POLYMERIZATION SIMULATOR
For Introductory Polymer and Material Science Courses

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One of the fundamental challenges in teaching a polymer science course is to develop the student's intuition regarding how this class of materials behaves. Professors often describe polymers as entangled masses of spaghetti or kite string to explain the unique behavior of polymers. The reason this is commonly done is that if students can visualize how polymer chains interact and function through tangible examples, then they are better able to understand many of the basic concepts in polymer science and engineering. Near the end of my graduate polymer engineering course, I tell my students that they are prepared for the final exam when they are able to "think like a polymer." Stated in a more didactic fashion, students must be able to visualize and understand the models used in polymer science in order to interpret microstructures, predict effects on properties, and derive the corresponding equations.

One important topic in polymer science is the kinetics of polymerization reactions. Modeling polymerization reactions does not typically require a detailed knowledge of the organic chemistry involved, since most polymerization reactions follow one of several motifs. For instance, in a typical stepwise growth polymerization, there are two monomer types such that each "type A" monomer will react with two "type B" monomers. Each type B monomer will react with two type A monomers, and each monomer does not react with its own

type. A stoichiometric reaction at high conversion will result in long polymer chains of alternating monomer types. A classic example of this reaction is the synthesis of polyester from a monomer with two alcohol groups and a second monomer with two carboxylic acid groups. Modeling the kinetics of the molecular weight development does not require knowing the details of the chemistry, except for knowing the aforementioned bonding rules.

With these thoughts in mind, two polymerization simulators were developed for two different polymerization types: stepwise growth and free-radical chain polymerizations. In these simulators, the details of the chemistry are neglected, and computer models of polymerization are created by

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considering monomers as simple spheres of different types that obey defined bonding rules. These simulators allow for students to quickly obtain an understanding of how these polymerization reactions occur and the differences between the two. For instance, at moderate conversions, the step-growth polymerization will result in a variety of oligomers, while the free-radical chain polymerization will result in a few long polymers along with unreacted monomers, as seen in Figure 1. An instructor can demonstrate these concepts more effectively and expeditiously with a computer simulation rather than with a blackboard. The simulators featured in this article are also convenient for instructors and institutions because they are free to use for academic, noncommercial purposes.

TARGET AUDIENCE

This simulator is an ideal tool for introducing polymerization reactions or simply the concept of a polymer. It has been found to be useful for at least two student groups. First, this module has been found to be effective in a basic materials science/engineering class to introduce polymer materials. Instead of simply giving the definition of a polymer, introducing polymers with the use of this simulator allows for the students to quickly develop an appreciation for what polymers are and how they are made.

The full potential of the simulator, however, can be realized in a graduate-level introductory polymers course, where basic polymer concepts and formulae can be quantitatively analyzed by the students by exporting their acquired data into spreadsheets. Students are likely to become more engaged in a class when there are live demonstrations of polymerizations, such as the "Nylon Rope Trick,"[1] or if they can use processing or characterization equipment themselves. These simulators offer much of the visual stimulus of a live demonstration with the convenience of a PowerPoint presentation, and they allow students to conduct their own simulated experiments.

From the students' perspective, the simulators represent an easier mechanism for learning the material that is more contemporary, visual, and interactive. One major benefit is that this method of instruction allows students with different learning styles that are less receptive to lectures to grasp the key concepts by executing their own model experiments. Surveys conducted at the end of my graduate polymer engineering courses confirm that the simulations help the students visualize and understand polymerization reactions and develop new insights as shown later in the "Results" section. Most professors have known some individuals who were rather lackluster students, yet they excel in more hands-on activities such as laboratory work, independent research, or future employment in industry. Similarly, instructors may find these students that do not respond well to passive learning in lectures may have a chance to excel if they are given an opportunity to perform their own model experiments and analyze the data that they collect.

