

# A NEW TAKE ON KINETICS: INITIATED CHEMICAL VAPOR DEPOSITION

## as a Chemical Engineering Capstone Laboratory

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Historically, chemical engineering reaction kinetics experiments have been liquid-phase reactions using primarily aqueous reagents in a batch reactor, a continuous stirred-tank reactor (CSTR), or a plug-flow reactor (PFR).<sup>[1]</sup> Students perform these reactions to determine kinetic parameters and gain hands-on experience with reactor design equations. While these systems are classical demonstrations of chemical reactors, and are usually safe and economical, novel or varied reactors and reactions can be considered when expanding the experiments in the capstone-level laboratory course. Chemical vapor deposition (CVD), with gas-phase reagents being transformed into a solid product, provides an interesting alternative to liquid-phase reactions while still allowing students to use basic elements of kinetic analysis. Additionally, CVD is widely used in various research and industrial applications, including functional thin films and coatings,<sup>[2-4]</sup> biocompatible materials,<sup>[5-8]</sup> and the semiconductor industry,<sup>[9,10]</sup> to name a few. As a learning tool, CVD exposes students to a wider range of reactor types and reaction mechanisms, as well as exposing them to a modern chemical engineering tool.

Initiated chemical vapor deposition (iCVD), a subset of CVD methods, is a novel polymerization method for fabricating many common organic polymers via a vapor-phase deposition process rather than traditional liquid-phase or spin-casting methods. A major advantage of iCVD is the high degree of structural fidelity with traditionally polymerized materials, which is in direct contrast to many previous CVD methods, such as thermal CVD or plasma-enhanced CVD (PECVD).

In these methods, the high energies involved often resulted in amorphous materials that did not resemble, structurally or behaviorally, materials produced via traditional polymerization

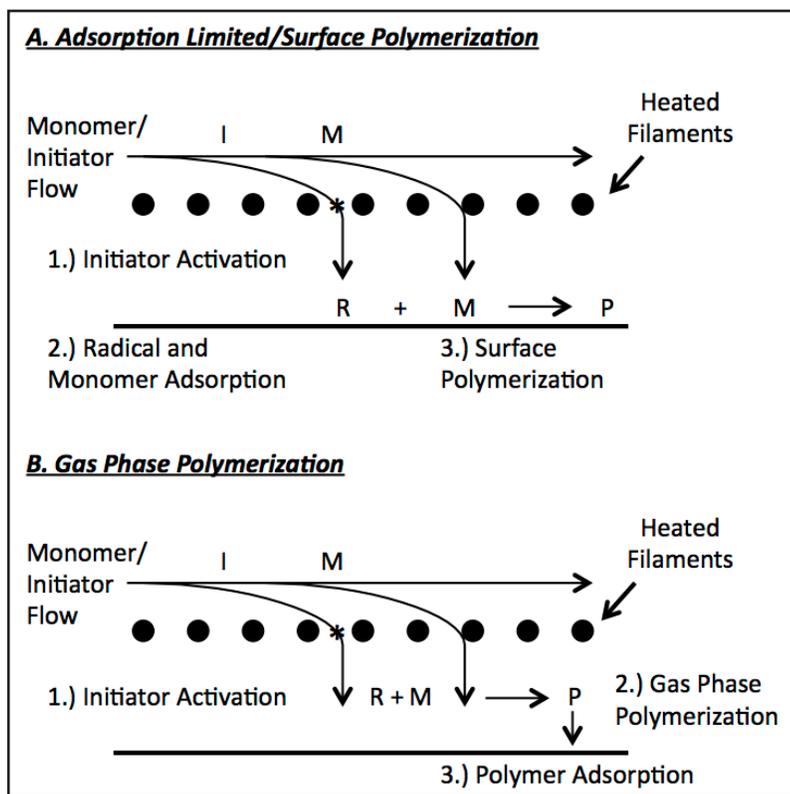
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**Figure 1.** Two proposed mechanisms for iCVD polymerization: A. An adsorption limited surface polymerization and B. A gas-phase polymerization. Figure is adapted from Lau, et al.<sup>[15]</sup>

techniques. By comparison, iCVD has been shown to produce materials that are virtually indistinguishable from their bulk counterparts.<sup>[11,12]</sup> This difference is largely due to the use of an initiator species that can be activated at substantially lower energies, which allows preservation of chemical functionalities in the monomer. Additionally, when compared to many other CVD processes, the substrate in iCVD is maintained at near-ambient temperatures. The advantages here are numerous, including the elimination of solvents and solvent waste, the ability to easily coat non-traditional substrates such as paper or cloth, and the ability to coat micro- and nano-scale high-aspect-ratio features due to the lack of surface tension and wetting effects.<sup>[13]</sup> From an educational perspective, students can apply basic kinetic analysis to determine rates, activation energies, and other kinetic parameters relevant to scale-up. For an excellent review of the state-of-the-art in iCVD and related techniques, see Alf, et al.<sup>[14]</sup>

In an iCVD process, the reactant monomer and an initiator are introduced into the reaction chamber at a constant flow rate and pressure. A series of resistively heated wires (filaments) inside the reactor supply thermal energy to activate the initiator. Most iCVD reactions follow a free-radical initiation pathway. The excitation source radicalizes the initiator, which then attacks the monomer and begins the polymerization process. Numerous studies have shown that

many iCVD reactions are adsorption limited, with the polymerization reaction occurring at the substrate surface rather than the gas phase.<sup>[15-17]</sup> For these cases, the monomer must be adsorbed at the substrate surface before the reaction occurs. Thus, as substrate temperature is *decreased*, the deposition rate will *increase* due to increased adsorption of reactants. This observation often surprises students, who typically expect chemical reactions to follow Arrhenius-type kinetics based on their undergraduate reaction engineering coursework.

