

Copolymerization of Divinylbenzene and 4-Vinylpyridine using Initiated Chemical Vapor Deposition for Surface Modification and its Applications

By

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ABSTRACT

This research investigates the copolymerization of divinylbenzene and 4-vinylpyridine into organic thin films that exhibit conformal, stable, and uniform surface properties. Thin films were grown using initiated chemical vapor deposition, a variant of hot-wire deposition using a chemical initiator. Readily variable monomer flow into the active stage of the reactor allows for directly tunable copolymer composition. This tunability extends onto the control of material surface properties of a substrate that is coated with these organic thin films. The conditions of iCVD allow a variety of delicate substrates to be coated and for the full retention of pendant functional groups. This leads to their application to many industries including water desalination membranes, microfluidics, photolithography, sensors, among many others. The focus of this paper is on the facilitated control of surface modification using iCVD techniques and some of its future applications are also discussed.

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I. Introduction

Initiated chemical vapor deposition (iCVD) has been used for several decades to produce high purity polymer thin films that are applicable to a variety of industries.^[1] iCVD has proven effective in surface copolymerization and has become desirable for its tunability, low energy input, retention of polymer functionality and speed of depositions.^[1] Being able to control exact compositions and thickness of thin films is useful as small variations in these parameters can lead to considerable changes in surface materials properties. This document will explore the copolymerization of two monomers, divinylbenzene and 4-vinylpyridine, and the applications of such coatings.

Initiated chemical vapor deposition is one of the many subtypes of CVD, specifically of hot-wire CVD. HWCVD uses an array of resistively heated filament wires to thermally decomposed molecules in the input gas which initiates polymerization. The hot filaments break down molecular bonds and create active centers that commence polymer chain growth.^[2] iCVD additionally uses a chemical initiator in the feed to facilitate polymerization. The temperature of the filaments is chosen sufficiently high to thermally decompose the initiator species but low enough to not decompose the monomer species. This is an important characteristic of iCVD to fully retain up to 100% of the functionality of the different monomer species being deposited onto a substrate. The conditions of iCVD are chosen

such that only the initiator species is transformed into active sites, which then transfer radicals to subsequent monomer building blocks. Other types of polymerization methods such as solution polymerization and even some types of CVD, such as Plasma-Enhanced CVD, will destroy functional groups through side reactions or harsh conditions such as elevated temperatures. [3]

iCVD is advantageous to these other polymerization methods due to its ability to function at lower temperatures, mild vacuum pressures, scalable dimensions, all-dry environment, and its generally mild environment with respect to substrate preservation. Consequently, it is possible to deposit very delicate substrates using iCVD such as paper, fabrics, carbon nanotubes and sensitive membranes, among other materials. This process has even been used to coat common tissue paper with superhydrophobic coatings. [1]

This process also enables uniformity in thickness across wide ranges of substrate width and geometry allowing full areal functionality due to the conformal nature of iCVD thin films. [3] The retention of monomer functional groups across the substrate allows for complete control over surface properties such as wettability, chemical responsiveness, and mechanical stability.

The formation of polymer thin films by iCVD follows the free-radical chain-growth mechanism. [3] Chain-growth polymerization is the process of creating a polymer by the single addition of a monomer unit onto an active site of a growing polymer chain. Free-radical polymerization encompasses a

three step process; initiation, propagation and termination of the polymer chain.^[4] A free radical molecule, in this case formed from an initiator molecule, is absorbed onto the surface of a substrate after decomposition. As the input monomer vapor is carried across the surface of a substrate, the monomer reacts with the initiator free radical making an active site on the monomer which will form the backbone of the polymer chain. Additional monomer flow causes new monomer units to interact with the initial reactive monomer which transfers its active site onto the new monomer. In this manner, every additional unit integrates onto the active chain by the spontaneous interaction of one of its functional group, such as a vinyl group, with the unpaired electron of its predecessor. This reaction continues until the flow of monomer gas vapor has stopped or until chain termination occurs. Chain termination will occur when two radical species meet, such as the interaction of a chain active site with a free radical initiator species or when two active polymer chains react with each other. Chain transfer will also terminate a polymer chain, but will itself initiate the creation of a second, separate polymer chain.^[5]

Mild vacuum pressures of 100-1000 mTorr are usually maintained during iCVD. This condition arises from a variety of reasons and also contributes to the advantage of iCVD. The low pressures inside the reactor chamber minimize three-body interactions required for bimolecular reactions. Due to this, monomers will favor surface polymerization instead

of polymerizing in the gas-phase before absorption onto the surface. [3] This prevents localized buildup of polymer from random chain absorption into the surface and results in the signature uniformity across iCVD samples. This condition also thermally favors the deposition process. Filament temperature is usually at least in the 200°C range for low temperature initiators such tert butyl peroxide (TBPO), and can be hundreds of degrees higher for other chemical initiators. [3] However, some of the substrates used in iCVD, specially paper and plastics, cannot withstand such elevated temperatures and are, in some reactors, within an inch of the hot filaments. The low pressure environment makes thermal diffusion harder and thus the substrate does not perceive the high temperature of the filaments. The cooled stage in iCVD reactors also play a minor role in this, but this condition is mostly use to facilitate absorption onto substrate surface.