MOLECULAR SIMULATION MODELS

The simulators demonstrated in this paper were developed as an Etomica molecular simulation module. These modules are available online, coded in Java, and free for purposes of academic research and instruction. The modules are publicly available at <www.etomica.org>. From the home page, the polymerization simulator can be found by navigating to "Modules" and then selecting the "Polymerization" module. The polymerization module may also be accessed directly at <http://rheneas.eng.buffalo.edu/wiki/Polymerization>. The module is designed to be self-explanatory with the essential background material included on the website with examples and problems. The module is even more effective when coupled with a formal polymer course, however.
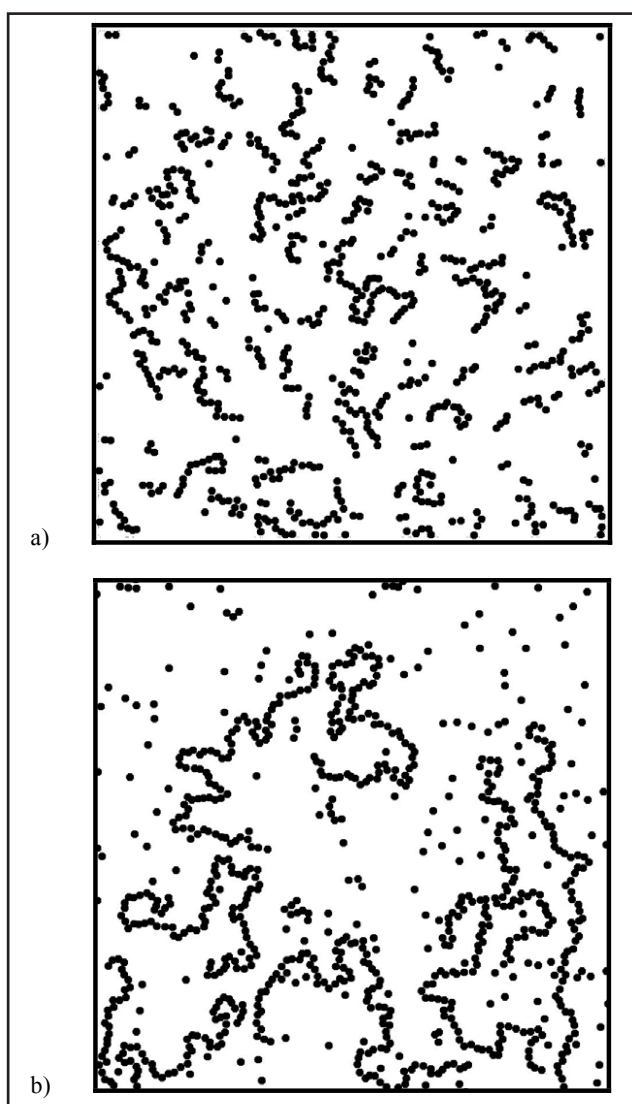

Figure 1. *Molecular simulation of a) a stepwise growth polymerization and b) a free-radical chain polymerization. Both simulations are at 80% conversion. Figures are reproduced in black and white, but the monomer types are color-coded in the simulation.*

In these models, the average speed of the particles is determined by the system temperature. The temperature can be controlled using a "thermostat" which will change particle speeds to obtain the set temperature for the system. The user is able to set adiabatic or isothermal conditions and change the temperature while the simulation is running. This allows the students to see the effects of temperature on polymerization reactions. The bond energy is also programmable, which affects both the strength of the bond and the heat released during reaction. Users can then monitor the number- and weight-average molecular weights, chain-length histogram, temperature, and conversion over time.

STEPWISE GROWTH SIMULATION

Stepwise growth polymers are created by reacting at least two different monomer types. In the simplest case, there will be a type A and a type B monomer, where each monomer will react and bond twice with the other type but not its own type. Monomers that form two bonds are known as di-functional. Specific chemical mechanisms are neglected in this simulation, but the monomers are given names for clarity. The type A monomers are di-functional alcohols, annotated as di-ols. The type B monomers are di-functional carboxylic acids, annotated as di-acids. Mono-ols and Mono-acids are mono-functional groups that act as end-capping agents. A tri-functional acid is also available as a cross-linking agent. The di-ols, di-acids, and cross-linking agents are represented as red, blue, and green dots, respectively. Using this simple model, a variety of basic concepts in stepwise growth polymerization can be demonstrated as discussed in the "Student Activities" section.