The adsorption-limited reaction initiates a discussion with students about two different potential mechanisms for the polymerization, as shown in Figure 1. As stated previously, the polymerization occurs at the substrate surface for the adsorption-limited case. Increasing filament temperature may increase the flux of reactive species to the surface, but the increased flux will not translate into increased reaction rate if there is nothing adsorbed. Conversely, changing the substrate temperature should have a profound effect. A low substrate temperature will result in increased adsorption, resulting in increased reaction. High substrate temperatures will retard adsorption, and hence slow the reaction rate.

In the second case, polymerization occurs in the gas phase and the products diffuse to the surface and deposit, forming the final film. Filament temperature should play a dominant role in the reaction, as increased energy at the filaments increases the probability of initiation and, thus, the reaction rate. Substrate temperature will play a minimal role—as long as the substrate isn't too hot, the products will adsorb.

These concepts can be quantified using the ratio of the monomer (reactor) pressure ( $P_M$ ) to its vapor pressure at the substrate temperature ( $P^{SAT}$  at  $T_S$ ). As  $P_M/P^{SAT}$  approaches zero, the monomer effectively has zero surface concentration, and the observed rate should also approach zero. For  $P_M/P^{SAT}$  approaching one, the monomer will condense and form a liquid film, at which point the process can no longer be classified as CVD. Lau, et al. have suggested that effective  $P_M/P^{SAT}$  ranges for iCVD deposition lie between about 0.3 and 0.8.<sup>[15,16]</sup> The CVD experiment thus forces the students to consider a number of factors related to core chemical engineering. They must apply thermodynamic principles such as vapor pressure and vapor-liquid equilibrium to determine the correct operating conditions for the source jars, as well as the experimental operating conditions with respect to the substrate temperature. They need to consider the implications of a mass-transfer limited process vs. a kinetically limited process, and they also need to use their basic understanding of chemical kinetics to determine the kinetic parameters for their reaction.