Many monomer species have been able to be deposited into thin films using iCVD. This includes acrylates, methacrylates, vinyl benzenes, and pyridines monomer types. [6-9] These monomers are capable of free radical polymerization due to the vinyl groups they contain which react with free radicals to form the covalent polymer backbones. Many of the monomer units also contain other functional groups, such homocyclic and heterocyclic compounds. These compounds can have a significant effect on the optical, electric, hydrophobic and mechanical properties of a film surface. In this document, the study of divinylbenzene and 4-vinylpyridine copolymerization

is studied. Divinylbenzene (DVB) is a homocyclic compounds that consists of a benzene ring with two vinyl groups. It is similar to styrene, the building block of the common industrially-used polystyrene plastic, but DVB comprises of an extra vinyl group. Divinylbenzene has been extensively studied with chemical vapor deposition due to its composition of two vinyl groups that can react with free radicals. The second vinyl group is also able to react with other units in a polymer chain and thus able to crosslink them together. On the other hand, 4-vinylpyridine (4VP) is a heterocyclic compound, with a functional pendant group similar to benzene but with a carbon atoms in the ring replace by a nitrogen one. 4VP only contains one vinyl group which is incorporated into the polymer chain through free-radical propagation. 4VP has also been extensively research in an iCVD setting and has even been used in functional nanodevices for selective sensing due to its absorption of nitroaromatic molecules. ^[10] When polymerized independently, both of these monomers readily form homopolymer thin films onto their respective substrates, with aromatic pendant groups on the surface. Additionally, unreacted vinyl bonds, especially with DVB, may also act as pendant functional groups. These groups can then crosslink polymer chains together and further improve materials properties, such as solvent resistance, heat distortion and hardness. ^[11]

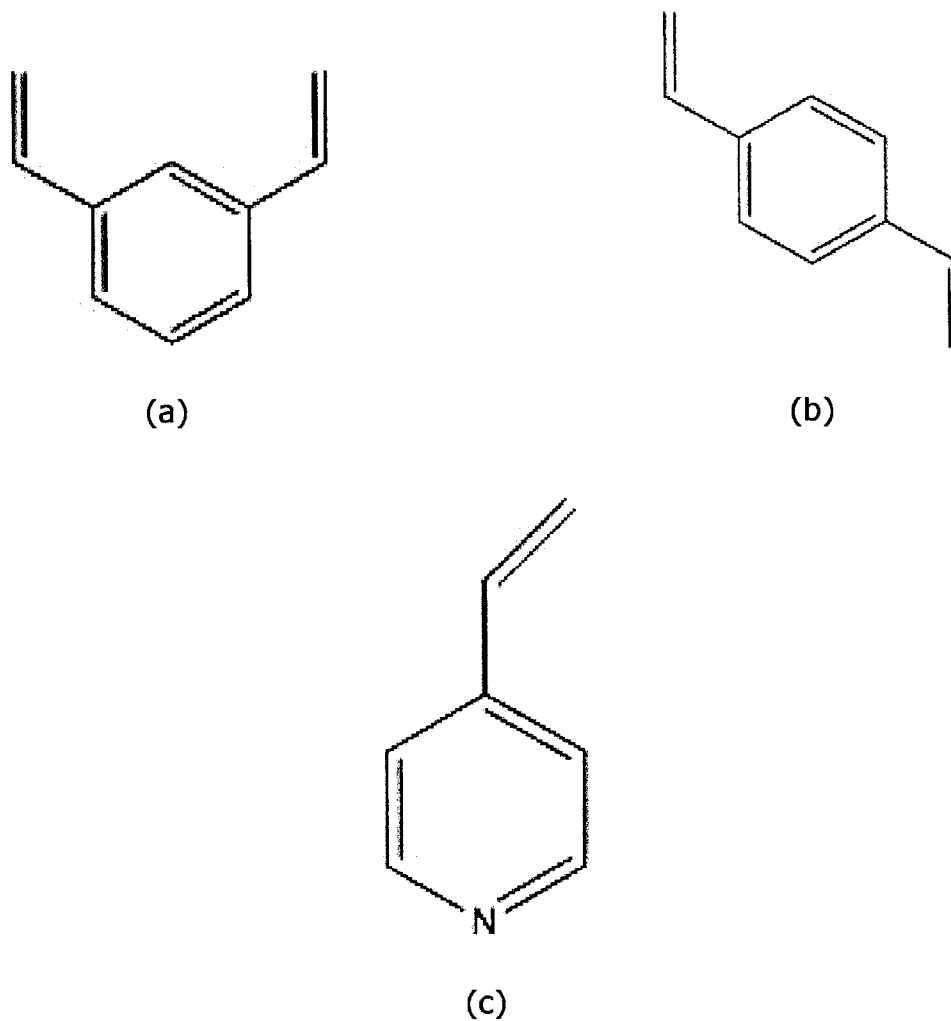


Figure 1: Chemical structures of (a) m-DVB monomer isomer, (b) p-DVB isomer, (c) 4VP monomer

