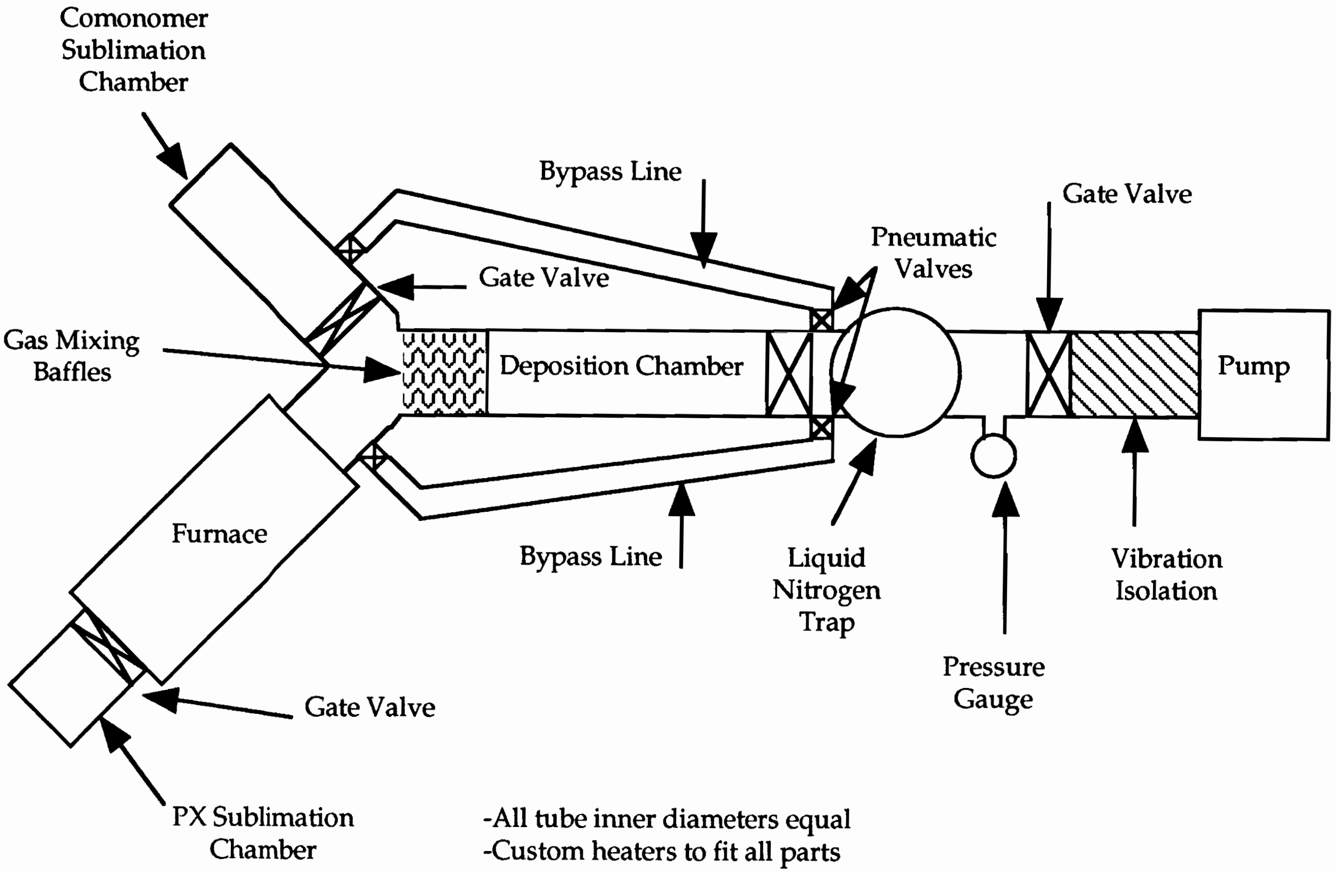


Figure 5: Exploded View of Trap/Pump Assembly



-All tube inner diameters equal
-Custom heaters to fit all parts

Figure 6: Schematic of "Ideal" Reactor

APPENDIX II

Using Wavelength Dispersive Analysis to Determine Compositions of Copolymer Thin Films

To model the kinetics of deposition and copolymerization, an accurate determination of chemical composition at different points in the reactor is required. The biggest problem encountered in these measurements was availability of suitable composition standards; in general, experiments were designed to measure changes in composition, rather than absolute composition, because acceptable standards could not be found. It is noteworthy that films produced by CVD were generally much more stable under electron beams than films prepared by more conventional methods.