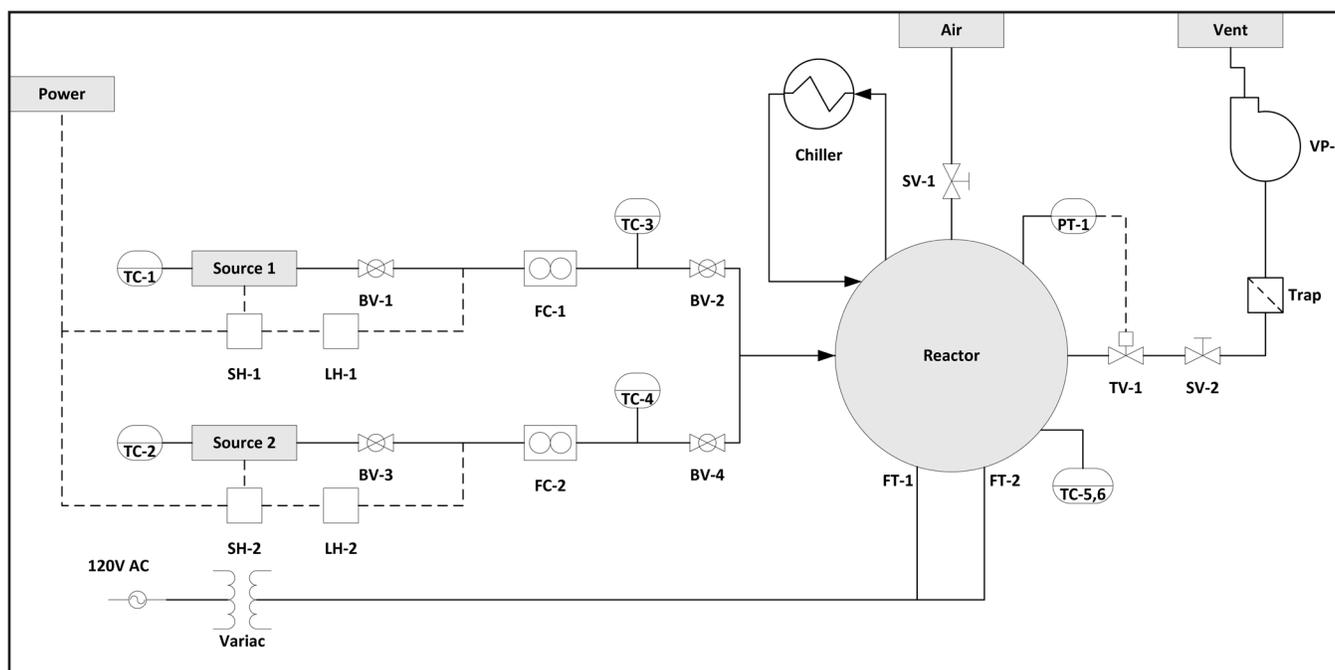
## LABORATORY DESCRIPTION

This experiment exposes students to iCVD, requiring them to determine the kinetic parameters for a polymerization reaction and compare their results to literature. The basic components for the experiment are a vacuum deposition chamber, vacuum roughing pump, an excitation source (either thermal or UV-based), heating vessels for the reagents (both monomer and initiator), as well as metering valves (or Mass Flow Controllers) to control the flow of reagents. A feedback control loop to monitor and maintain chamber pressure and temperature are also included. For the system in the laboratory at the University of Connecticut (UConn), shown in Figure 2, we purchased a turn-key system from GVD Corporation (<[www.gvdcorp.com](http://www.gvdcorp.com)>), located in Cambridge, MA. GVD specializes in the design and fabrication of these research-quality systems. Through collaboration with the company, a balanced system that incorporated both manual operation and computer control loops was created. The total cost for the system at UConn was approximately \$120K, but wide variation in price is possible depending upon the options chosen; for example, significant cost reductions can be realized by favoring more manual control loops over automated ones. There always is the option to construct a system in-house based on needs. Having a good machine shop available on campus is beneficial to a project of this scope. A process schematic is included as Figure 3, and Table 1 lists the major components from the process schematic, as well as potential vendors. The authors ([daniel@enr.uconn.edu](mailto:daniel@enr.uconn.edu)) would be happy to answer more detailed questions about in-house construction of such an experiment.



**Figure 2.** The integrated iLab chemical vapor deposition experiment at UConn. Photo courtesy of GVD Corporation.

In a typical experiment, students will control five variables: chamber pressure, stage temperature, filament temperature, monomer flow rate, and monomer identity. Astute students may recognize that the  $P_M/P_M^{\text{SAT}}$  ratio is a combination of the



**Figure 3.** Process schematic for an iCVD deposition reactor.

monomer pressure and stage temperature, which can be used as a variable as well. In the pre-lab briefing, the instructors explain the general concept of CVD, and then give the students the challenge of deducing the reaction mechanism as well as kinetic parameters based on a combination of variables of their choosing. The CVD experiment serves as one of the “anchor” laboratories in the capstone laboratory sequence at UConn, and as such, students have three weeks (six 4-hour laboratory periods) in which to collect their data. However, more or less time can be dedicated to the experiment to adapt to other laboratory schedules.

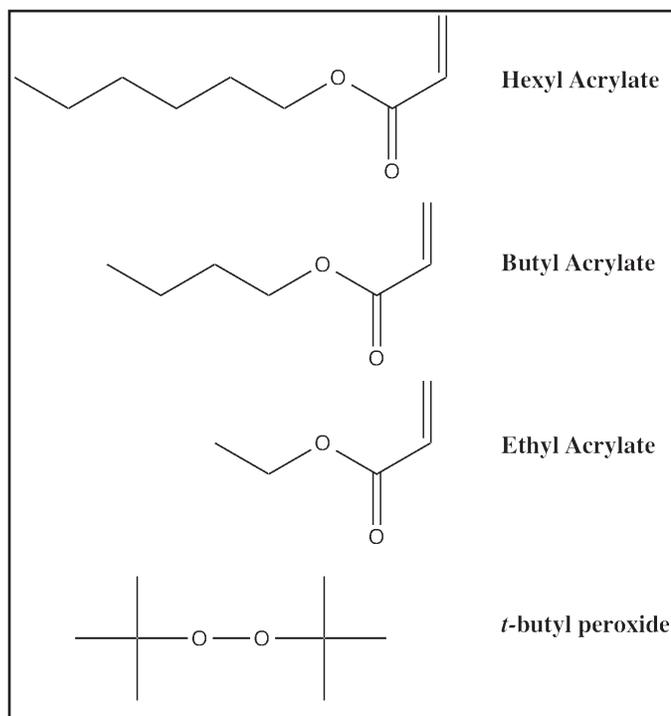
## MATERIALS AND METHODS

Alkyl acrylates were chosen as the monomer for this experiment. The unsaturated bond in alkyl acrylates is susceptible to free-radical initiated polymerizations, due to the electron-

withdrawing carbonyl group in close proximity. In most cases, the pendant group on the ester side of the molecule is left untouched, making iCVD polymerization a convenient way to produce functionalized thin films by changing the identity of the acrylate pendant group. For example, a perfluorinated pendant group can render the films hydrophobic, whereas hydroxyl-terminated pendant groups can render them hydrophilic. Ethyl Acrylate (CAS 140-88-5, Sigma-Aldrich), Butyl Acrylate (CAS 141-32-2, Sigma Aldrich), and Hexyl Acrylate (CAS 2499-95-8, Sigma Aldrich) were all used without further purification, and each student group selected one of these acrylates for their study. For the initiator, alkyl substituted peroxides, such as *tert*-butyl (CAS 110-05-4, Sigma-Aldrich) or *tert*-amyl (CAS 10508-09-5, Sigma-Aldrich) were used. The peroxide bond is very weak and, under mild heating by the filament, degrades into two alkyl peroxy radicals capable