With certain monomers and iCVD reactor designs, it is also possible to easily copolymerize two monomer species into a thin film in a single dry step exactly as with homopolymers. ^[12] Copolymerization of two species requires the influx of both monomer vapors to the reactor chamber along with the initiator species. As before, free radical transfer will happen between

monomers as they are absorbed onto the substrate surface, and between identical and different monomer species, depending on monomer reactivity. Polymer composition can then result in alternating sequences of A and B monomers, sections of A monomer repeat units and B monomer repeat units, or random copolymers. ^[13] Copolymerization can be useful as monomers with different pendant groups can be selected and simultaneously deposited onto a thin film which will then both contribute to the performance of the polymer. Secondary monomers can be introduced as a form of crosslinking to increase chemical stability, or to introduce surface responsive groups onto the surface of a substrate for sensing purposes. The introduction of a second monomer can also improve the mechanical properties of a film and change the wettability of a polymer film while retaining the first monomers purpose. iCVD is one of the best methods of copolymerizing thin films as it does not require extra chemicals or procedures in order to introduce an additional species, all that is required is the additional flow of another monomer vapor that has responsive functional groups to polymerize and compatibility with the initial monomer type. The applications of iCVD copolymer thin films are numerous and are important for industries such as photolithography, biomedical implants and devices, water desalination, flexible displays, and generally protective coatings for vehicles or devices in aqueous environments. ^[1]

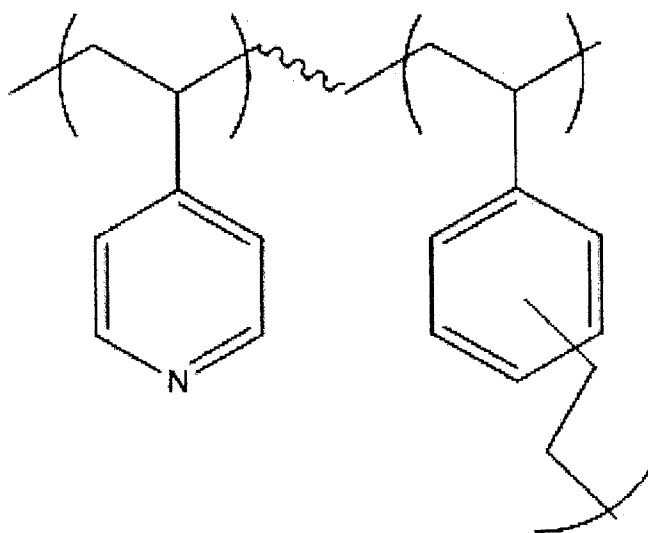


Figure 2: Copolymer unit of P (DVB-co-4VP)

The most prevalently used and researched application for organic thin films is their use as protective coatings. Biosensors, implants, microfluidic devices, reverse osmosis membranes and other technologies require the prevention of protein adsorption or the attachment of microorganisms onto a surface. Microorganism attachment can be detrimental to ship hulls or underwater structures. Protein adsorption can interfere with the performance and lifetime of biomedical diagnostic tools or membranes for water desalination technologies ultimately lower their effectiveness and efficiency. ^[14] The solution for many of the degradation of the technologies mentioned above is the incorporation of protective barriers between the environment containing proteins or microorganism and the surface of the

device or membrane. At the same time, the barrier must not interfere with the function or performance of the technology in a significant way. iCVD copolymer thin films offer a great solution for this issue due to their conformality, uniform thickness, highly tunable properties, variety in composition capabilities, and stability. It is also worth mentioning that most of the monomers, including the ones discussed above, are relatively inexpensive to procure but also to deposit as iCVD is a low energy input process. Poly (DVB-co-4VP) copolymer films, processed with propane sulfonate for the creation of a zwitterionic coating, are proposed for use as antifouling layers for reverse osmosis (RO) membranes and for bacterial attachment prevention using microfluidic devices. P (DVB-co-4VP) can form zwitterionic layers which can bind water onto its surface more tightly than conventional hydrophilic materials by strong localized electrostatic interactions. ^[15] A zwitterionic molecule is one which is overall neutral yet contains localized positive and negative charges within it. Thus a zwitterionic film has no net charge over its surface, yet can prevent nonselective protein attachment by strongly binding to water molecules. As it is conformal to substrate surface, deposition of polymer film will not interfere with membrane pores or with fluid flow in microfluidic devices due to unwanted roughness.

II. Experimental

Copolymer thin film synthesis

Copolymer thin films were deposited using a custom iCVD reactor system. The full specifications of the reactor are described elsewhere.^[16] Films were deposited onto 100mm wide silicon wafers (Wafer World, Incorporated). Filament temperatures were kept at 220°C for all of the depositions. The reactor stage in which the substrate rested was kept at 20°C. The pressure of the reactor chamber was maintained at 800 mTorr using a throttling butterfly valve. The film thickness was monitored live using laser reflection interferometry with a 633nm helium neon laser (JDS Uniphase).

DVB and 4VP liquid phase monomer were purchase from Sigma Aldrich and contained Copper (II) Chloride, also purchased from Sigma Aldrich to prevent polymerization while in the attached monomer jar. Both monomers were delivered with heated mass flow controllers (MKS Instruments 1152C). The DVB monomer was kept at a constant temperature of 65°C and 4VP was kept at 50°C in order to create volatile monomer vapors. According to the supplier, the DVB source comprised of 80% DVB isomers (p-DVB and m-DVB) and 20% ethylvinylbenzene (EVB). EVB incorporation onto a PDVB homopolymer has been shown to be equivalent to the amount present in the liquid monomer.^[11] Tert butyl peroxide (TBPO, 98%) was used as the

chemical initiator and deliver using a mass flow controller (MKS Instruments 1479) at room temperature.