FREE-RADICAL CHAIN ADDITION SIMULATION

Free-radical chain addition is an entirely different mechanism of polymerization that has completely different reaction kinetics and results in a different distribution of molecular weights. The first step in a free-radical chain addition simulation is known as the initiation step, where an initiator molecule forms free radicals. In this simulation, the initiator is considered to behave as a typical peroxide initiator, which splits to form two free radicals when heated. This simulation models each initiator as two particles that are not reactive when they are together. The initiators are held together by a finite bond energy, however, so that as the temperature is increased, more bonds are spontaneously broken by the thermal energy. When an initiator splits, it forms two free radical species, each of which can react with a monomer. Once the free radical reacts with a monomer, the formerly reactive particle permanently bonds to the monomer, which then becomes reactive towards other monomers, and the initiation step is complete.

The initiation step results in the nucleation of a growing polymer chain and leads to the second stage in this polymerization: propagation. In the propagation stage, monomers are added one by one to the growing chain. Each time a monomer is added, the radical (reactive) nature of the chain is passed to the newly added monomer so that the unit on the end is the only chemically active unit in the chain. The last stage of this polymerization is termination, where the propagation is terminated in one of two ways when the active ends of two propagating chains collide. In termination by combination, the active ends will bond with each other, effectively doubling the average molecular weight in this step. Alternatively, the chains can terminate by disproportionation, where the radical is transferred from one chain to the other, killing the reactivity of both chains and resulting in two polymer chains with the same average molecular weight as before the termination step. The probability of combination vs. disproportionation is an input parameter.

STUDENT ACTIVITIES

These computer simulations can serve to teach students over a range of levels from a sophomore materials science course through a graduate-level introduction to polymers. Since the detailed reaction mechanisms have been replaced by simple bonding rules, the level of chemistry included in the corresponding lecture can be tailored to fit the learning objectives of the course.

For a materials science course where the students have never been formally exposed to polymer science or organic chemistry, the details of the chemistry can be neglected and only the bonding rules of the monomers need to be discussed. This may be particularly advisable if the course includes a significant number of students from disciplines other than chemistry or chemical engineering. These simulations will still serve to give the students a firm, intuitive grasp of what is a polymer and how they are formed. After a demonstration in front of the class, which may take less than 30 minutes, the students should be able to describe how initiator concentration affects the conversion rate and the final molecular weight of a polymer, the three basic steps of a free-radical chain polymerization, effects of termination mechanism on molecular weight, effects of temperature, the importance of stoichiometry in stepwise growth polymerizations, the effect of mono-functional groups, and the concept of gelation. These critical concepts can be covered quickly and effectively by using this simulation as a visual aid. After this brief tutorial, students will be better prepared for polymer work in undergraduate research projects, industrial internships, or graduate-level polymer courses. The students can then be referred to the website if they wish to learn more about polymerization reactions.

The full potential of the simulation can be used in a graduate-level polymers course. The simulations are not ideal for advanced graduate work or for research purposes since they are two-dimensional, contain a small number of molecules (with respect to the statistics of large numbers of polymers), and the

specific chemical mechanisms are neglected. This simplicity, however, makes the simulations ideal for illustrative purposes for an introductory polymer science or engineering course, because most of the fundamental polymer formulae still apply. The students can then use the simulations to collect their own data, copy the data to a spreadsheet, analyze the data, interpret the results, and discuss how their results agree or disagree with theoretical predictions.