**TABLE 1**  
Major System Components

Process Diagram ID	Example Part No.	Description	Source	Approximate Price
BV-1	SS-63TVCR8	½” Ball Isolation Valve	Swagelok	\$340
BV-2	SS-63TVCR8	½” Ball Isolation Valve	Swagelok	\$340
BV-3	SS-62TVCR4	¼” Ball Isolation Valve	Swagelok	\$224
BV-4	SS-62TVCR4	¼” Ball Isolation Valve	Swagelok	\$224
Chiller	101101010000006	ThermoFlex 900W Recirculating Chiller	ThermoScientific	Quote
FC-1 (Manual Alternative)	SS-4BMG	¼” Needle Valve, Regulating	Swagelok	\$371
FC-1	1152C	MKS 1152 Heated Mass Flow Controller	MKS Instruments	Quote
FC-2 (Manual Alternative)	SS-4BMG	¼” Needle Valve, Regulating	Swagelok	\$371
FC-2	1479A01312CR1BM	MKS 1479A Mass Flow Controller	MKS Instruments	Quote
FT-1	EFT0113058	KF16 Copper Pin Electrical Feedthrough	Kurt J. Lesker	\$60
FT-2	EFT0113058	KF16 Copper Pin Electrical Feedthrough	Kurt J. Lesker	\$60
LH-X	SRT101-040	Example: Omega Silicone Rubber Heating Tape (or similar)	Omega Engineering	\$86/ea.
PT-1	622B11TDE	10 Torr MKS Baratron Pressure Transducer	MKS Instruments	Quote
Reactor	Custom	Various Designs Possible	Kurt J. Lesker	Quote
SH-X	SRT101-040	Example: Omega Silicone Rubber Heating Tape (or similar)	Omega Engineering	\$86/ea.
SV-1	SS-DSS4	Diaphragm Valve (Repressurization)	Swagelok	\$170
SV-2	SA0150MVQF	KF 40 Manual Sealed Bellows Isolation Valve	Kurt J. Lesker	\$320
TC-X	SA1-K-72	Low Profile K-Type Thermocouple	Omega Engineering	\$84/pack of 5
Trap	TSR4MS150QF	KF 40 Molecular Sieve/Activated Carbon Foreline Trap	Kurt J. Lesker	\$450
TV-1	253B-1-40-1	KF 40 MKS 253B Exhaust Throttle Valve	MKS Instruments	Quote
Variac	ST3PN1210B	Variac 120V Variable Autotransformer	Variac	\$432
VP-1	A36401935	Edwards E2M40 Rotary Vane Vacuum Pump	Edwards	\$8400



**Figure 4.** Chemical structure of hexyl, butyl, and ethyl acrylate, as well as *t*-butyl peroxide, the monomers and initiator used in this study.

of initiating polymerization. Figure 4 shows the chemical structure of all of the monomers and initiator used.

An 80/20 nichrome alloy wire connected to a 120 V Variac power supply heated the filaments. A K-type thermocouple in contact with the filament monitored temperature, and the power supplied was adjusted manually. Filament temperatures were normally kept in the range of 200 °C to 400 °C. An external recirculating chiller controlled substrate temperature, which was monitored via a low-profile K-type thermocouple adhered directly to the stage close to the substrate being coated. Stage temperatures between 0 °C and 50 °C are generally possible with water cooling. Other temperatures (higher and lower) may be achieved with appropriate changes to the recirculating fluid (*i.e.*, glycol mixtures or silicone oils).