TBPO undergoes thermal decomposition at temperatures higher than 100°C. Once the initiator makes contact with the hot filaments at 220°C it undergoes homolysis at the peroxide bond site and creates two molecules with free radical properties. Figure 3 shows the thermal breakdown of TBPO.

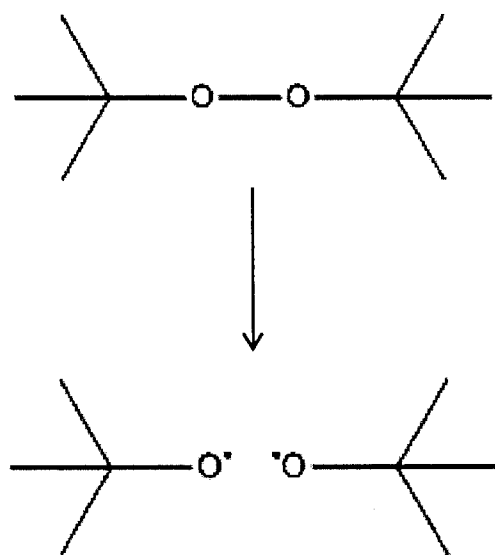


Figure 3: di-Tert butyl peroxide molecule undergoing chemical breakdown of the peroxide bond in the middle, resulting in the creation of 2 new radical molecules which will be the starting point of a polymer chain.

Tert butyl peroxide was retained at a flow rate of 1.8 sccm and 4VP at a rate of 4 sccm, with varying flow rate of DVB monomer. A patch flow of Argon gas was also delivered to the reactor chamber using a mass flow controller (MKS Instruments 1479) to ensure residence time. The flow rate

of all combined gases was held constant at 10 sccm. After desired thickness was accomplished, monomer flow was stopped but TBPO flow was sustained in order to promote initiator free radicals to react with active chain sites and promote chain termination.

Thin Film Characterization

After deposition, P (DVB-co-4VP) thin film thickness was measured using a J.A. Woollam M-2000 variable angle spectroscopic ellipsometer at incident angles of 65°, 70°, and 75°. The data obtained from the three angle measurements was then fit with a Cauchy-Urbach model in the WVASE32 software. Copolymer composition was analyzed using FTIR spectra. Spectra was collected using a Thermo Scientific Nicolet iS50 FT-IR spectrometer in transmission mode with KBr detector. The spectra was collected at a range of 400-4000 cm^{-1} at 4 cm^{-1} resolution over 256 scans. The data was processed and baseline corrected using OMNIC software and normalized over sample thickness.

Experiments on the performance of the polymer films at the specific applications of antifouling layers for RO membranes and anti-bacterial attachment are ongoing. For the antifouling application, RO membranes have not yet been deposited and tested, but preliminary baseline permeation and salt rejection tests for uncoated commercially available membranes have been done. These tests were performed using a commercially available stirred cell (Sterlitech, HP4750) with DI water at room temperature. The

feed pressure was controlled using a pressure control valve. The permeate flow rates was calculated by measuring the amount of permeate at 5 minute intervals over 30 minutes. A conductivity meter was used afterwards to perform salt water rejection calculations. For bacterial attachment tests on microfluidic devices, 1 inch by 2 inch glass slides were coated in a similar fashion as the films on the Si wafers above and were sent to a contributing lab for the bacterial attachment tests. The bacterial solution was run through the samples at a flow rate of 2ul/min at room temperature. A bacterial solution consisting of *Vibrio cyclitrophicus* was used. Experiments on the applications side are still ongoing.

III. Results

Poly (DVB-co-4VP) copolymer thin films were deposited onto 100mm Si wafer films. Figure 4 shows the spectra of PDVB homopolymer, P4VP homopolymer and four different compositions of P (DVB-co-4VP) copolymers. The area under the peak at 710 cm^{-1} was measured in order to calculate the amount of DVB incorporation onto the copolymer film. This peak relates to the C-C vibration in phenyl groups. The equation used to calculate the amount of DVB in copolymer was derived elsewhere. ^[11] Equation 1 yields the mole fraction of DVB in the copolymer samples of varying DVB compositions:

$$(Y_{\text{DVB}})_{\text{Cn}} = \frac{(A_m)_{\text{Cn}}}{(A_m)_{\text{Hn}}}$$

$(A_m)_{\text{Cn}}$ is the measured area under the peak at 710 cm^{-1} and $(A_m)_{\text{Hn}}$ is the average area under the peak at 710 cm^{-1} obtained elsewhere. ^[11] As the amount of DVB increases in the composition of the thin film, the 710 cm^{-1} peak in the spectra can be seen to increase in area, where it reaches the maximum at the PDVB homopolymer spectra. This change in DVB mole fraction is directly controlled by the DVB feed fraction of the total gas flow into the chamber. The Fineman-Ross equation relates the composition in the copolymer to the monomer mole fraction, however, it only takes into account monomers with single vinyl groups and does not consider divinyl molecules such as DVB. For this reason, a revised version of the Fineman-Ross equation ^[17] must be used that considers the system as a monomer with 2 vinyl groups and another with a double bond:

$$\frac{f_A(1-2F_A)}{F_A(1-f_A)} = r_B + \left[\frac{f_A^2(F_A-1)}{F_A(1-f_A)^2} \right] r_A$$

where f_A is the DVB gas mole fraction in the feed, F_A is the mole fraction of DVB in the deposited film, r_A is the reactivity ratio of DVB and r_B is the reactivity ratio of 4VP. Using FTIR to measure F_A , and knowing f_A of DVB from the deposition conditions, the relationship between the two was plotted in figure 5, which shows a clear linear relationship between the two parameters.