Students in a polymer science course should be able to quantitatively predict the results of the given polymerization from the concentrations of the reactants. For instance, in an unbalanced step-wise growth polymerization consisting of two di-ols for each di-acid monomer, a student should predict that the maximum number-average degree of polymerization would be three, which is verifiable by the simulation. Furthermore, the simulation would also help the student visualize that while the number-average degree of polymerization approaches three, there is significant polydispersity. Students should also be able to quantitatively predict the effect of mono-functional groups. The number- and weight-average molecular weights can be pasted into a spreadsheet, plotted
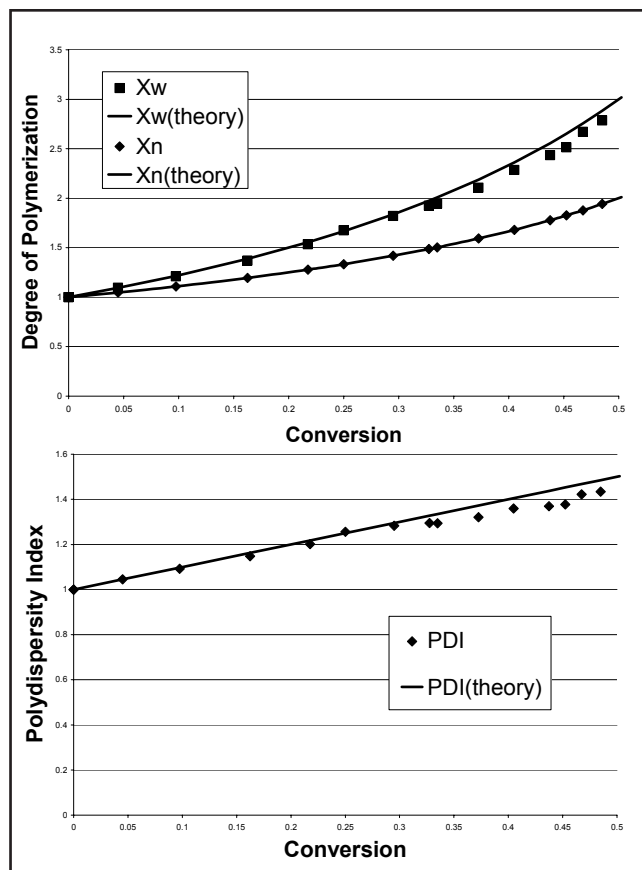
as in Figure 2, and compared to theoretical predictions from the following equations.[2]

$$\bar{X}n = \frac{1}{1-p}, \quad \bar{X}w = \frac{1+p}{1-p}, \quad PDI = 1+p \qquad (1)$$

where $\bar{X}n$, $\bar{X}w$, PDI, and p represent number-average degree of polymerization, weight-average degree of polymerization, polydispersity index, and conversion, respectively.

In a free-radical chain polymerization, the students should be able to predict the final number-average molecular weight for a polymerization reaction if the initiator-to-monomer ratio and termination mode are given.

Gelation can be modeled by using the step-wise growth simulator. Gelation occurs when the polymer network reaches an infinite average molecular weight, which can be easily visualized with the periodic boundary condition by pressing "1" as seen in Figure 3 (next page). If the average monomer functionality, f, is greater than two for a stoichiometric mixture of reagents, then gelation will typically occur at a high conversion. The critical conversion at which gelation will occur (where a polymer of infinite size appears) can be predicted as $p_c = (f-1)^{-\frac{1}{2}}$ for a large number of monomers in a stoichiometric, 3-D system.[3] Since the simulator features a relatively small number of monomers in a 2-D system for visualization purposes, however, this equation only works as an approximation.

The effects of temperature on the polymerization can also be observed. The simulations can be run under isothermal or adiabatic conditions, and students can plot the conversion over time for both conditions. Under adiabatic conditions, the heat of reaction will raise the temperature during the polymerization reaction, resulting in faster reaction rates. In the stepwise growth simulator, however, the reactions are reversible, so the larger temperatures generated in the reaction will cause depolymerization, which will result in a lower final molecular weight. This auto-acceleration is a real effect as is the thermal degradation which can result at high temperatures. One unrealistic aspect, however, is that the thermally broken polymer chains are able to reform bonds. In reality, thermally degraded polymers typically result in chain ends that are not reactive with monomers or other polymer ends.

A student can copy the conversion data over time by right-clicking on the plot and then pasting the data into a spreadsheet where the reaction rate kinetics can be analyzed. A reaction rate equation for the consumption of monomer can be proposed such as $\frac{d[M]}{dt} = -k[M]^n$, where M, t, k, and n are the monomer concentration, time, rate constant, and order of reaction, respectively. The student can perform his/her own analysis to then determine the values for the rate constant and the order of reaction. The student can also investigate the effect of temperature on the rate constant.