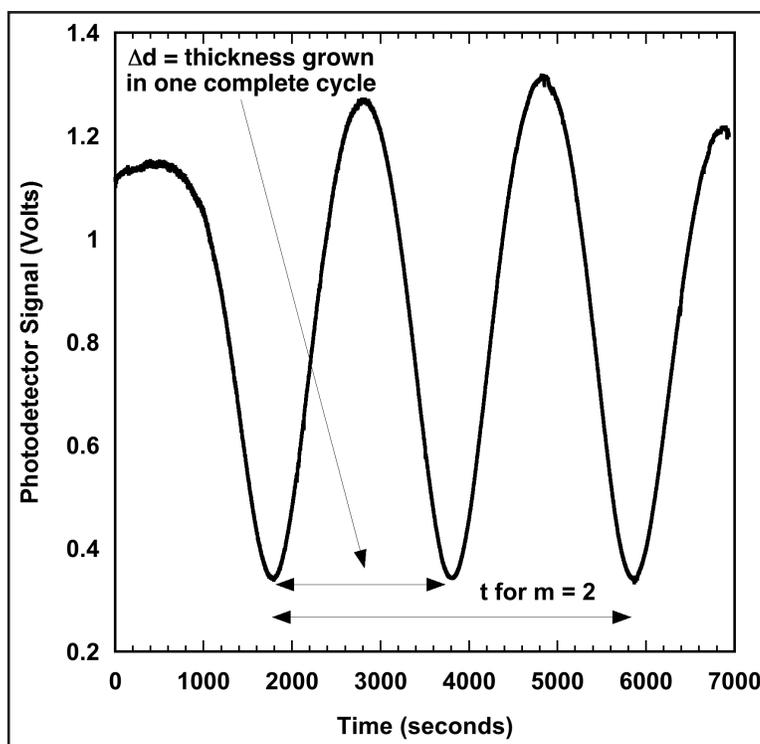
Chamber pressure was normally kept between 100 mTorr ( $\sim 1.3E-4$  atm) and 1000 mTorr ( $\sim 1.3E-3$  atm), depending upon the properties of the monomer being studied. Students were encouraged to determine the vapor pressure behavior of the monomers using data available from the suppliers as well as from the NIST database or other sources to establish the appropriate operating ranges for their experiments.

The substrates were typically small (2 cm  $\times$  2 cm) chips of <100> silicon wafer placed in the center of the reactor. Care was taken to avoid contaminating the surface of the substrate. Real-time thickness measurements were carried out using a laser interferometry technique, which allows the determination of deposition rate and, thus, determination of kinetic parameters. Rate can also be determined *in situ* via a quartz crystal oscillator, or post-deposition, and *ex situ* by measuring thickness via profilometry or ellipsometry.

During a typical experimental run, student groups first tried to determine whether the reaction was gas-phase or surface-dominated by selecting a fixed substrate temperature and running a number of trials at varying filament temperatures. Next, they selected a filament temperature and ran a number of trials at varying substrate temperatures. Other groups looked at fixing filament temperature and then varying the  $P_M/P^{SAT}$  ratio through manipulation of the total pressure or substrate temperature.

## RESULTS

Each student group was asked to investigate a different monomer, and then pool their results at the end of the semester to determine the impact of monomer type. Deposition rate was measured via the laser interferometry technique and the raw data from the experiment is shown in Figure 5. Briefly, as the thin film is deposited, the incident



**Figure 5.** Interferometry plot showing thin film growth as a function of time. Students calculate the cycle thickness ( $\Delta d$ ) and from there, the polymerization/reaction rate.

laser beam is both reflected and refracted by the polymer. The refracted beam passes through the growing film, reflects off the silicon substrate, passes through the polymer again, and then exits the film. As this refracted beam has travelled further than the beam that was reflected off the film, a phase differential exists when beams are received at the photodetector, resulting in constructive/destructive interference. As the film grows, the phase difference goes through a full  $2\pi$  cycle, and a sinusoidal curve characteristic of the film growth is observed in the intensity of the laser signal. The cycle thickness can be calculated using Eq. (1) and Eq. (2),

$$\Delta d_{\text{film}} = \frac{\lambda}{2n \cos(\theta_2)} \quad (1)$$

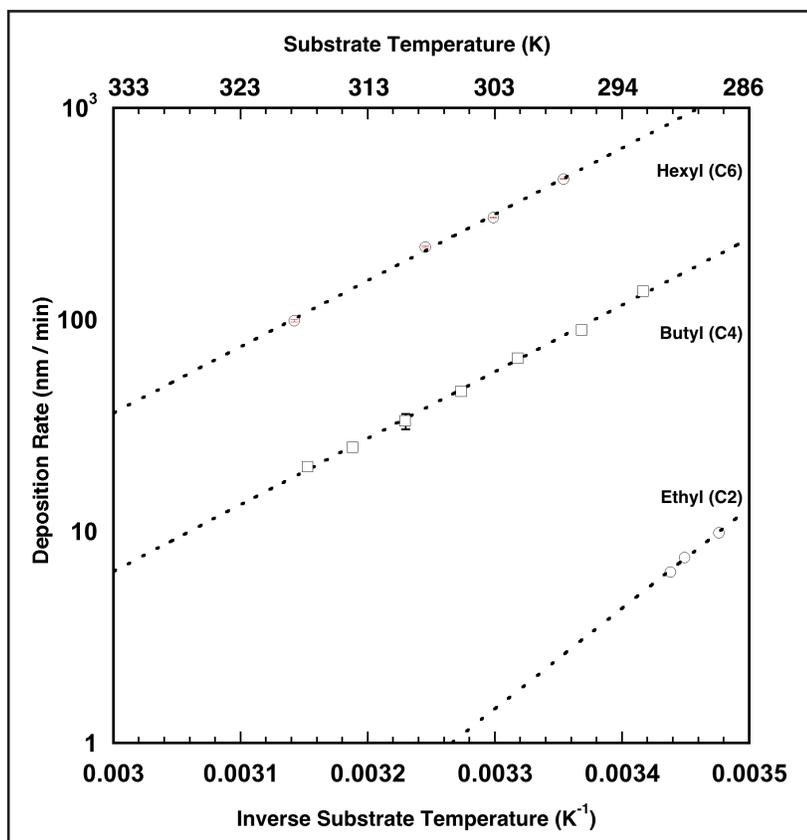
$$\cos(\theta_2) = \sqrt{\left(1 - \left[\frac{\sin(\theta_1)}{n}\right]^2\right)} \quad (2)$$