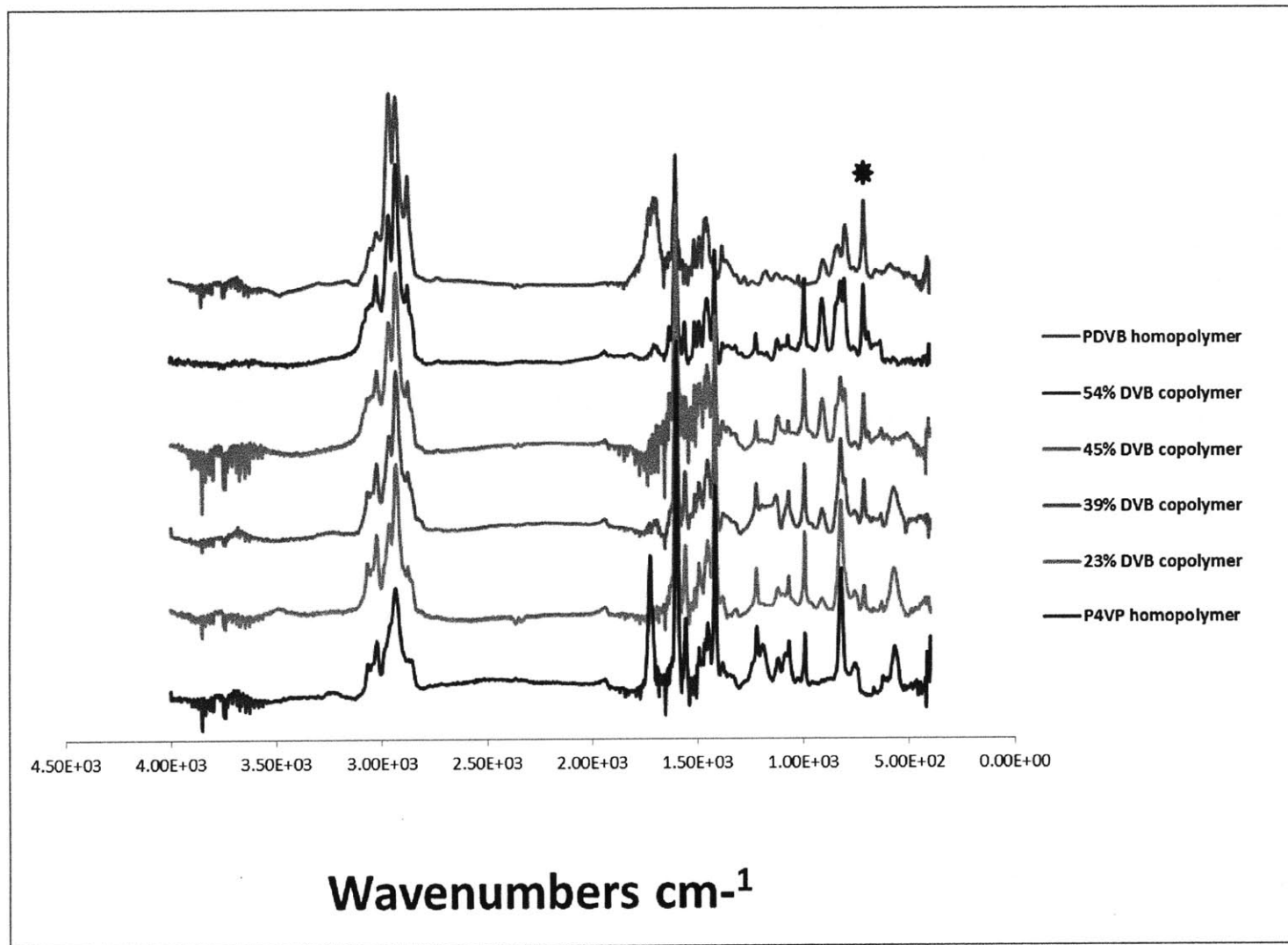


Figure 4: FTIR spectra of P (DVB-co-4VP) of varying compositions alongside the respective homopolymers.