Figure 2. a) Simulation results for number- and weight-average degrees of polymerization plotted vs. conversion and compared to theory. b) Polydispersity index of simulation plotted vs. conversion and compared to theory.

Acid catalysis causes the reaction order for many stepwise polymerizations to be third order (n = 3).[4] Since acid catalysis is not included in the simulation mechanism, however, a second-order reaction is expected, which has a solution of the form:

$$\frac{1}{M} = \frac{1}{M_0} + kt ,$$

where M_0 is the initial monomer concentration.[5] From this equation, k can be readily calculated by taking the slope of 1/M plotted over time as shown in Figure 4a. A model of
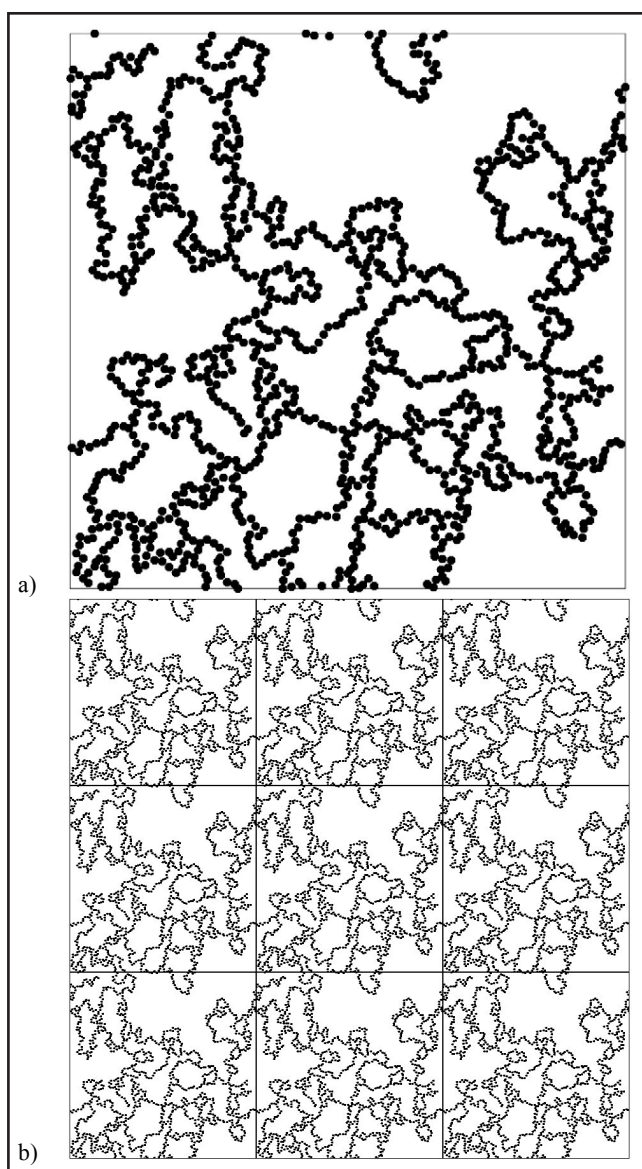

a)

b)

Figure 3. a) Simulation of gelation caused by tri-functional monomers. b) View of the simulation with the periodic boundary condition showing 3 × 3 unit cells. Note that the chain continues from one unit cell to the next and is of infinite size after gelation.

the second order reaction using the fitted k value is shown in Figure 4b. Students can alternatively fit k and n without assuming a reaction order.

For a multidisciplinary polymer engineering course, a minimum amount of organic chemistry may be included in the course. In my CHEE 417(G): "Polymer Engineering" course, I remind the students that alcohols react with carboxylic acids to form esters, which leads to showing how a di-ol and a di-acid can react to form a long chain of polyester. At minimum, this amount of chemistry is required to understand polymer nomenclature, because a student may have some difficulty in understanding what a polyester is and how it is made without the basic understanding of an esterification reaction. Students should similarly be able to identify common polymers and the types of monomers used to synthesize them. This will help the students become conversant in polymer terminology so that they may better comprehend research papers and presentations relevant to polymers later in their careers.