where  $\Delta d_{\text{film}}$  is the thickness deposited in one  $2\pi$  cycle,  $n$  is the index of refraction of the polymer (unknown, but typically estimated between 1.2 and 1.5),  $\lambda$  is the wavelength of the laser (633 nm in this case), and  $\theta_1$  is the angle of the laser

with respect to the film surface normal (about  $25^\circ$  in this setup). To determine the overall deposition rate, the students then take the cycle thickness, multiply by the number of complete peaks observed,  $m$ , and divide by the total time,  $t$ . The deposition rate (and hence the reaction/polymerization rate) is thus  $(m \cdot \Delta d_{\text{film}})/t$ . Students should typically observe 5-6 complete cycles at minimum and ensure the peaks have a consistent frequency to guarantee steady-state deposition conditions. Once the students have the rate data, they can begin to manipulate it as they would any kinetic data.

Figure 6 shows the effect of varying substrate temperature while holding filament temperature constant. This represents the aggregate data collected by eight students working in three groups (3, 3, and 2 students) over the course of a three-month semester. Each group used a different monomer (ethyl, butyl, and hexyl acrylate), and the groups helped each other between sessions in troubleshooting and determining appropriate operating conditions. A number of features are immediately apparent when looking at Figure 6. The first is the effect of monomer. At similar substrate temperatures, there is a clear ordering of the species by molecular weight, with the highest

molecular weight species (hexyl acrylate) having the highest deposition rates. If the reactions are substrate-dominated then this result is expected. At a given substrate temperature, vapor pressure of the higher molecular weight species is lower, resulting in increased adsorption and hence increased rate. The other feature that is apparent is the effect of the substrate temperature itself. As the substrate temperature is decreased, the deposition rate increases significantly for all of the monomers, further suggesting that the iCVD reaction is adsorption limited. Students should find that this result agrees with the literature. Lastly, if students fit the data and calculate an apparent activation energy for this process, they find a value of approximately  $-90$  kJ/mol for ethyl acrylate, which, considering the uncertainties present in the students' technique and measurements, is very close to the  $-82$  kJ/mol as calculated by Lau, *et al.* for the same monomer.<sup>[15]</sup> Performing the same calculation for the butyl and hexyl acrylates, students find values of approximately  $-60$  kJ/mol, which, as Lau points out, is within the range of physisorption enthalpies for small molecules. Furthermore, the enthalpy of adsorption is expected to decrease with increasing molecular weight. Thus, over the course of the semester, the students were able to show a clear effect of substrate temperature and monomer identity on reaction and polymerization rate, and compare these favorably with data from the literature.<sup>[15,16]</sup>



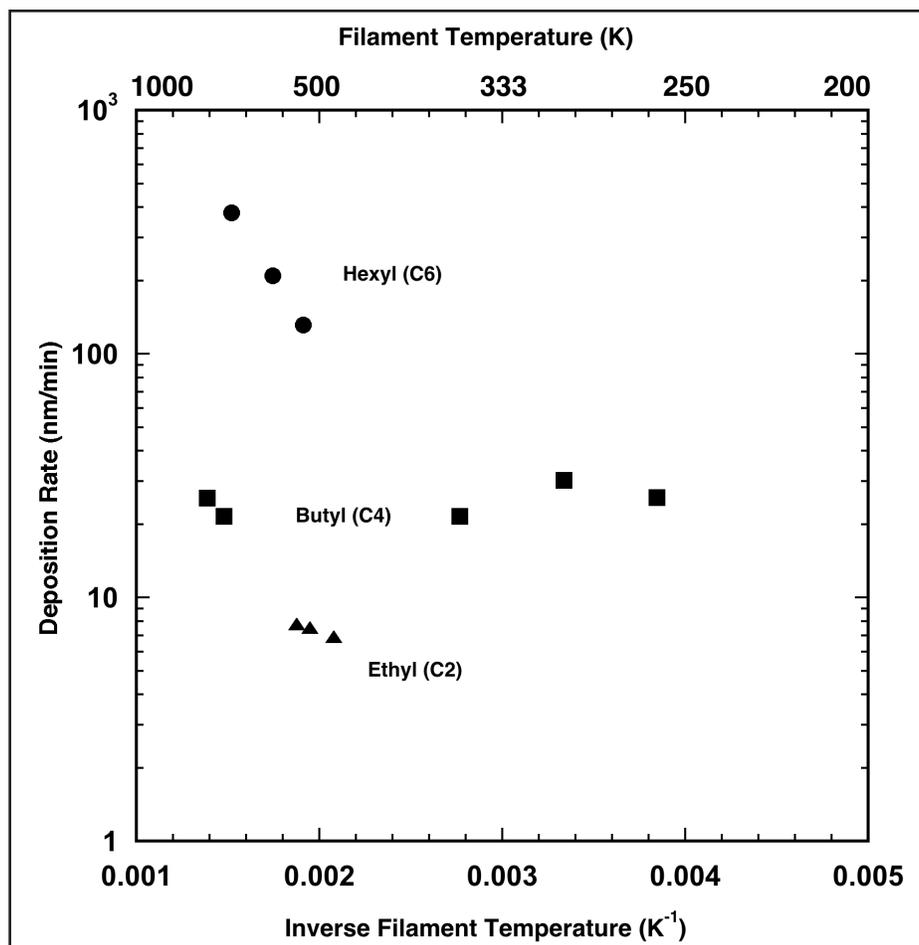
**Figure 6.** Deposition rate vs. inverse substrate temperature for the three monomers studied. Rate increases with increasing molecular weight, as well as with decreasing substrate temperature, indicating an adsorption limited process.