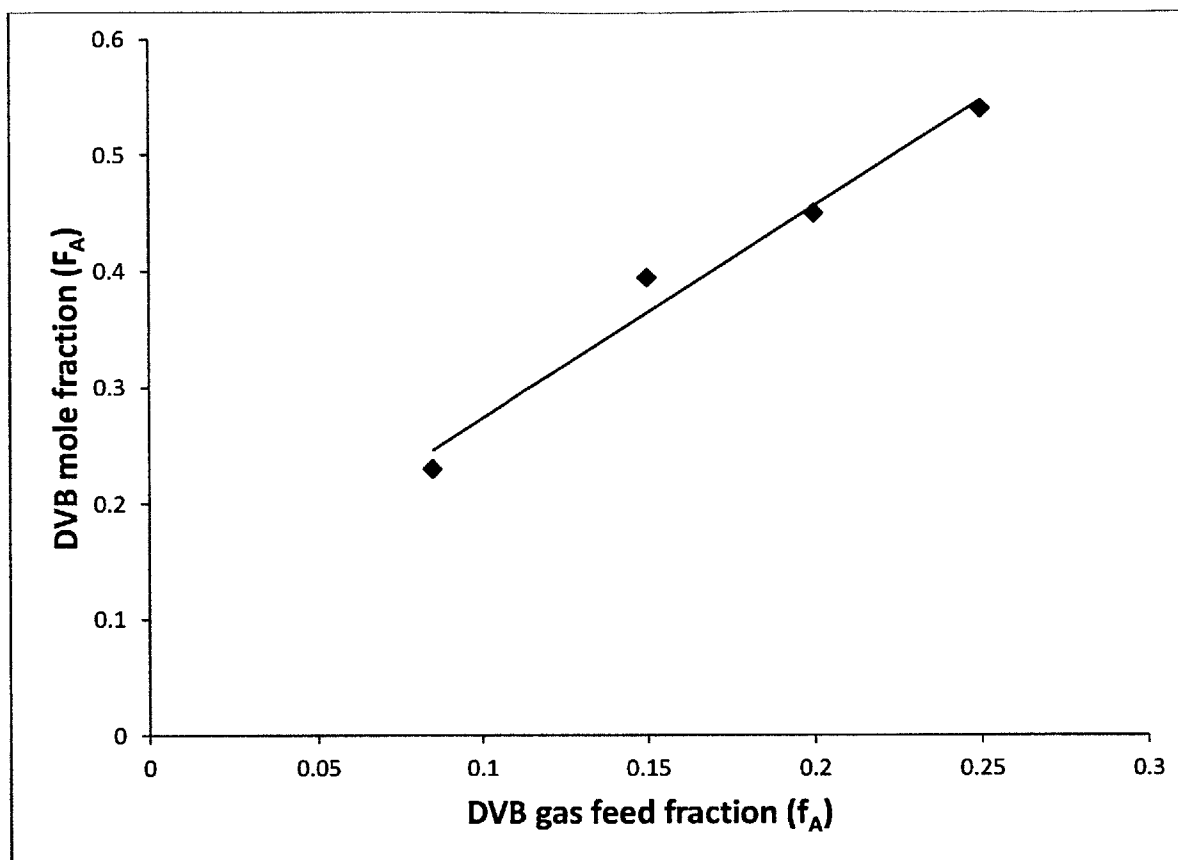


Figure 5: Correlation between DVB mole fraction (F_A) in the resulting thin film and DVB gas feed fraction (f_A).

Furthermore, linear regression of the Fineman-Ross equation leads to estimated DVB and 4VP relative reactivity values, which can be compared to the theoretically calculated values from the Q-e scheme. ^[18] Reactivity ratios are the ratios between reaction rate constants, k , of a propagation sequence. In free radical copolymerization, there are two monomer species being added to a polymer chain, denoted as A and B. As stated above,

during initiation, the free radical initiator transfers its radical to a monomer unit. Assuming this monomer is of the A species, one of two possible reactions can happen, monomer A reacts with an incoming monomer A unit to form an AA sequence, or monomer A reacts with monomer B, forming an AB sequences, these two reactions have a reaction rate constant of k_{AA} or k_{AB} , respectively. The same holds true if monomer B is the initial monomer to react with the free radical initiator, with reaction rate constants of k_{BB} or k_{BA} . Thus $r_A = k_{AA}/k_{AB}$ and $r_B = k_{BB}/k_{BA}$. A reactivity ratio of greater than 1 indicates that AA or BB reactions are kinetically favorable than AB or BA interactions, and less than 1 means the opposite is true. Such information can give insights into the preferred mechanisms for chain growth in a particular copolymerization reaction, whether perfectly alternating sequence, block chains, or random copolymerization will occur. However, due to the fact that iCVD operates by free-radical *surface* polymerization and not gas-phase polymerization, f_A in the equation above must be changed to f'_A :

$$f'_A = \frac{P_t f_A / P_{A,0} M_A}{P_t f_A / P_{A,0} M_A + P_t (1-f_A) / P_{B,0} M_B}$$

such that it will reflect iCVD surface kinetics. ^[19] Thus more approximate relative reactivity values are found in the linear regression of equation 2, with f_A substituted with the calculated value from equation 3. This relationship is shown in figure 6.