In a graduate-level polymer chemistry course with an organic chemistry prerequisite, the chemistry mechanisms would be an essential element of the corresponding lectures. In such a course, the students might be asked to critique this
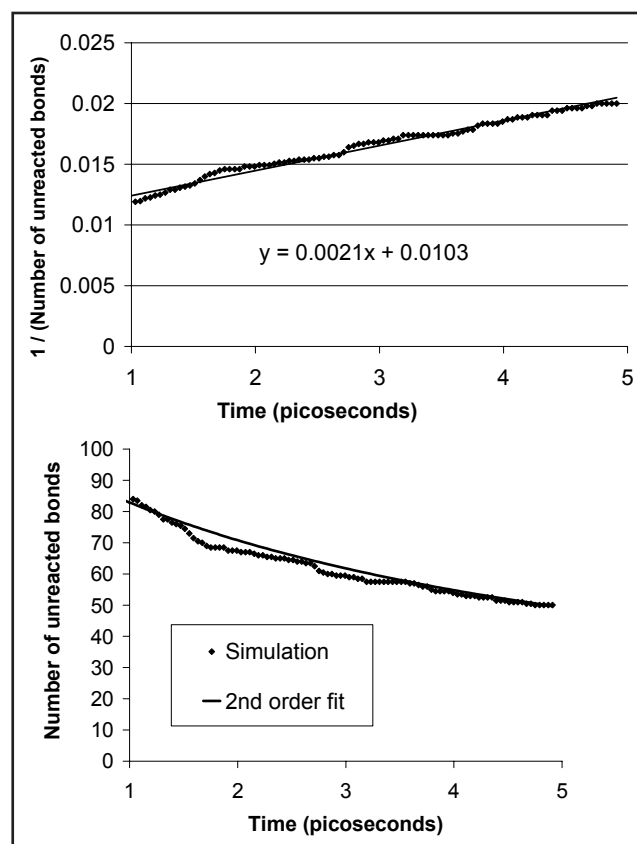

Figure 4. a) The inverse of the number of unreacted monomer bonds is plotted vs. time to find k. b) The fitted reaction constant can be used to compare the 2nd order kinetics equation to the simulation data.

polymerization model by discussing some of the unrealistic ramifications of removing the chemical mechanisms. For instance, the students may predict how the removal of the acid-catalysis mechanism in the polyesterification reaction affects the order of the reaction. An instructor might also explain how polymer chains may thermally degrade through a beta-scission mechanism or discuss other unfavorable side reactions.

RESULTS

The use of these simulations had a positive impact on the effectiveness of instruction. As an instructor, I found this was an enjoyable variation from the usual PowerPoint and chalkboard lectures. The students welcomed this change in the medium of instruction even more so. This alternation in medium alone can help an instructor avoid "Death by PowerPoint" as described by Felder and Brent.[6] Furthermore, the students garner other benefits through doing their own simulated experiments, analyzing their own data with spreadsheets, and performing the critical thinking required to interpret the results and compare them to theoretical predictions. Incorporating these tasks is also valuable for achieving accreditation outcomes and improving course evaluations.

Instructors should find, as with any model or simulation, that some theoretical equations will work exactly, some approximately, and others not at all due to the assumptions and approximations of the model and how it fails or succeeds in representing reality. One unrealistic aspect of the simulation is that all of the monomers in the simulation were given a molecular weight of 1 g/mole. Therefore, the degree of polymerization is equal to the molecular weight. This was done for the sake of simplicity; however, it was found that it could be confusing to the students when the terms "degree of polymerization" and "molecular weight" are used interchange-

ably. Emphasizing this caveat early in the introduction of the simulation briefly, but clearly, should alleviate this issue.

Equations derived specifically for 3-D systems may only work as approximations in this simulation. Equations derived based strictly on stoichiometry and extent of conversion should work exactly, however. Allowing students to predict which equations will work or fail with this model exercises their critical-thinking skills and will give them a deeper understanding of the equations and their implied assumptions.