To confirm the adsorption-limited mechanism, students then varied filament temperature while holding substrate temperature constant. If the reaction is wholly surface-dominated, then at constant substrate temperature the relative surface coverage of the substrate with monomer should be the same, regardless of the filament temperature. Students were careful in adjusting the stage temperature with the chiller, as the proximity of the filaments also tends to increase the substrate temperature. Some increase in rate may be expected as increasing filament temperature can increase the flux of radical initiator to the substrate, but this effect is often small. The results from the three student groups for variable filament temperature with constant substrate temperature are presented in Figure 7. For ethyl acrylate and butyl acrylate the data shows that over a wide range of filament temperatures studied there is relatively little change in the deposition rate when the substrate temperature is held constant. For hexyl acrylate, there is a more pronounced effect, with rate increasing with increasing filament temperature, although the lack of replicate data on the first data point makes it difficult to determine whether this effect is real or an outlier. Future student groups can re-examine this data point to further fill out the deposition space.

## EXPERIENCES AND ASSESSMENT

The CVD experiment has been run for a total of four full semesters (Fall 2011, Spring 2012, Fall 2012, and Spring 2013). In the first semester of use, it was originally scheduled as a three-day experiment. The overall consensus (from both the students and the course instructors) was that more time with the equipment was desirable to generate more data with which to draw meaningful conclusions. In

the second semester, the experiment was allowed six class periods, becoming one of the six “anchor” experiments in the UConn senior laboratory course. The laboratory at UConn has 14 different experiments, and traditionally students have completed a small set of these over the course of their senior year, selected to try and provide as much diversity in topics as possible. In order to keep group sizes manageable (2-3



**Figure 7.** Deposition rate vs. inverse filament temperature. The general lack of correlation indicates that the reaction is largely not dominated by gas-phase growth of the polymer chains.

TABLE 2 Post-Experiment Survey Questions		
Question	Level 1 Response	Level 5 Response
How much did you know about chemical vapor deposition prior to this experiment?	1 = Nothing at All	5 = A Lot
Compared to other experiments in the lab you have performed, how would you rate the CVD experiment?	1 = Not Interesting at All	5 = Very Interesting
How much do you feel you learned during the CVD experiment?	1 = Nothing at All	5 = I Learned A Lot
Please rate how you felt overall about the CVD experiment.	1 = It was terrible – no one should have to do this.	5 = It was great – everyone should have a chance to do it.

students per group), each student completes a subset of the available experiments (two anchor and four shorter experiments), with the CVD experiment being one of the anchor six-day experiments. Typically, 8-9 students completed the CVD experiment per semester at UConn, although the experiment can be adapted depending on curricular needs.

During its first run as a six-day experiment, the true potential of the system was realized. Students had sufficient time to collect enough data as well as perform replicate trials to establish confidence intervals on some of their data. In the most recent semesters, students were encouraged to share information and operational tips across groups. Having each group test a different monomer or different conditions avoided concerns about sharing or copying of data.

As such, each group had different, but comparable, results. Several different monomers are possible, limited only by their thermodynamic characteristics. For our system, accessible pressures range between 100 and 1000 mTorr, and accessible substrate temperatures between 0 °C and 50 °C. This variability allows the instructors to easily select monomers with an appropriate  $P_M/P^{SAT}$  ratio, ensuring not only that deposition will occur, but will occur in a reasonable time frame. One of the primary difficulties this semester was the use of ethyl acrylate, which has a relatively high vapor pressure, and as such, a low value of  $P_M/P^{SAT}$ , which makes the depositions significantly slower than the other monomers at the conditions available in our system. The vapor pressure represents the major reason why there are few if any replicates of the ethyl acrylate data points, as the runs for that monomer lasted several hours.