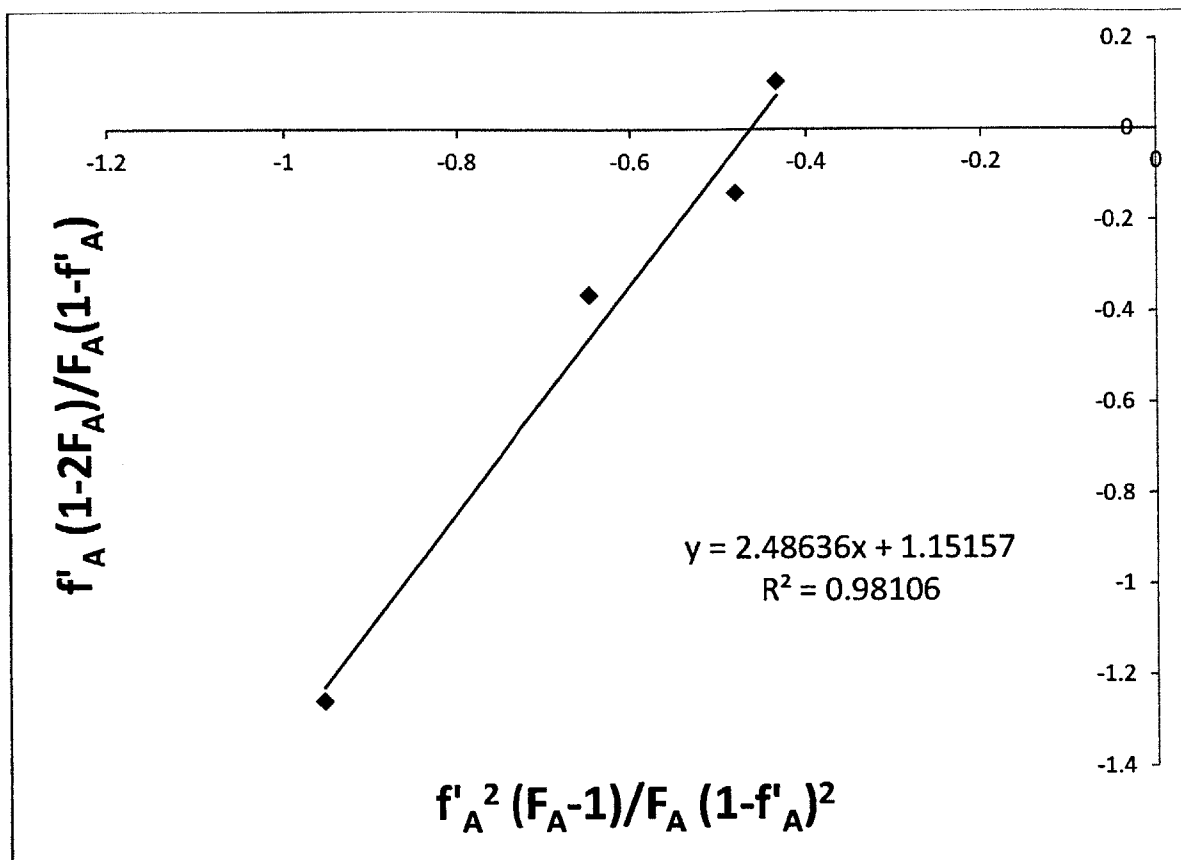


Figure 6: Fineman-Ross adjusted correlation for surface polymerization

Experimental relative reactivity values for 4VP were 2.482 and 1.151 for DVB. This indicates that 4VP monomers are mostly likely to polymerize other 4VP monomers instead of DVB units, since it's much greater than 1. At 1.151, the reactivity ratio for DVB is close to unity, signifying that both reactions are likely to occur with DVB. Due to this, an alternating ABABABABAB sequence of DVB and 4VP is ruled out as the mechanism for copolymerization. This is also supported by FTIR analysis of the samples,

which indicate a varying amount of DVB, from 22% to 54%, ruling out an alternating sequence because such a mechanism would yield a 50/50 composition of 4VP and DVB. Since the reactivity ratio of 4VP is greater than 1 and DVB is shown to vary in copolymer composition, it is clear that there is significant homopolymerization occurring in the samples, yielding higher 4VP content in three of the samples. Using the Q-e scheme, however, resulted in reactivity values of .204 for 4VP and .005 for DVB. The discrepancies in relative reactivity values can arise from different kinetic rate constants in the mild vacuum of the iCVD chamber. In surface copolymerization, partial pressures of the monomers relate to the surface concentrations of said monomers, which then translate into ease of adsorption of these monomers onto the surface of a substrate.

Test samples, created in earlier depositions, were sent to a collaborating lab for initial bacterial attachment tests which will be later formalized into controlled tests of P (DVB-co-4VP) films inside microfluidic devices. However, preliminary data was promising in the ability of the copolymer films to hinder the attachment of microorganisms. Figure 7 shows qualitative snapshots of side-by-side coated and bare glass slides during a bacterial attachment test. The image to the left is a display of a glass slide that has been coated with a thin film of the copolymer described above, to the right is the one which remained uncoated. The first set is taken after 1.75 hours of bacterial flow. In this image, you begin to see

signs of bacterial attachment on the right side, while the left side is relatively unscathed. Even after more than 3 hours, in the fourth image, you can see a considerable amount of bacterial buildup, while still observing minimal attachment in the left side. These results are quite promising for this copolymer's use in anti-bacterial attachment applications. Further tests, more rigorous and well-defined, are currently taking place.