Many surface characterization techniques, such as ESCA, only measure the top few nanometers of a sample, and were therefore unsuitable for these studies. Techniques such as FTIR, while performed for qualitative information, were not suited for quantitative composition determination. In this dissertation, wavelength dispersive analysis (WDA) was chosen because of its high spatial resolution and large measurement volume.

WDA uses an electron beam which is stopped within the sample, producing x-rays from the various elements present. The sample is transparent to the x-rays, which are collected by a series of detectors. The wavelengths of the x-rays are measured; from this information, quantitative information about the presence of various elements can be determined. Compared to energy dispersive x-ray analysis, much smaller beam currents are typically used. In addition, the detectors offer superior resolution. This makes the technique especially suitable for detection of light elements.

Measurements were taken with a Cameca SX-50 electron probe. The pressure in the measurement chamber was about 10^{-10} Torr. Samples were coated with 20-25 nm of carbon to render them conductive. An electron beam, between 5 and 10 nA, was produced from a tungsten filament. Electromagnetic lenses were used to focus and raster the beam. The beam was rastered to prevent extensive damage to the sample; measurements were typically made by rastering a relatively diffuse 500nm diameter beam through an area of about 30μm by 30μm. Kα X-rays were measured with a PC1 pseudo diffracting crystal for C, N, O and F atoms, pentaerythritol (PET) for Cl atoms and with thalium acid phthalate (TAP) for Si atoms.

When measuring thin films, care was taken to ensure the analytical volume did not exceed the volume of film sample. Different elements have different analytical volumes, potentially yielding misleading composition measurements. Figure 1 of this appendix illustrates this problem. This is the same sample discussed in Figure 3 of Chapter 3. In that figure, the amount of silicon detected is negligible until the film thickness falls to about 1800nm. The concentration of fluorine, which had been increasing, appears to plateau here. In fact, this is an erroneous measurement caused by insufficient sample thickness.

Whenever possible, absolute compositions were determined from chlorine concentration data. Its signal is easily resolved from those of other elements and it has a small analytical volume. The other elements were used as checks. For a given sample, the change in composition with distance was generally consistent regardless of which element was used for the calculation; the absolute values, however, varied considerably, as shown in figure 2 for a 5-7μm thick film of PX/NPMI.