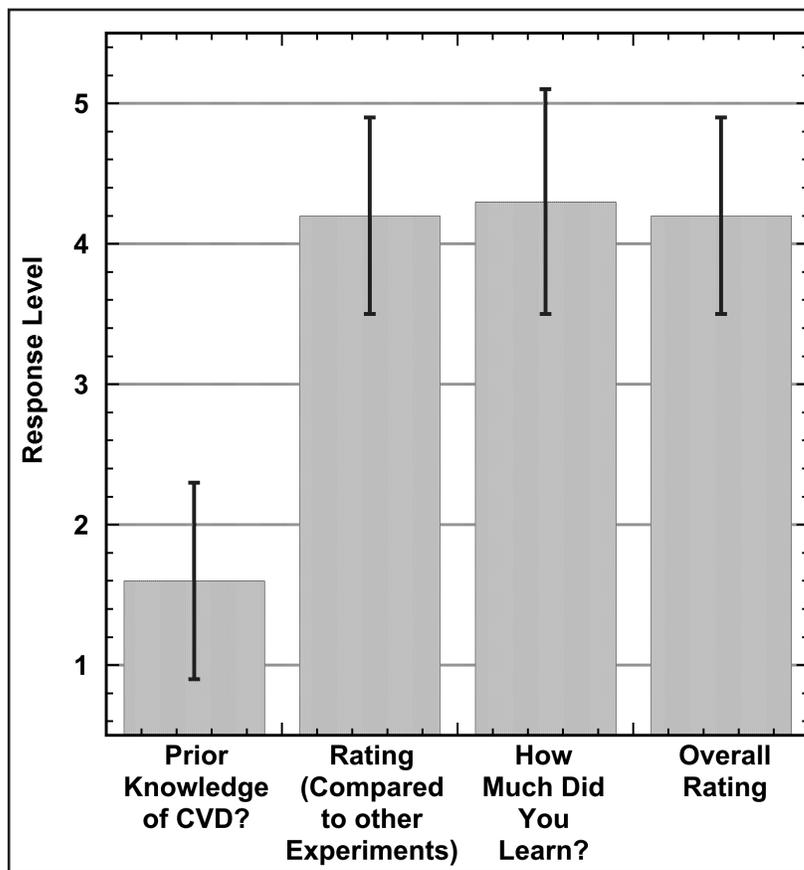
All students who completed the experiment in Fall 2012 and a subset who completed the experiment in Spring 2013 (at the time of this writing) were surveyed for a total of 12 respondents. Table 2 shows the questions that we asked of the students and the answer choices, which were on a 5-point Likert scale.

Figure 8 shows the responses to these questions as provided by the students. As shown, most students had very little exposure to or knowledge of CVD as a technique prior to the lab. As exposing students to new and modern chemical engineering tools and techniques was one of the major goals of implementing this experiment, it would seem this goal is being accomplished. Students generally responded favorably to the experiment as compared to others they had performed, as well as overall. Students also felt they had learned a good deal about CVD after performing the experiment. Response levels to these questions were all over 4 out of the 5-point scale used. Students were also given an

opportunity to discuss what they liked about the experiment as well as things that they disliked or could use improvement. Most of the positive responses focused on the “newness” or novelty of the technology, but that their basic chemical engineering knowledge could still be used to analyze the data. Most of the comments about ways to improve the experiment focused on speeding up the process and eliminating downtime in waiting for steady states to be achieved.

## SAFETY

The alkyl acrylates used in this experiment are typically considered irritants, and as such, proper PPE, such as gloves and eyewear, are recommended. Students should refer to the MSDS for other specific information. The lab staff should note that some acrylates require storage at lower temperatures, so having a chemical refrigerator nearby is helpful. The alkyl peroxides used as the initiator are also reactive, and general guidelines for the storage and handling of peroxides should be followed. Because of the small quantities used, charging the reactant containers with enough material for several runs can usually be carried out prior to an experiment by lab personnel, thus minimizing student handling of the reactants.



**Figure 8.** Student responses to survey regarding the CVD experiment. Questions and response levels are given in Table 2. Data represents the average of 12 students surveyed.

To avoid possible electric shock, students should ensure that the filament power source is disconnected prior to opening the reactor to place or retrieve samples. Students should also monitor the temperature of various components, such as the filament array, to ensure that they have reached ambient temperature before attempting to work in the reactor. Lastly, students should be aware of the orientation of the laser used in the interferometry setup to avoid placing their head or eyes near the beam.

## SUMMARY AND CONCLUSIONS

With the iCVD experiment, we have added an interesting and modern chemical reaction engineering experiment to the curriculum, which gives us the ability to demonstrate vapor-phase and heterogeneous reactions, adsorption-limited reactions, and a variation on classical polymerization reactions. Student reaction to the experiment has been generally positive, and the results of the work over several semesters have shown that the students are more than capable of running the apparatus and generating high-quality results similar to those obtained in the literature. While the initial investment in a system such as this can be costly, there are a number of variations on the general theme that can be performed at a lower cost, making iCVD experiments feasible over a wide range of budgets. We have found that it provides an excellent counterpoint to the traditional batch and CSTR/PFR liquid-phase reaction experiments we also have in the lab, and it exposes students to a polymer fabrication technique that is of growing interest and importance in the field.

## ACKNOWLEDGMENTS

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