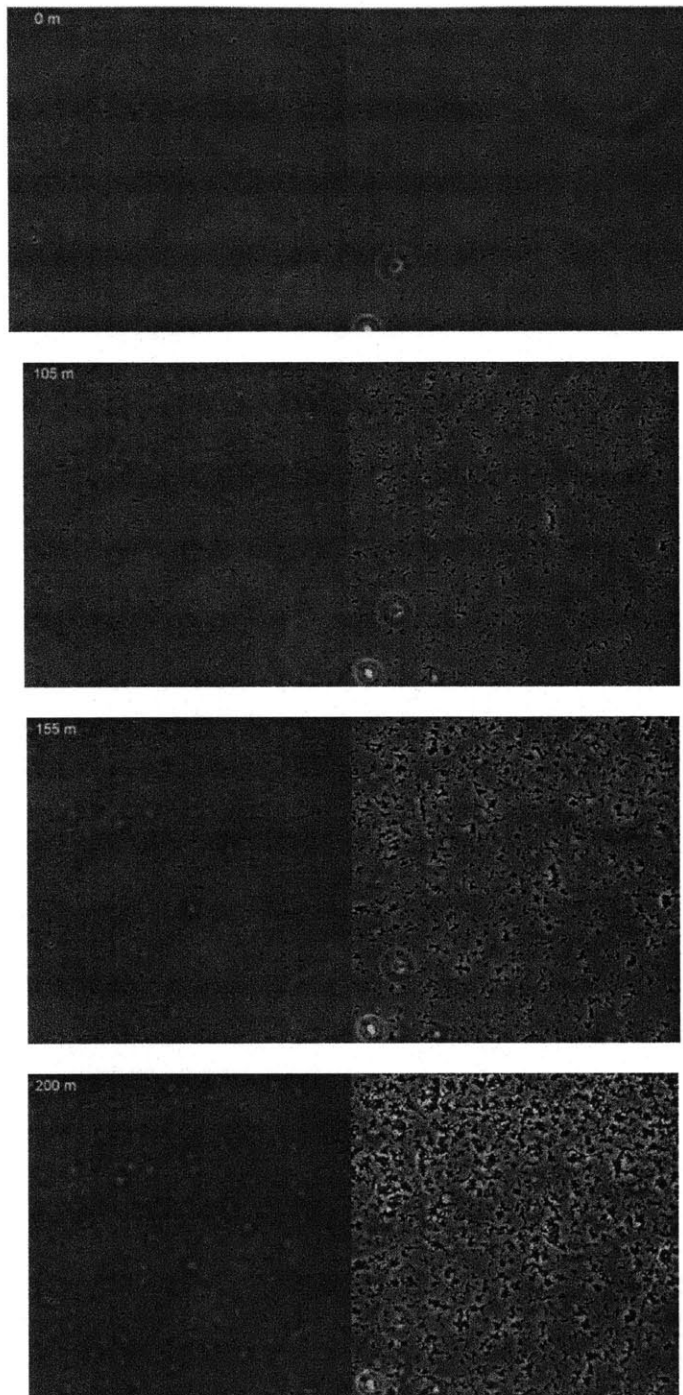


Figure 7: Snapshot progression of bacterial attachment tests on coated and bare glass slides. Left side is coated with copolymer, right side is not.

IV. Discussion

iCVD provides a well-defined tunability for copolymerization of organic thin films. Using analytical methods such as Fineman-Ross correlations, it is possible to create a polymer of desired composition of different species onto a substrate by varying monomer flow rates. This allows for tunable materials properties on highly conformal, stable thin films for a wide variety of applications, especially those requiring the protection of the original surface of a substrate from its environment. The dry and thermally stable conditions of an iCVD chamber also allow for the deposition of polymer material into a variety of materials, including sensitive ones that would otherwise not survive harsh chemicals used in solution polymerization, or high temperatures of other deposition methods. Its low energy input and low cost of monomers also makes it economically advantageous for scaling up the process onto an industrial scale. This means many industries such as biomedical diagnostics, in situ devices, and sensitive membranes can benefit from coatings that can increase their performance and lifetime. Further research into the development of thin films using this process will allow highly specialized materials of complex geometry, composition, or sensitivity to be protected by organic barriers and to be created with reactive groups which can make functionalized surfaces without a large change in dimensions or effectiveness.

V. Recommendations

Further testing needs to occur in order to test the full extent of P (DVB-co-4VP) coatings in anti-bacterial attachments for microfluidic devices and other surfaces that persistently encounter such activity. Mechanical testing of the films on the substrates in question can also be beneficial in determining the stability and function of these coating in situ. Further needs in materials properties of these devices can also be addressed once the attachment activity is fully understood by investigating other monomers that are able to polymerize with DVB, 4VP, or both. Optical response, heat resistance, and abrasion resistance can all be studied with the investigation of copolymerization and crosslinking of polymer chains that are deposited onto such surfaces.

Full characterizations of the zwitterion surfaces that P (DVB-co-4VP) can form are also needed in order to implement zwitterionic copolymer coatings onto them for antifouling purposes. Electrostatic surface characterizations would be beneficial in order to predict the applicability of these surfaces. After coating depositions, salt rejection and permeation tests should be carried out on the protected membranes to confirm their retention of effectiveness in the water desalination objective.

The next step after the processes are fully controlled in the creation of these copolymer thin films would be to begin scaling up the process with bigger dimensions of chamber surface and bigger arrays of filaments in

order to deposit films onto large areas or on a considerable amount of substrates simultaneously. It is unclear whether thickness and composition uniformity would be preserved in larger scales but this may be an issue of reactor design rather than monomer or initiator selection. The initiator of choice of P4VP and PDVB and its copolymers has so far included only TBPO and a consideration of other initiators may improve deposition rates these polymers, yet there hasn't been a need for such improvement in the current stages of research into these films.

VI. Acknowledgments

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