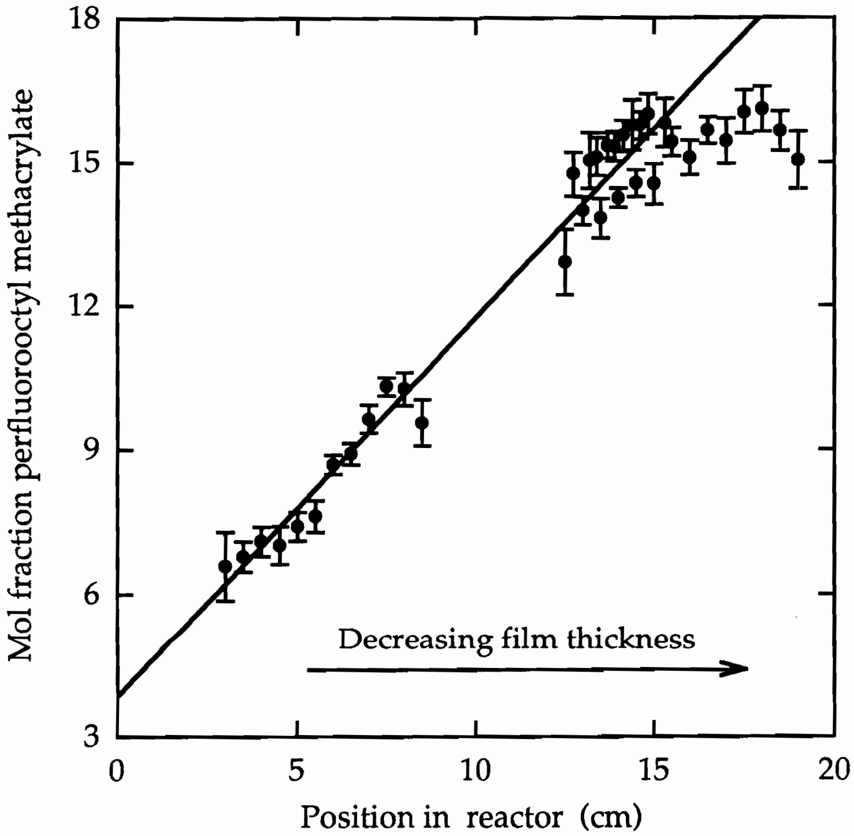


Figure 1: Illustration of misleading results caused by insufficient film thickness.

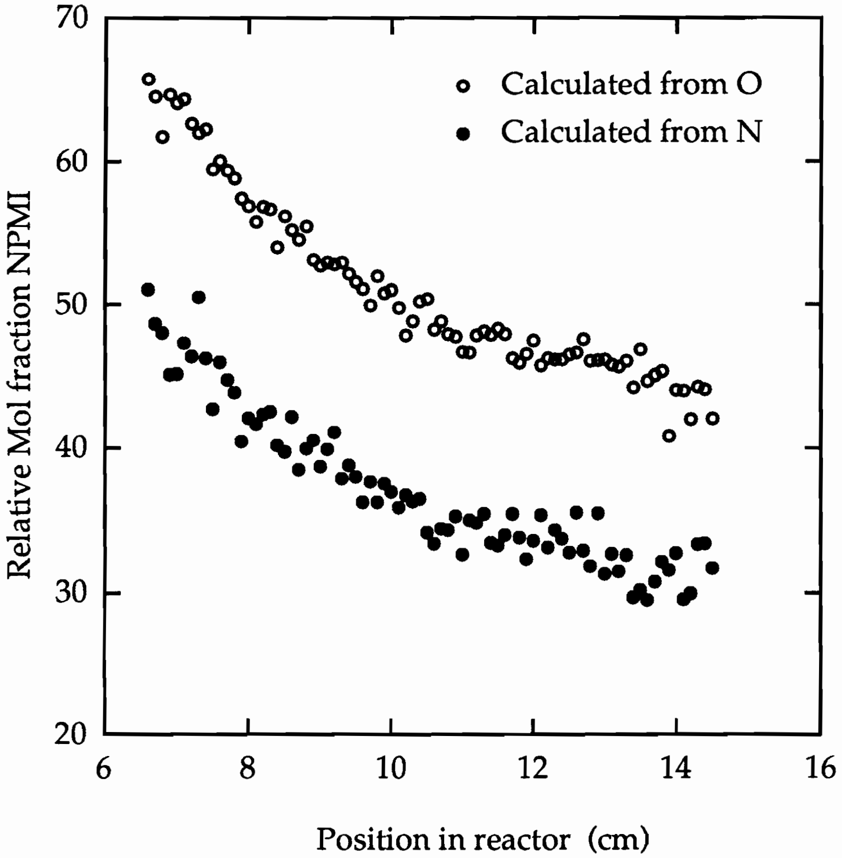


Figure 2: Composition determination of PX/NPMI copolymer, illustrating lack of suitable standards for absolute composition measurements.

VITA:

The author was born in Gainesville, Florida in 1965. After high school in New Smyrna Beach, Florida he attended Daytona Beach Community College until 1985, after which he enrolled in the University of Florida. His junior year was taken at the University of Bonn, Germany, where he studied German and physics. He received his bachelor's degree in physics in 1989. He then began research in the High Energy Physics group under James Walker and Julie Harmon at the University of Florida. He began graduate studies under Paul Holloway of the Department of Materials Science and Engineering and received his Master's degree in 1992, studying the effects of high energy radiation on polymeric fluorescent optical fibers, funded by the Superconducting Supercollider. He received a Cunningham Doctoral Fellowship and began his doctoral studies under Seshu Desu at the Virginia Polytechnic Institute Department of Materials Science and Engineering. Upon completion of his Ph. D., he will join the Texas Instruments Semiconductor Process and Device Center in Dallas, Texas.