Beyond my anecdotal observations, an anonymous survey consisting of 49 questions (38 multiple choice and 11 open response) was taken by an independent party to evaluate the effectiveness of this model for the CHEE 417(G): "Polymer Engineering" course in the Fall of 2008. A sub-selection of the questions is shown in Table 1 for brevity. The class only had seven students, which is excellent for instruction and discussion, but poor for survey statistics even with all seven students responding. Regardless, the feedback was very positive for all of the students. The survey data for the questions in Table I was collected again in the Fall of 2009 with 12 out of the class of 18 students responding with similarly positive results.

In addition to the quantitative survey data, the students were asked open-ended questions regarding the simulation and its implementation. These results were similarly favorable. Many of the students found the simulations aided their ability to visualize the polymerization reactions and found the simulator easy to use. Some students also appreciated the opportunity to practice spreadsheets skills in the analysis of the kinetics. While most students found the interface easy to understand and use, especially with the supporting documentation and examples on the website, it was recommended that the instructor take time at the start to explain the features to be controlled using the interface. Some students have suggested

#	Statements	Fall 2008 Average	Fall 2009 Average
	TABLE 1 **Survey Results of the Simulation Module for CHEE 417(G): "Polymer Engineering"**		
1	The computer simulation was an effective use of my time.	4.14	4.25
2	I find this computer simulation helped me visualize molecular motion better than I could before.	4.43	4.50
3	This simulation was a valuable experience.	4.43	4.25
4	This computer simulation allowed me to study a problem in a way not possible with a conventional experiment.	4.14	4.13
5	The use of this module aided in my understanding of the material.	4.43	4.08
6	I believe this module should be used next year.	4.71	4.25
7	The use of this simulation module was a valuable use of class time.	4.43	4.00
8	The content covered in the simulation was appropriate to the course.	4.71	4.17
9	The computer simulation provided me insights I had not had before.	4.29	4.25
10	I feel the computer simulation was effective in increasing my understanding of molecular motion.	4.29	4.25
	The individual responses were scored as: 5–Strongly Agree, 4–Agree, 3–Neutral, 2–Disagree, 1–Strongly Disagree. The averages of the responses are shown.		

the model should be more complex, featuring more realistic chemical mechanisms, larger numbers of monomers, and making the simulation three-dimensional. This would necessarily make the simulator more complicated to setup and slower to run, however. There was a fair balance of comments that the simulator was too simplistic vs. being too complicated to set up, which seems to indicate that a good balance has been achieved for students at this level. A trial version of a 3-D simulator was partially developed, but it was not used, because the molecules and interactions were harder to see, even though it was more aesthetically impressive.

Some students would prefer the assignments be assigned to small groups; however, an equal number of students preferred working individually. Running multiple simulations to high conversions can take a considerable amount of time, so allowing data sharing among groups might be a reasonable option if large take-home projects are assigned. Instructors, as in any experiment or assignment, are advised to conduct the simulations themselves before assigning them to make sure that the time demands are reasonable and that the expected results are produced. This simulator was primarily used in individual take-home assignments to ensure that each student had an equal opportunity to use the simulator and received an individual assessment of their work. The ability to work in teams is an important career skill and accreditation outcome, however, and this could be an opportunity to implement a team-based project in a polymer course.

CONCLUSIONS

Courses generally benefit from tangible visual aids, demonstrations, and laboratory experiments. Unfortunately, many of these course supplements are not implemented due to the material cost, preparation time, safety considerations, or laboratory space required. The simulations presented here allow students to accrue most of the benefits of running their own experiment as they set experimental parameters, collect and analyze data, exercise spreadsheet skills, and then interpret their own results. The only investment required is a small amount time by the instructor to become familiar with the simulator and to make sure that the students have access to a computer.

Overall, the simulations were found effective in explaining the fundamentals of polymerization in a 30-minute demonstration for a materials science and engineering course. The simulations were also successful for teaching a polymer engineering graduate course over the course of the month in which lecture topics, demonstrations, and assignments were conducted and reviewed using the simulations and spreadsheets. An instructor can use these simulators as a brief qualitative introduction to polymer science or as an opportunity for rigorous derivation, analysis, and testing of polymer equations, or any intermediate between these extremes that fits the learning objectives of the course.

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